

THE PATERNÒ-BÜCHI REACTION

Maurizio D'Auria and Sonia Stoia

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TABLE OF CONTENTS

List of Tables.....	vii
Chapter One.....	1
Introduction	
The Paternò-Büchi reaction	1
Historical background	3
Chapter Two.....	5
Mechanism and stereochemistry	
Mechanism.....	5
Kinetic data	6
Spectroscopic studies	10
Calculations.....	11
Regioselectivity and diastereoselectivity	13
Use of chiral auxiliaries.....	24
Stereochemical behavior in organized media.....	27
Hydroxyl group directing effects	29
Effect of viscosity and temperature	37
Chapter Three.....	43
Scope and limitations	
Intermolecular reactions.....	43
Reactions with electron-poor unsaturated compounds	43
Reactions with electron-rich unsaturated compounds	73
Reactions of carbonyl compounds with alkenes, dienes, and alkynes	73
Reactions of carbonyl compounds with enol ethers and enol thioethers	209
Reactions of carbonyl compounds with enol esters, enol silyl ethers and enamine derivatives	281
Reactions with heterocyclic compounds.....	292
Reactions with five-membered heterocycles.....	292
Reactions with six-membered heterocycles	452
Intramolecular reactions.....	473
Limitations attributable to the properties of the carbonyl compounds....	478
Limitations attributable to the structure of the unsaturated compounds..	513

Chapter Four.....	515
Application to synthesis	
Cycloreversion.....	515
Cleavage of C-C bond to give alcohols.....	519
Other ring opening reactions.....	522
Rearrangements of oxetanes.....	523
Miscellaneous reactions.....	526
Synthesis of preussin.....	529
Synthesis of (±)-avenaciolide.....	530
Synthesis of (±)-asteltoxin.....	531
Synthesis of (±)-oxetanocin A.....	522
Chapter Five.....	533
Comparison with other methods	
Ring closure through aliphatic nucleophilic substitution.....	533
Ring contraction.....	535
Ring closure through electrophilic additions.....	536
Chapter Six.....	539
Experimental conditions	
Source of light.....	539
Solvent.....	540
Tables.....	540
Bibliography.....	541

LIST OF TABLES

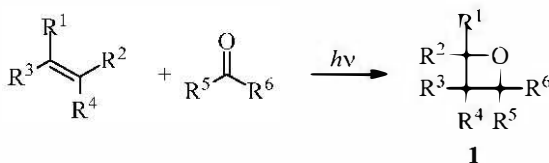
Table 1. Intermolecular reactions with electron-poor unsaturated compounds	44
Table 2. Intermolecular reactions with electron-rich unsaturated compounds. A. Alkenes and dienes	74
Table 3. Intermolecular reactions with electron-rich unsaturated compounds. B. Alkynes	210
Table 4. Intermolecular reactions with electron-rich unsaturated compounds. C. Allenes and other cumulated double bonds	228
Table 5. Intermolecular reactions with electron-rich unsaturated compounds. D. Enol ethers	244
Table 6. Intermolecular reactions with electron-rich unsaturated compounds. E. Enol thio- and selenyl ethers	276
Table 7. Intermolecular reactions with electron-rich unsaturated compounds. F. Enol esters	282
Table 8. Intermolecular reactions with electron-rich unsaturated compounds. G. Enol silyl ethers	293
Table 9. Intermolecular reactions with electron-rich unsaturated compounds. H. Enamine derivatives	327
Table 10. Reactions with substrates bearing both electron-withdrawing and electron-donating groups	339
Table 11. Intermolecular reactions with five-membered heterocyclic compounds	345
Table 12. Intermolecular reactions with six-membered heterocyclic compounds	456
Table 13. Intramolecular reactions	479

CHAPTER ONE

INTRODUCTION

The Paternò–Büchi Reaction

The Paternò–Büchi reaction originally referred to a [2+2]-photocycloaddition between an alkene and the excited state of a carbonyl compound to give the corresponding oxetane **1** (Scheme 1). As outlined in this chapter, this reaction can be further generalized as a photochemical reaction between an unsaturated compound and a compound with a carbon–heteroatom double bond, mainly aldehydes and ketones. Also, the notion that the reaction occurs through interaction of the excited state of the carbonyl compound with the ground state of the alkene does not always hold. Examples of the converse situation are also presented where the excited state of the alkene reacts with a carbonyl compound in its ground state [1].



Scheme 1

The Paternò–Büchi reaction represents a method for preparing small, heterocyclic rings, some of which are contained in natural and biologically active compounds (Figure 1). Among such compounds are paclitaxel (**2**), an antitumor drug [2] isolated in *T. brevifolia* [3], merrilactone (**3**) (isolated in *Illicium merrillianum* and showing neurotrophic activity) [4], and oxetanocin (**4**) (isolated in *Bacillus megaterium* NK84-0218 [5] and possessing anti-HIV activity) [6]. In addition, thromboxane A₂ (**5**), mitrephorone A (**6**) (isolated in *Mitrephora Glabra Scheff* and possessing anticancer activity) [7], and

maoecrystal I (**7**) (isolated in *Isidon japonicus* and showing cytotoxic activity) [**8**], all contain oxetane rings.

Furthermore, oxetane **8** displays several biological activities [**9**], dictyoxetane (**9**) (isolated in *Dictyoadatichotoma algae*) [**10**], oxetin (**10**) (isolated from the fermentation broth of *Streptomyces* sp.●M-2317) [**9a**], bradyoxetin (**11**) (a bioactive compound isolated from *Bradyrhizobium japonicum*) [**11**], laureatin (**12**) (isolated from *Laurentia nipponica* and showing larvicidal activity) [**12**], parthoxetine (**13**) (isolated from *Parthenium fruticosum*) [**13**], and a sesquiterpene dimer (**14**) (isolated from *Xylopia aromatic*) [**14**] all contain an oxetane ring.

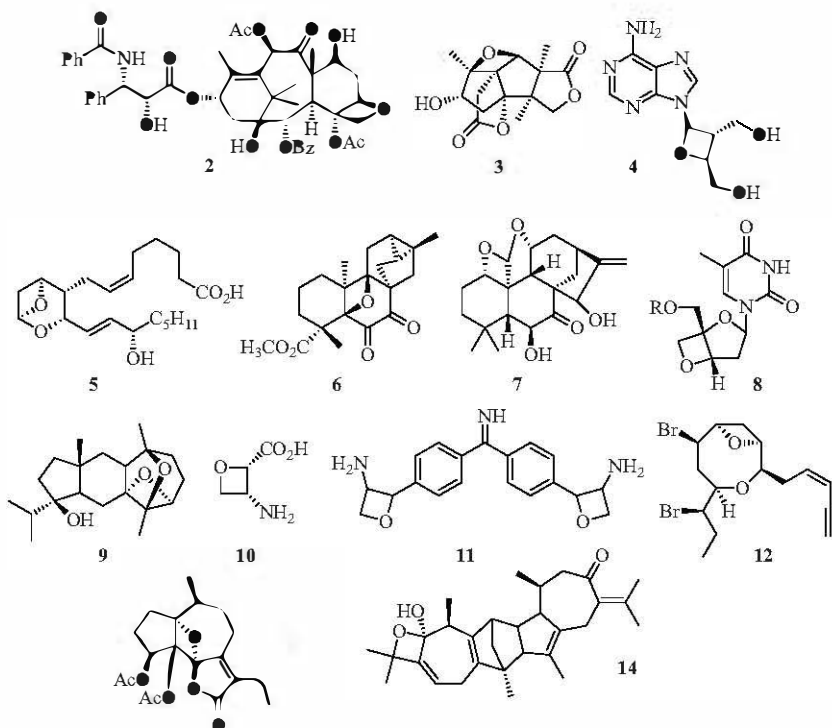


Figure 1. Bioactive compounds containing the oxetane ring.

It is noteworthy that several patents for new drugs containing an oxetane ring have been registered [15]. Interestingly, only compound **4** and oxetin (**10**) have been synthesized to date using a Paternò–Büchi reaction. However, the compounds reported in Figure 1 represent future challenges for synthetic applications of this photochemical reaction.

Several reviews have previously been published covering different aspects of the Paternò–Büchi reaction [16].

Historical Background

The exact origin of the Paternò–Büchi reaction is not easily discerned because the discovery of this process involved a controversy between Ciamician and Paternò [17]. In 1909, Paternò, while studying the photochemical reaction of benzaldehyde with amylene (2-methyl-2-butene), showed that the corresponding [2+2]-cycloadduct was formed [18]. It was not possible for Paternò to distinguish between the two possible constitutional isomers of the oxetane and all of the possible stereoisomers could not be determined.

In 1909, Ciamician also reported a reaction where the same type of photochemistry was described involving the photoreaction of safrole and isosafrole with benzaldehyde and claimed the formation of addition products [19]. However, structures were not provided for the photoproducts.

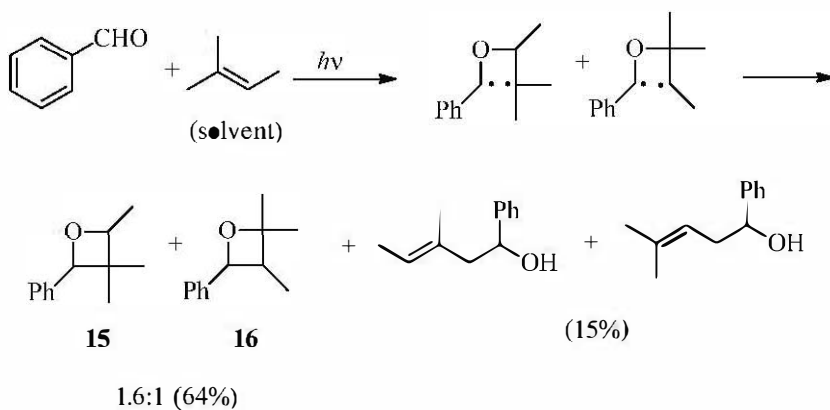
Despite its potential, the Paternò–Büchi reaction was essentially forgotten. In 1949, it was reported that aliphatic aldehydes (ethanal) irradiated in a quartz tube in the presence of an alkene (1-octene) gave, after distillation of the crude product, little of the corresponding ketone (2-decanone). However, no oxetane product was isolated [20]. It was only in 1954 that Büchi repeated the reaction described by Paternò, and identified the oxetane product [21].

CHAPTER TWO

MECHANISM AND STEREOCHEMISTRY

Mechanism

Since the first reports on this subject, the reaction of benzaldehyde with 2-methyl-2-butene was suggested to involve the triplet state of the carbonyl compound reacting with the alkene ground state to form the most stable biradical intermediate (Scheme 2) [21]. However, the photoisomerization of 5-hexen-2-one (see below) and the absence of any effects due to the presence of oxygen allow one to speculate that a triplet state is not involved in this reaction [22].



Scheme 2

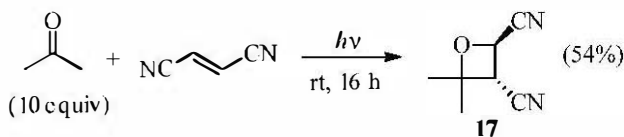
In the reactions of biaryl ketones, the cycloaddition occurs only with carbonyl compounds that can access $n \rightarrow \pi^*$ triplet states [23]. The reaction of benzaldehyde with 2-methyl-2-butene gives mainly the corresponding

oxetanes (64%) along with a mixture of 1-phenyl-3-methyl-3-penten-1-ol and 1-phenyl-4-methyl-3-penten-1-ol (in a combined yield of 15%) as well as some dihydrobenzoin (11%) [24]. The oxetane mixture is mainly compound **15**, but some of the isomer **16** is also present ($15/16 = 1.6:1$) (Scheme 2). The relative stereochemistry of these products has not been determined.

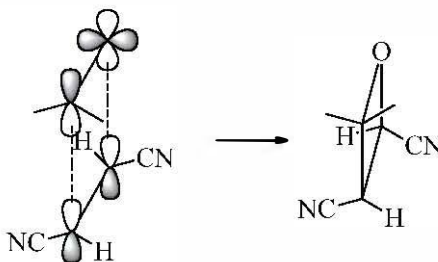
The quantum yield for the formation of the oxetanes **15** and **16** is 0.45 ± 0.05 . Benzophenone and acetophenone react with 2-methyl-2-butene to give the corresponding oxetanes higher regioselectivity (>90%) than for benzaldehyde. The quantum yields for oxetane formation are similar to those obtained with benzaldehyde when benzophenone is the carbonyl compound, while acetophenone gives a lower value (0.1). All of these carbonyl compounds can access an $n \rightarrow \pi^*$ triplet state. 1- and 2-Naphthaldehyde give the corresponding oxetanes (70%) when reacting with 2-methyl-2-butene. The regioisomeric ratio between the two possible oxetanes is 3:2 in favor of that corresponding to **15** and the quantum yields are 0.05. 2-Naphthyl phenyl ketone reacts with 2-methyl-2-butene to give the oxetanes in 62% overall yield with a regioselectivity similar to that shown by benzophenone and with a quantum yield of 0.005. 1- and 2-Acetylnaphthalene do not react with all the alkenes tested. Naphthaldehyde and naphthyl methyl ketone have a π, π^* triplet state. 9-Anthraldehyde also shows the involvement of a $\pi \rightarrow \pi^*$ triplet state. However, it gave a Paternò-Büchi reaction when irradiated in the presence of 2-methyl-2-butene. To justify the reactivity of this compound, the internal conversion between the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplet states could be lower than that for the naphthaldehydes, leading to a higher reactivity. The $n \rightarrow \pi^*$ triplet state of 9-anthraldehyde reacts with 2-methyl-2-butene, giving the corresponding oxetane with high regioselectivity, giving only the regioisomer derived from the most stable biradical intermediate.

The triplet excited state of the carbonyl compound can undergo an electron transfer process with an alkene to provide the corresponding radical-ion pair. This process occurs with electron-rich alkenes and carbonyl compounds in polar solvents [25].

Kinetic Data. Some aliphatic ketones such as acetone react with (*E*)-1,2-dicyanoethene, giving the corresponding oxetanes in good yields (54%) while maintaining the configuration of the alkene in the product (Scheme 3) [26]. The fluorescence of acetone is quenched by the addition of dicyanoethene.



Scheme 3



Scheme 4

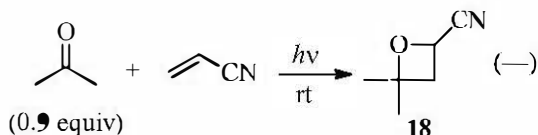
Oxetanes are also obtained in the reaction of the same aliphatic ketones in the presence of maleic anhydride in good yields (67%). Triplet quenchers (1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, and naphthalene) do not inhibit the reactions. Thus, the reactions seem to occur from a singlet excited $n \rightarrow \pi^*$ state either through a concerted process or through a rapid closure of an intermediate biradical species.

The formation of **17** is only slightly affected by the addition of 1,3-pentadiene (a triplet quencher), and the reaction is quite inefficient ($\phi = 0.026 - 0.054$). The Stern–Volmer plot of the formation of **17** as a function of (*E*)-1,2-dicyanoethene concentration is in agreement with the formation of an exciplex intermediate.

The cycloaddition occurs through a concerted or a "quasi-concerted" attack of the nucleophilic π system of the singlet $n \rightarrow \pi^*$ state of acetone on the π system of the ground state of 1,2-dicyanoethene (Scheme 4). The observed stereospecificity demands that bond formation is faster than bond rotation.

In the Paternò–Büchi reaction between acetone and acrylonitrile, only oxetane **18** is formed (Scheme 5) [27]. This observation is more consistent with an addition of the higher electron-density carbon lobe of the LSO orbital

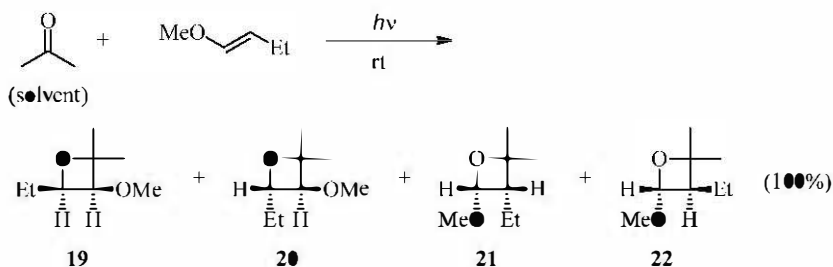
of the ketone to the most electron deficient end of the acrylonitrile double bond. The reaction occurs *via* the formation of an exciplex.



Scheme 5

Kinetic data confirms the involvement of the triplet state in the Paternò-Büchi reaction of benzaldehyde with 2,3-dimethyl-2-butene. The overall reaction follows 0th-order kinetics. A Stern–Volmer plot of the reaction taking place in the presence of piperylene shows that the reaction occurs via a single reactive state ($n \rightarrow \pi^*$ triplet) with a quantum yield of 0.55 [28]. Furthermore, when 9-anthraldehyde is used as a starting material, a quantum yield of 0.024 is found. A Stern–Volmer plot of the quenching experiment of the reaction between 9-anthraldehyde and 2,3-dimethyl-2-butene in the presence of di-*tert*-butyl nitroxide indicates that there are two different reactive species. The energy gap between the $n \rightarrow \pi^*$ singlet state and the low-lying triplet state of anthraldehyde is considerably larger than that of benzaldehyde, and the rate of radiationless transition between these two states may become sufficiently slow to be competitive with the rate of singlet state reaction. In the case of anthraldehyde, both states could be responsible for the reaction.

In the reaction between acetone and (*E*)-1-methoxy-1-butene, an electron rich alkene, the ratio of **19/20** and **21/22** is found to be dependent on the initial concentration of the alkene (Scheme 6) [29]. Compounds **21** and **22** are removed from the reaction mixture through acid hydrolysis. The ratio of **19/20** extrapolated to zero concentration of the alkene is 1.06, whereas at high concentration of the alkene the ratio is *ca.* 2.5. At low concentration of the alkene, a mechanism involving a total loss of the configurational identity of the alkene seems to be operative, whereas at high concentration of the alkene, some preservation of the configuration is observed, probably indicating a different mechanism.



Scheme 6

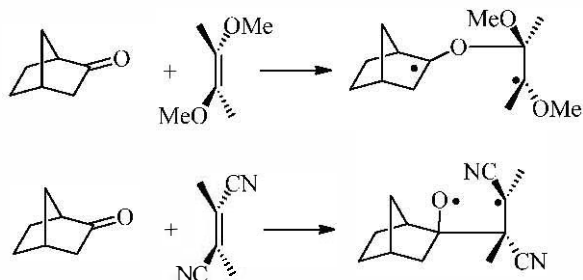
The amounts of **19** and **20** are reduced in the presence of variable amounts of piperylene (quencher of triplet acetone), with the observation that quenching is not linearly related to concentration. Thus, the formation of **19** and **20** are not inhibited at the same rate. At high concentrations of piperylene, the only mechanistic pathway available is the addition from the singlet excited state of acetone.

These reactivity patterns can be explained by assuming that both the singlet and triplet state of acetone undergo the [2+2] cycloaddition. The formation of singlet and triplet biradical intermediates are proposed. The singlet biradical intermediates (a mechanism operative at high alkene concentration) retain the information of the configuration of the alkene (cyclizing rapidly to the oxetane). Triplet biradicals are expected to have a greater lifetime, allowing rotation of the carbon atom bearing the free-radical site.

Benzophenone phosphorescence is quenched by the addition of enol ethers [30]. The k_q and the energy of the HOMO of the enol ethers are correlated. Quenching data shows that the primary step in the quenching process is π -complex formation and not bond formation. Partial charge donation from the olefin to the ketone produces the initial exciplex. These results are relevant because they show that the formation of an exciplex is not limited to the processes involving the first excited singlet state, but also in those where triplet states are involved. Several articles have appeared on the kinetic behavior of the reaction [31].

A general way to rationalize the observed regioselectivity in the addition of (*E*)-1,2-dicyanoethene and (*E*)-1,2-dimethoxyethene to norbornanone derivatives has been proposed. In the case of electron-rich substrates, the reaction occurs through an attack of the carbonyl n orbital on the olefin in a

perpendicular relationship. When using electron-poor alkenes, the attack occurs via a parallel conformation, allowing the formation of the corresponding C-C-C•biradical (Scheme 7) [32].



Scheme 7

Spectroscopic Studies. Spectroscopic studies of the Paternò-Büchi reactions allowed to determine evidences on the formation of the 1,4-biradical intermediate, when it is present. Furthermore, they can confirm the presence of radical ions due to the presence of an electron transfer mechanism. The mechanism of the reaction between quinones and quadricyclane or norbornadiene has also been studied using CIDNP measurements. The results are in agreement with the formation of a biradical intermediate [33]. CIDNP experiments were also performed to characterize the biradical intermediate in the reaction between acetylene and quinone [34].

Benzophenone shows a transient absorption due to the triplet at 525 nm. In the presence of dioxene, the transient triplet spectrum is quenched with $\tau_{1/2} = 175 \pm 25$ ps, and a new absorption appears at 535 nm [35]. This transient absorption has been identified as the triplet biradical. In fact, the triplet state of benzophenone is quenched by charge transfer to form a contact ion pair that rapidly collapses to give the biradical. The picosecond-resolved spectrum of the biradical intermediate has also been reported [36].

The triplet state of vinylformyl[2.2]paracyclophane derivatives has been studied using femtosecond time-resolved photoelectron spectroscopy [37]. Additionally, transient vibrational spectroscopy has been used to follow the decay of the biradical intermediate [38].

In the reaction between biacetyl and an electron-rich olefin, electron transfer accounts for the observed reactivity. The ESR spectra of the radical

cation and the radical anion can be observed [39]. The radical ion arising from an electron transfer process has also been observed in another related study [40].

Calculations. A study on the Paternò–Büchi reaction has been performed with ab initio calculations at the ST-3G level using Gaussian 70 [41]. The alkene is assumed to approach the ketone in such a manner that its π orbitals lie in the plane defined by the ketone carbonyl group. In the reaction between formaldehyde and ethylene, the surface crossing is shown to occur at a C–O bond distance of approximately 1.9 Å. Activation energies of 24 and 29 kcal mol⁻¹ are required for the excited reactant to leave this well and reach the biradical product. The effects of substituents can be deduced by tracing the molecular energy level variations and orbital coefficient changes that are induced by the substituents. Substituents can be broadly grouped into electron-donating, electron-attracting, and conjugative categories. Electron-donating substituents raise the molecular energy levels. Electron attracting substituents lower all energy levels. The energy of the n-orbital [F(n)] is changed only by a second-order inductive effect. In general, conjugative substituents lead to a spreading of π energy levels, with the highest occupied π level raised, and the lowest vacant level being lowered in energy. In addition, a much lower electron density is found at the reactive sites in either the π or π^* orbitals. In this way, an electron-donating group on the alkene favors the formation of a 1,4-biradical intermediate, whereas an electron-withdrawing group on the alkene favors a concerted mechanism [42].

Theoretical calculations show that in the reaction of benzoquinone with 2,3-dimethyl-2-butene to give the corresponding oxetane, an n $\rightarrow\pi^*$ triplet state is involved [43]. In contrast, the tetramethyl derivative, duroquinone, gives the corresponding cyclobutane. In this case, calculations show the lowest triplet state is a $\pi\rightarrow\pi^*$ triplet state. In the case of naphthoquinone, which gives both products, calculations show that both the n $\rightarrow\pi^*$ triplet and the $\pi\rightarrow\pi^*$ triplet are close in energy.

A description of the Paternò–Büchi reaction using the Woodward–Hofmann rules has been reported [44]. The effect of spin-orbit coupling in oxygen-containing biradicals was studied [45]. A conformational analysis of the biradical intermediate shows that the previously postulated conformational dependence of spin-orbit coupling in the biradical based on the "90-degree rule" is not satisfactory for quantitative estimates [46].

In the reaction between 1,4-dioxene and benzaldehyde, theoretical calculations indicate that the only transition able to give the observed transient absorption is that from the LSO₂MO to the LUMO (549 nm); the same result is obtained for the reaction between furan and benzaldehyde [16af].

The regioselectivity of the reaction can be explained invoking hard-soft acid and base theory, and this approach is in agreement with the experimental results [47]. Another way to explain the regiochemistry of the Paternò-Büchi reaction considers that atoms arrange themselves so that the obtained product reaches the minimum electrophilicity, that is considered the driving force in the reaction [48].

Another theoretical study of the Paternò-Büchi reaction shows that there are two conical intersection points located near the C-C and C-O bonded biradical regions of the ground state. These two conical intersections support a mechanism in which the decay from the excited state is accompanied by a geometric rotation of the terminal group, in the case of C-O attack, and by an orbital rotation at the oxygen center, in the case of C-C attack. Furthermore, for C-O attack, the triplet surface must cross the singlet to reach a biradicaloid minimum. For C-C attack, the triplet biradical minimum is located at the same geometry as the conical intersection between the two singlet states, and the efficiency of the intersystem crossing will be determined by the nature of the spin-orbit coupling. Thus, for the triplet, the reaction path can be predicted by the most stable biradical rule [49].

A CAS SCF geometry optimization using the TZV basis set of the intermediate biradicals shows that the biradical region corresponding to the C-C attack lies about 10 kcal mol⁻¹ lower in energy than the C-O region [45]. This result, however, is not in agreement with reported experimental results. An AFIR method has been used to obtain a predictable model for the reaction between formaldehyde and ethene. The reaction product is obtained by minimizing the AFIR function. The O-C bond formation is more favorable than the C-C bond formation, and the oxygen atom forms a bond with the less bulky site of the alkene [50]. The same behavior has been observed by using the atomic zero steric potential (AZSP). AZSP can be considered as a measure of charge heterogeneity [51].

An electron transfer process can occur when the HOMO of the alkene is very near the LSO₂MO of the excited carbonyl compound [52].

Regioselectivity and Diastereoselectivity

The reaction of acetaldehyde with acrylonitrile is considered to be a concerted [2 + 2] cycloaddition in which the regioselectivity is controlled by the dipole-dipole orientation. Another hypothesis involves the formation of an oriented exciplex intermediate able to give only one possible constitutionally isomeric singlet biradical [31j].

The regioselectivity of the reaction of carbonyl compounds with furan derivatives is explained on the basis of the relative stability of the biradical intermediates [53]. The regioselectivity of the attack is postulated to depend on the frontier orbital coefficients [47].

The minimum electrophilicity principle [$\omega' \approx (\varepsilon_L - \varepsilon_H)^2 / 4(\varepsilon_L + \varepsilon_H)$], wherein ω' is the electrophilicity, ε_L is the energy of LUMO, and ε_H is the energy of the HOMO, correctly predicts the most stable constitutional isomer formed in the reaction. This is based on the assumption that there is a tendency for atoms to arrange themselves such that the observed product reaches the minimum electrophilicity [48]. Thus, in the theoretical reaction between formaldehyde and 1,3-butadiene, two possible constitutional isomers can be obtained (Scheme 8). The electrophilicity values are 0.21210 for the first oxetane product and 0.20269 for the second one. Finally, the electron density on the reactive carbon atoms is assumed to determine the regioselectivity of the reaction [54].

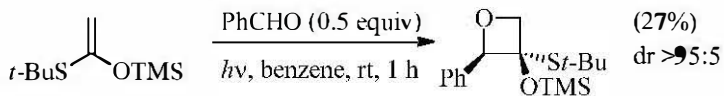


Scheme 8

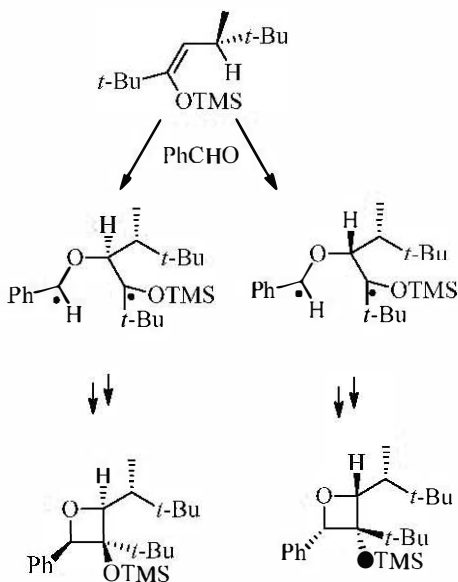
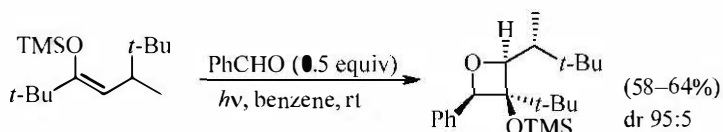
The stereoselectivity of the Paternò–Büchi reaction has attracted the attention of several researchers. Stereoselectivity in the alkenes bearing electron-withdrawing or electron-donating substituents are interpreted on the basis of the main interactions between the orbitals in the excited state [55].

3-(Silyloxy)oxetanes are successfully prepared from silyl enol ethers containing additional carbon-chlorine, carbon-silicon, or carbon-sulfur bonds (Scheme 9) [16ah, 56]. Ethers, esters, and simple alkenes are compatible with the reaction. When a β -alkyl-substituted silyl enol ether is used, a *trans* relationship between the C-2 and C-3 substituents in the oxetanes is observed.

This result does not depend on the geometry of the alkene. The products are obtained with high diastereoselectivity (dr 87:13 – 98:3) [57].



Scheme 9

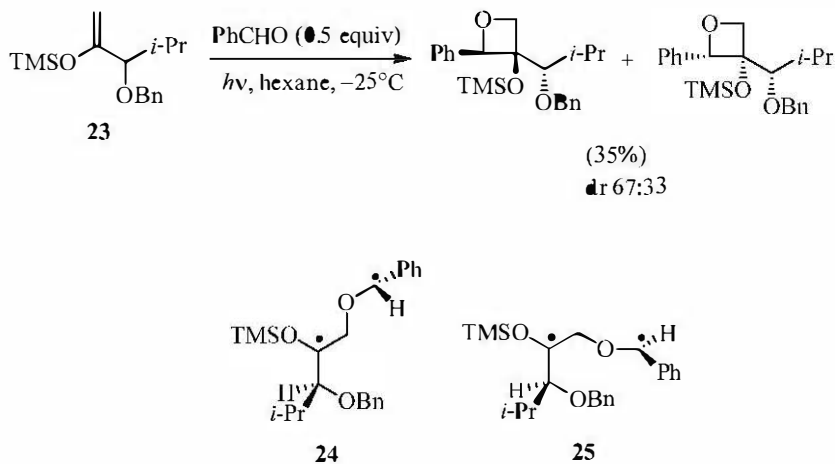


Scheme 10

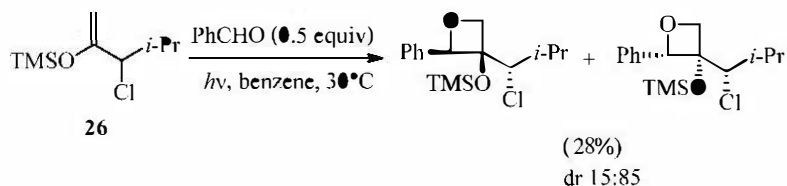
In the triplet biradical, free rotation leads to the sterically least congested conformation. A further reaction pathway of this species includes intersystem crossing (ISC) and an assumed selection step (cleavage vs. ring closure) at the singlet 1,4-biradical level, which accounts for the high diastereoselectivity at C-2/C-3.

The presence of a stereogenic center in the β -alkyl group induces facial diastereoselectivity. In some cases, high diastereoisomeric ratios are observed (Scheme 10) [58]. The observed diastereoselectivity probably arises because of a conformational preference represented in Scheme 10. This conformation allows the attack by benzaldehyde on the enol ether on the less shielded face [59].

Good diastereoselective results are obtained by using silyl enol ether **23**, which gives the corresponding adducts with a dr of 67:33 (Scheme 11), and compound **26**, giving the adducts with a dr of 15:85 (Scheme 12) [60]. In the former reaction, two conformers of the biradical intermediate can be obtained. Conformer **24** is calculated to be more stable than **25** by 3.11 kcal mol⁻¹) [61].

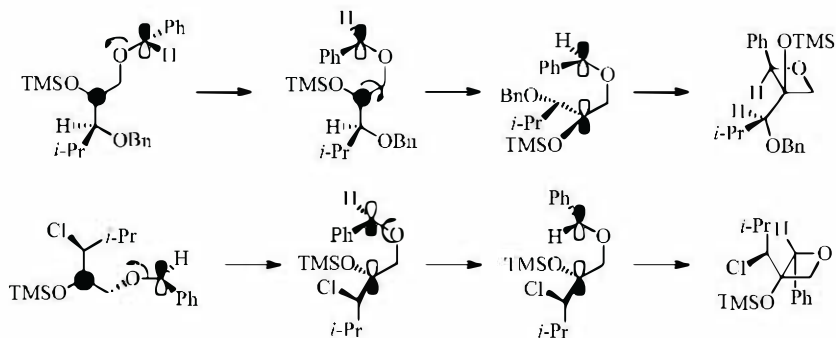


Scheme 11



Scheme 12

The LSO $\bullet\bullet$ of the biradical **24** is at -0.077 H, while the HSO $\bullet\bullet$ is at -0.073 H. The coupling of the radical carbon atoms gave two new orbitals in the product. The new orbitals are a σ orbital and a σ^* one. To obtain the σ orbital, considering the atomic coefficients at the radical carbon atoms on the involved orbitals, the coupling of these carbon atoms can occur only as depicted in Scheme 13, where the in-phase superposition of the p orbitals allows the formation of only one stereoisomeric product.

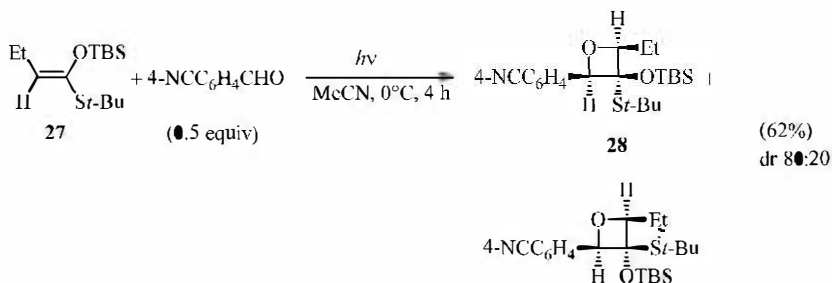


Scheme 13

Conformer **24** gives the major stereoisomer observed in the reaction (Scheme 13). The calculations are in agreement with the experimental results, showing that the course of this reaction is strictly frontier orbital controlled. The other biradical conformer (**25**) gives the other diastereoisomer which is observed in the reaction. The observed diastereoisomer ratio (67:33) can be explained by the small difference between the energies of the conformers of

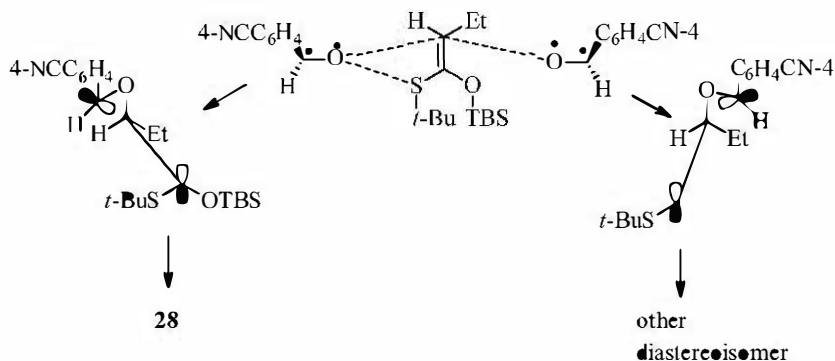
the biradical intermediate ($3.11 \text{ kcal mol}^{-1}$). To confirm this result, the behavior of **26** has been examined (Scheme 12). In this case, the authors observe an inverse diastereoselectivity [59b]. Also in this case, two conformers of the biradical intermediate are possible. The energy difference between these two conformers is $4.6 \text{ kcal mol}^{-1}$. The coupling between the carbon atoms, considering the atomic coefficients, allow the formation of the observed diastereoisomers, where the most stable conformer of the biradical intermediate is able to give the major observed diastereoisomeric product, while the other conformer of the biradical intermediate can give the minor observed diastereoisomeric product (Scheme 13). The larger diastereoisomeric ratio (85:15) observed in this case is in agreement with the larger energy difference between the conformers of the biradical intermediate.

When silyl \odot ,S-ketene acetal (*E*)-**27**, is used, **28** is obtained as the main product (Scheme 14) [62].

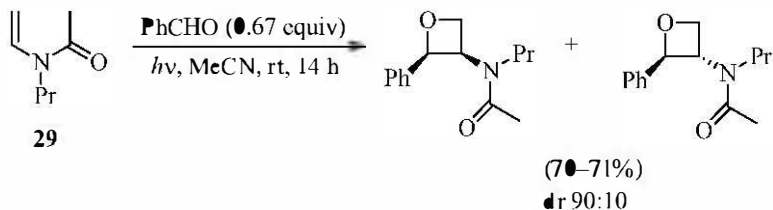


Scheme 14

The stereochemical behavior of the reaction of **27** with aromatic carbonyl compounds is explained by considering the ability of the sulfur atom to coordinate the oxygen atom of the carbonyl compound [62]. The presence of such an interaction induces attack of the excited carbonyl compound on the side of the alkene bearing the sulfur atom (Scheme 15). The same regio- and stereoselectivity is observed when silyl \odot ,Se-ketene acetals are used [63].

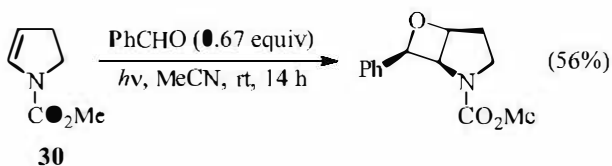


Scheme 15



Scheme 16

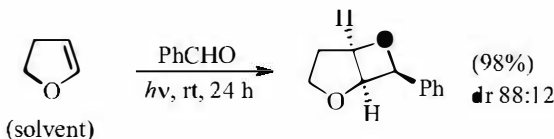
Oxetanes are obtained in the Paternò–Büchi reaction of *N*-acyl enamines **29** and **30**. *N*-Acyl derivatives are used to reduce the electron density of enamines without changing the electronic properties of the double bond (σ_{para} of $-\text{NH}_2$ group is -0.66 , while that of the $-\text{NHCMe}$ substituent is -0.15). These compounds give the corresponding adducts with high regio- and stereoselectivity (Schemes 16 [160, 64] and 17 [65]). The main product in each case is the thermodynamically less stable isomer [66].



Scheme 17

Sometimes, chiral enamine derivatives do not give the corresponding adduct with high diastereoselectivity [16r, 67]. For example, (*R*)-phenylethylamine reacts with acetaldehyde in the presence of acetic anhydride to give the corresponding *N*-acylenamine, that is irradiated in the presence of benzaldehyde to give the corresponding *cis*-oxetanes in 2:1 ratio [67].

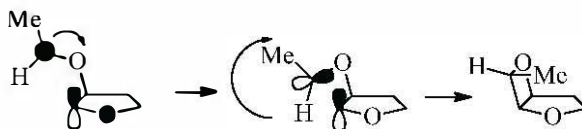
The Paternò-Büchi reaction of 2,3-dihydrofuran with benzaldehyde shows a significant *endo* stereoselectivity (Scheme 18) [68].



Scheme 18

When acetone is used as the carbonyl compound, the adduct with 2,3-dihydrofuran is obtained in 52% yield as a mixture of two constitutional isomers in a 200:1 isomeric ratio [69]. However, when acetaldehyde is used as the carbonyl compound, the adduct is obtained in 63% yield as a mixture of stereoisomers. The selectivity in this case depends on 2,3-dihydrofuran concentration, involving a switch from a triplet mechanism to a singlet mechanism at higher concentration [16u, 16v, 16z, 68e, 70]. The best interaction between the frontier orbitals is that from the LSO of acetaldehyde and the HOMO of 2,3-dihydrofuran [16am]. The atomic coefficients on the olefinic carbon atoms in 2,3-dihydrofuran are -0.26 at C-2 and -0.38 at C-3. The atomic coefficient on the oxygen atom in the LSO of singlet excited acetaldehyde is 0.48 , while the atomic coefficient at the C-1 of acetaldehyde in the HSO is 0.49 . The nature of the LUMO of 2,3-dihydrofuran excludes the possibility of a concerted mechanism. The reaction

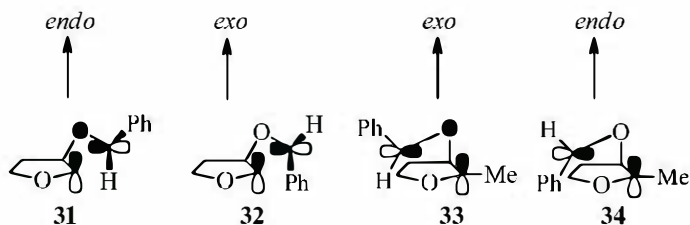
leads to the formation of an extremely reactive singlet biradical. In this case, the oxygen atom of acetaldehyde attacks the C-3 carbon atom in 2,3-dihydrofuran to give the more stable biradical intermediate. The reaction, in this case, allows the formation of only the *exo* isomer. This logical scheme explains the observed reactivity assuming that, when the reaction is performed in a concentrated solution, the excited singlet state will give the *exo* isomer, while the excited triplet state is responsible for the formation of the *endo* isomer. In the triplet state, the main interaction is that between the LSO• of the triplet state acetaldehyde and the HOM• of the dihydrofuran. This interaction leads to the formation of the corresponding C-C 1,4-biradical intermediate (Scheme 19). The HS• on the biradical intermediate is mainly localized on the aromatic ring. The LSO• is mainly localized on the dihydrofuran ring. Coupling between the radical carbons in these two orbitals to give the new σ orbital is possible only if the *endo* isomer is formed (Scheme 19).



Scheme 19

When benzaldehyde is used as the carbonyl component, the reaction with 2,3-dihydrofuran shows good regio- and stereoselectivity. The adducts are isolated with an overall yield of 98% as a >98:2 constitutional isomer mixture with the major isomer obtained as an 88:12 *endo/exo* mixture. The reaction of dihydrofuran with benzaldehyde is the first example where spin-controlled selectivity is observed [16v, 16ae]. In singlet photoreactions, stereoselectivity is often controlled by the optimal geometries for radical-radical combinations. By contrast, in triplet photoreactions, the optimal geometries are those able to favor the intersystem crossing from the triplet excited state to the singlet excited state. The singlet biradicals should be too short-lived to enable rotation about the endocyclic C-C or C-C bonds, and, therefore, conformational memory effects on the stereochemistry are expected. The geometries in the triplet state can be quite different from the former ones because of differences

of the spin-orbit coupling (SOC) values. The lifetimes of many triplet biradical intermediates are definitely high enough to enable bond rotations. Therefore, the formation of the thermodynamically favored product can be expected because the radical-radical combination step should not be influenced by the approach geometry. “Memory effects” should be erased because of the relatively long biradical lifetimes. After transition from the triplet to the singlet potential energy surface, immediate product formation is expected. Thus, the intersystem crossing (ISC) proceeds in a concerted fashion with the formation of a new bond or by cleavage of the primarily formed single bond. As a consequence, the stereoselectivity of the Paternò–Büchi reaction is the result of a combination of several rate constants for cyclization versus cleavage reactions.

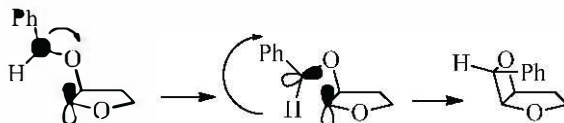


Scheme 20

Benzaldehyde reacts with 2,3-dihydrofuran in its triplet state and a triplet biradical intermediate is formed. To obtain the oxetane products, intersystem crossing into the singlet manifold is necessary. The most important factor influencing an intersystem crossing for flexible triplet biradicals is spin-orbit coupling. The angle between *p* orbitals at the radical centers is approximately 90° for maximum spin orbit coupling. For the pronounced *endo* selectivity in the reaction between aromatic aldehydes and 2,3-dihydrofuran, the two biradical conformers **31** and **32** can be considered to be responsible, **31** being more populated because of fewer steric interactions (Scheme 20).

When a methyl group at C-2 is present, the increasing *gauche* interactions with the β -alkyloxy substituent lead to a certain concentration of **33** and **34**, with **33** being preferred because of fewer steric interactions. Another explanation for the regio- and stereochemistry proposes that the HSOMO is mainly localized on the aromatic ring and the LSOMO is mainly localized on

the dihydrofuran ring [71]. Coupling between the radical carbons in these two orbitals to form a new σ orbital is thus possible only if the *endo* isomer is formed (Scheme 21).



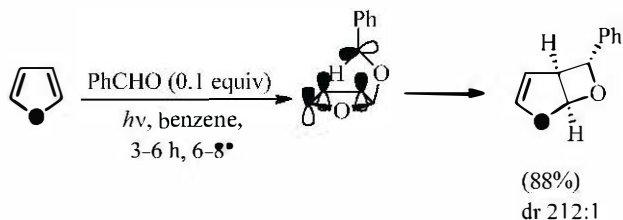
Scheme 21

α - and β -Naphthaldehydes, on the contrary, give high *exo* selectivity in the reaction with 2,3-dihydrofuran [72]. The cycloaddition occurs in the presence of triplet quenchers, while in the presence of 2,3-dihydrofuran fluorescence quenching is observed. In this case, the singlet excited state is responsible for the high *exo* selectivity [16z, 72], and the coefficients on the HSO and LSO allow coupling of the radical carbons to only give the *exo* isomer [61].

Furan and 2-methylfuran react with propanal and benzaldehyde [73]. In this case, the *exo* configuration at C-6 of the dioxabicyclo[3.2.0]heptene skeleton is observed [74]. Good regioselectivity is observed using silyl- and stamylfuran derivatives, and the reaction occurs on the less hindered side of the molecule [75]. When 2-silyloxyfuran is irradiated in the presence of aliphatic carbonyl compounds or with benzaldehyde, a 1:1 mixture of constitutionally isomeric products is formed. In contrast, when benzophenone is used, only the product derived from attack on the most hindered side of the molecule is formed. The same result is observed with acetone in a reaction where a low concentration of furan is used. In all these cases, *exo* selectivity is observed [76]. In contrast to the above reported data showing a good regioselectivity of the reaction of substituted furan derivatives with carbonyl compounds, 2-furylmethanol and the corresponding silyl ether give rise to low regioselectivity in the reaction with benzaldehyde [76, 77].

The high *exo* stereoselectivity of the reaction of furan with benzaldehyde has been extensively studied; the formation of the product occurs via a triplet 1,4-biradical which biradical must be converted (intersystem crossing) into a singlet biradical to give the product. To explain the pronounced *exo* stereoselectivity, a secondary orbital effect is postulated. Thus, an interaction

between the rather flexible α -oxy radical center and the allyloxy ring-localized radical most likely plays a major role to induce the observed stereoselectivity (Scheme 22) [16m, 68d].



Scheme 22

Considering the regioisomeric biradical intermediates **35** and **36** (Figure 2), resulting from the head-to-head and head-to-tail addition, respectively [71], the biradical **35** is calculated to be more stable than **36** by 16.5 kcal mol⁻¹.

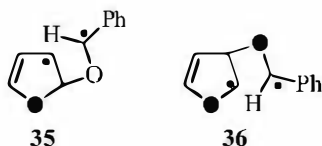


Figure 2. Possible biradical intermediates in the reaction of benzaldehyde with furan.

The HSOMO is mainly localized on the benzaldehyde fragment of the biradical, while the LSOMO is mainly localized on the furanoid part of the molecule. The coupling between the radical carbons in these two orbitals to form a new σ orbital can give only the *exo* isomer, in agreement with the experimental results (Figure 3).

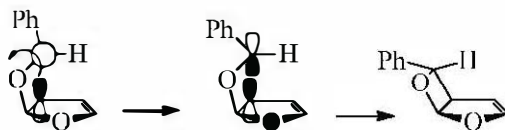
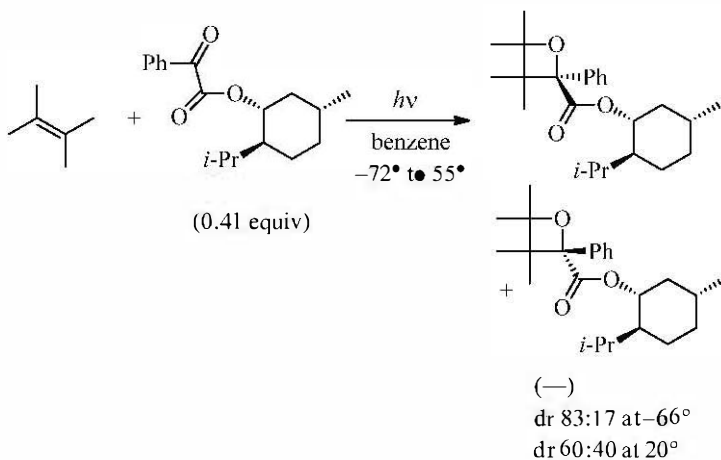


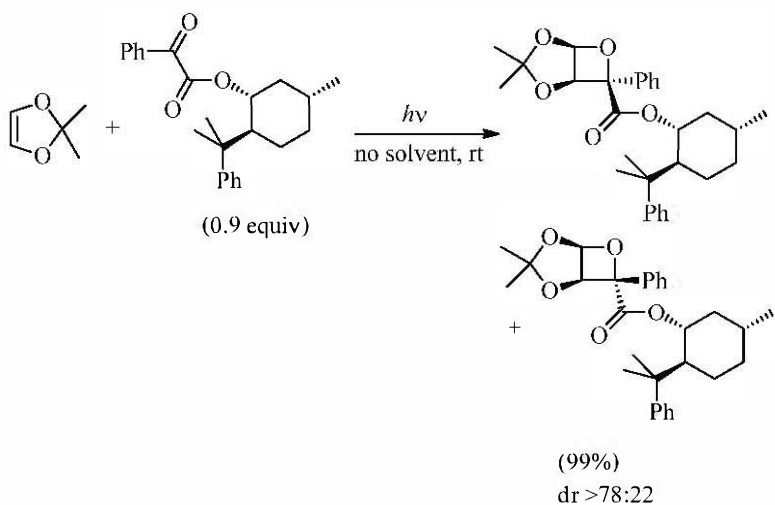
Figure 3. Rationale of the stereoselectivity of the reaction between benzaldehyde and furan.

Use of Chiral Auxiliaries. 2,3-Dimethyl-2-butene reacts with neomenthyl phenylglyoxylate in benzene to give the corresponding adduct with a dr of 83:17 at -66° (Scheme 23) [78].



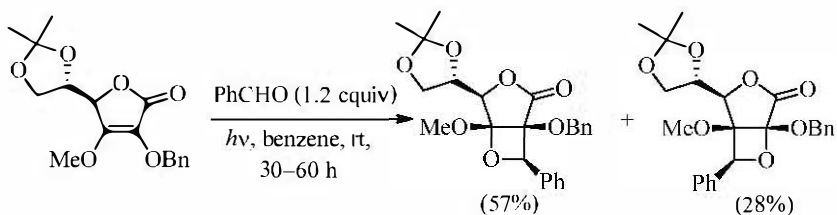
Scheme 23

The same type of reactions with chiral phenylglyoxylates are performed with 1,1-diphenylethene [79]. In this case, a good dr can be obtained (88.5:11.5), but the products are formed in very low yields. Better results are obtained by using enol ethers in reactions with chiral phenylglyoxylate derivatives (Scheme 24) [78a, 78b, 80].



Scheme 24

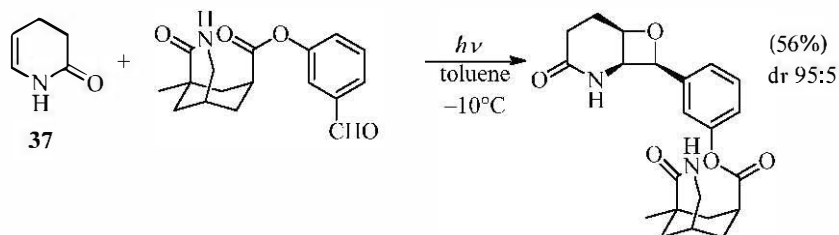
In some cases, the use of chiral enol ethers give results with good regio- and stereoselectivity in reactions with aromatic aldehydes (Scheme 25) [81].



Scheme 25

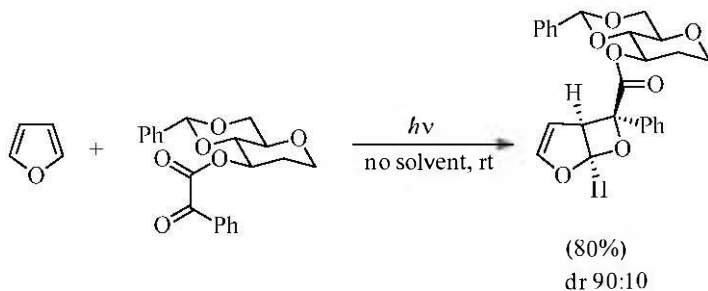
The reaction of cyclic enamide derivative **37** with a chiral aromatic aldehyde in toluene at -10° gives the corresponding adduct with high diastereoselectivity (Scheme 26) [82]. This result can be explained by assuming the presence of a hydrogen bond between the lactam moieties, thus

inducing the attack of the carbonyl compound on only one diastereotopic face of the alkene.

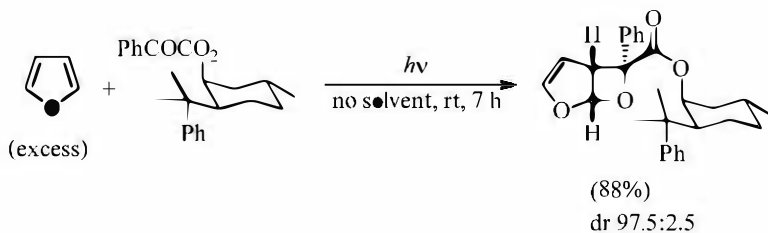


Scheme 26

Furan reacts with glyoxylate derivatives bearing chiral auxiliary groups in the alcoholic part of the molecule, giving the corresponding adducts [83]. However, only low selectivities are obtained. Chiral alkyl esters of phenylglyoxylic acid give the corresponding adducts with a low diastereoisomeric excess [84]. Better results are obtained when furan reacts with a phenylglyoxylate derivative esterified with a carbohydrate derivative (Scheme 27) [85] and β -phenylmenthol (Scheme 28) [84].

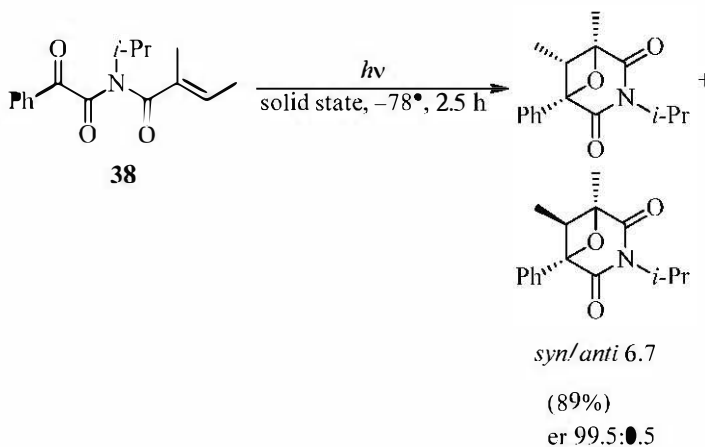


Scheme 27



Scheme 28

Chiral phenylglyoxylates also react with 2-furylmethanol derivatives, giving the corresponding adducts with high diastereoselectivity [84].

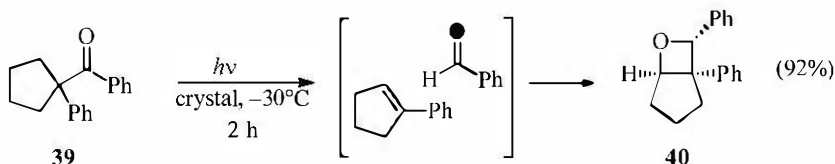


Scheme 29

Stereochemical Behavior in Organized Media. High diastereoselectivity can be obtained in intramolecular Paternò-Büchi reactions performed in the solid state. For example, the reaction of substrate **38** at -78° gives the corresponding product with a high enantiomeric excess (Scheme 29). The

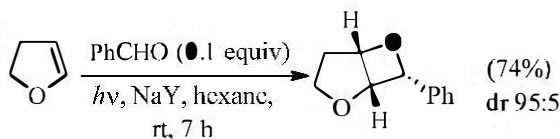
observed enantioselectivity is due to the fact that **38** crystallizes in a chiral space group [86].

The irradiation of crystalline ketone **39**, furnishes oxetane **40** with high diastereoselectivity (Scheme 30) [87]. In this case, the reaction requires an initial α -cleavage of the carbonyl group with the formation of an aldehyde and an alkene.



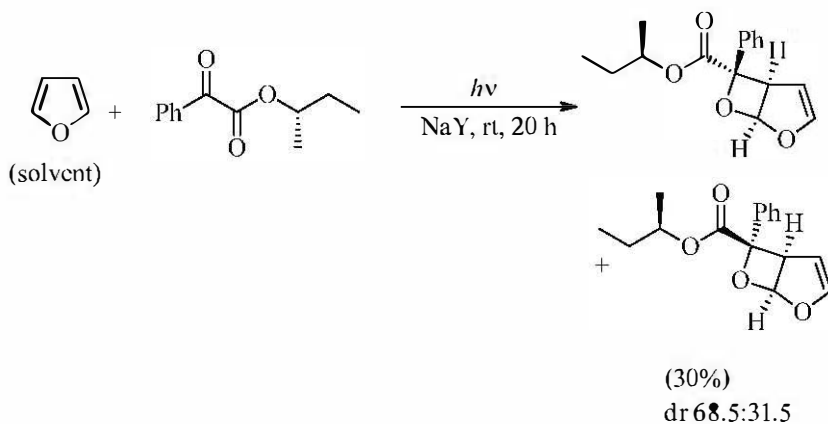
Scheme 30

The reaction of 2,3-dihydrofuran with benzaldehyde can be performed in NaY zeolite. The dr increases from 88:12, when the reaction is performed in benzene, to 95:5 when carried out in hexane (Scheme 31) [68g]. The reaction presumably occurs in the cavity of the zeolite where 2,3-dihydrofuran is adsorbed, and the dimension of the cavity allows the formation of the product with the smallest volume (the *exo* isomer occupies a larger volume in the cavity than the *endo* isomer).



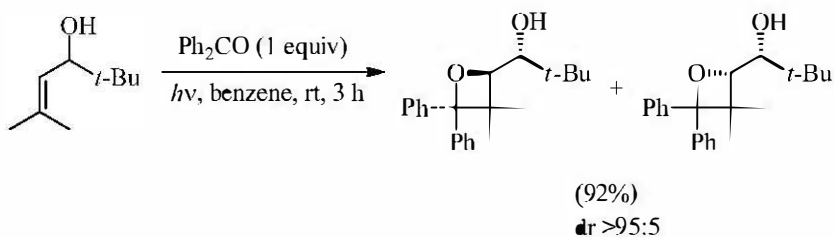
Scheme 31

Furan reacts with phenylglyoxylates bearing chiral auxiliary in the alcoholic part of the molecule in Y zeolites, showing that, when phenylglyoxylate ester is adsorbed on NaY, the dr increases from 57.5:42.5, when the reaction is performed in solution, to 68.5:31.5 (Scheme 32) [84, 88].



Scheme 32

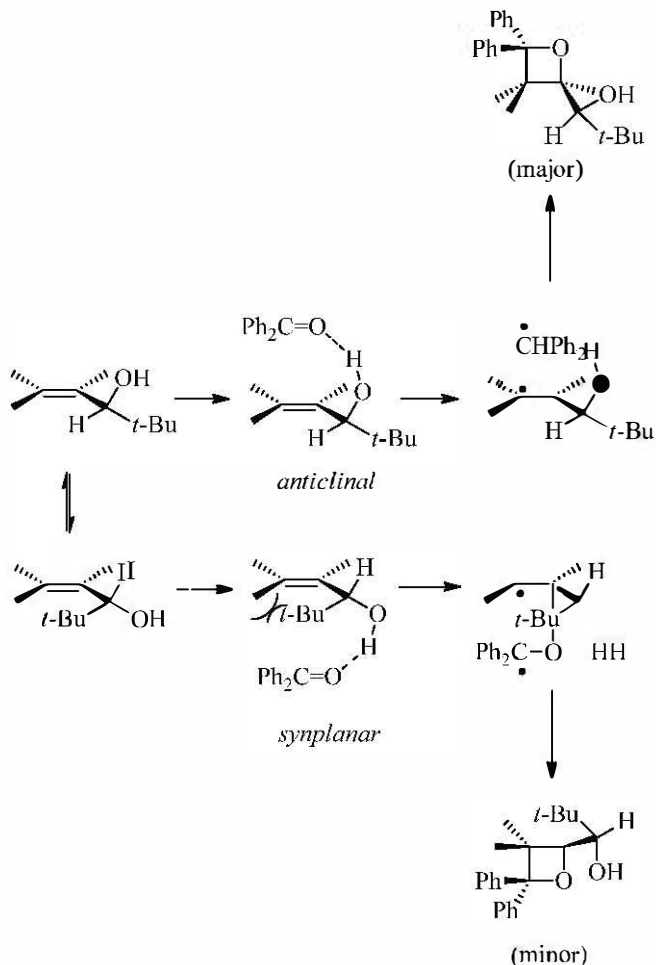
Hydroxyl Group Directing Effects. Reactions of benzaldehyde with homoallylic alcohols are not diastereoselective [16z]. However, allylic alcohols react with benzophenone to give the corresponding adducts with high regio- and diastereoselectivity (Scheme 33) [89].



Scheme 33

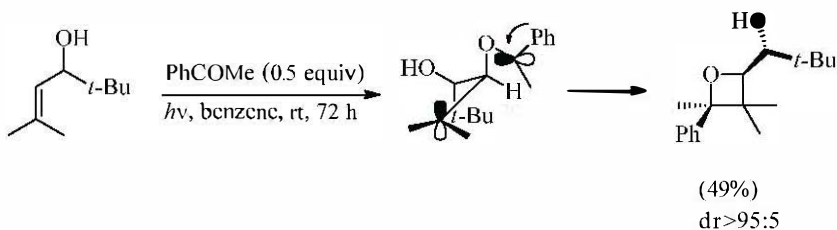
In the presence of methanol, the diastereoselectivity in this cycloaddition drops drastically, and disappears completely when using the corresponding silyl ethers. These data are in agreement with the presence of a hydroxyl

directing effect. Thus, the formation of a hydrogen bond between triplet excited benzophenone and the substrate in the exciplex favors the formation of the anticlinal isomer. In contrast, the formation of the synplanar stereoisomer is disfavored because of allylic strain (Scheme 34).

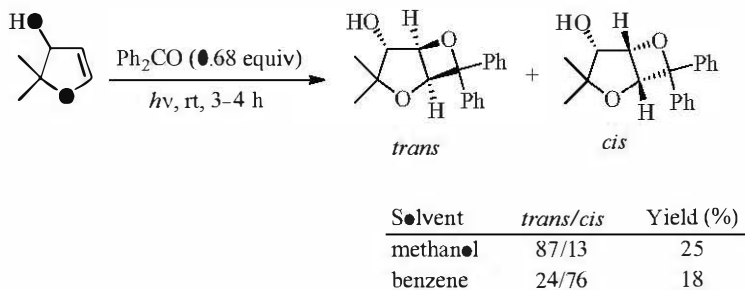


Scheme 34

Hydrogen bond-directed diastereoselective cycloadditions occur using a chiral enamide [82, 90] and in the reactions of cyclic allylic alcohols with benzophenone [91]. When unsymmetrical carbonyl partners such as acetophenone or benzaldehyde are used, the obtained oxetanes show the phenyl group and the alcoholic side chain in *cis* relationship and are obtained with high diastereoselectivity (Scheme 35). The regioselectivity is high with acetophenone (>95:5) but lower with benzaldehyde (59:41) [92].



Scheme 35

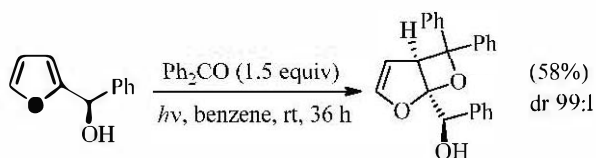


Scheme 36

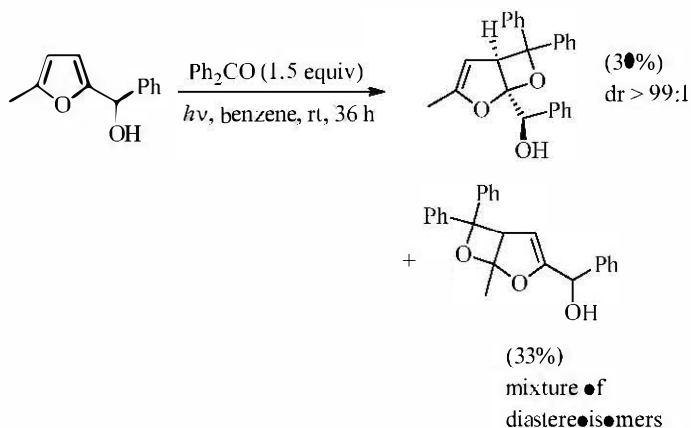
cis-Diastereoselectivity can be explained considering the conformation of the postulated triplet biradicals formed in the reaction [93]. Steric interactions are minimized when the biradical assumes the optimal conformation showed in the Scheme 35, and this conformation accounts for the formation of the observed stereoisomer [93].

The reaction of 2,3-dihydrofuran-3-ol derivatives (a type of allylic alcohol) with benzophenone gives the corresponding adducts. In methanol, a *trans* relationship between the oxetane ring and the hydroxyl group is observed, while in benzene, the *cis* isomer prevails (Scheme 36). An Eyring plot shows that the *trans* isomer proportion increases with a non-linear behavior upon decreasing the temperature [91].

The directing effect of alcohols was also tested on 2-furylmethanol derivatives. The furan ring can be considered as a particular case of electron rich alkene. In this case, the presence of large substituents on the carbon bearing the hydroxy group in the side chain of the furan ring allows high regioselectivity and stereoselectivity (Scheme 37) [94].

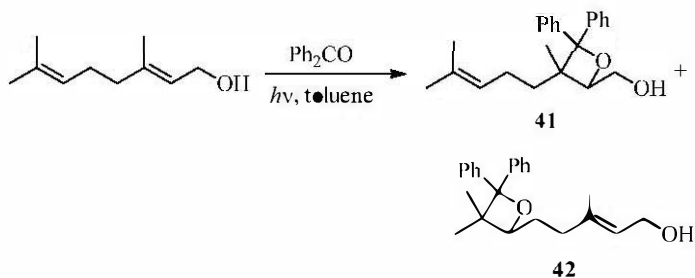


Scheme 37



Scheme 38

5-Methyl-2-furyl derivatives have been used as substrates to reveal features of the regioselectivity of the cycloaddition. 1-(5-Methyl-2-furyl)benzyl alcohol gives approximately a 1:1 mixture of constitutional isomers when irradiated in the presence of benzophenone (Scheme 38), and a single constitutional isomer (that obtained through the cycloaddition of the carbonyl compound on the furan double bond bearing the methyl group) in the presence of benzaldehyde [95]. In agreement with the results obtained with 2-furyl derivatives, the products deriving from the attack on the side bearing the hydroxy group are obtained as a single diastereomer, while those deriving from the attack on the side bearing the methyl group are obtained as a mixture of diastereomers.



Temp	41 Yield (%)	42 Yield (%)
-75	13	44
-40	14	38
2	16	26

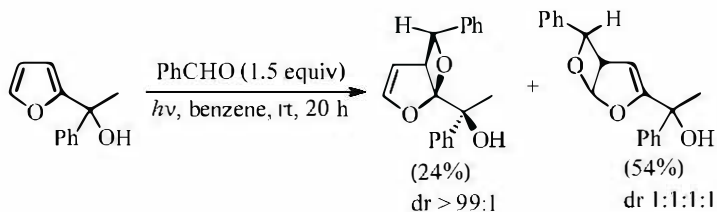
Scheme 39

The reactions described above with furans show that although two possible constitutional isomers can possibly be obtained, in some cases the reactions occur mainly on the side of a hydroxyl-bearing substituent group. The reason for this behavior is due to kinetic factors that depend on the differences in stability of the biradical intermediates. For example, in the substrate in Scheme 39, two different double bonds are present which can both give a tertiary radical intermediate. At -75° , oxetane **41** is obtained in 13% yield, while product **42** is obtained in 44% yield. Furthermore, at 20° , the yields are 15%

and 29%, respectively. In this case, then, the attack on the terminal double bond is favored [96]. These results are explained considering aggregation effects due to the temperature used in the reaction.

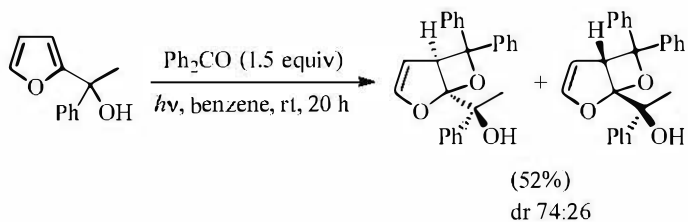
The reaction of 2-furylmethanol derivatives with aliphatic aldehydes and ketones gives the corresponding adducts with high regioselectivity: the reaction occurs on the most substituted side of the furan ring. However, no diastereoselectivity is observed [97]. The relative stability of the biradical intermediates rationalizes the regioselectivity of the reaction. A computational study (DFT) shows that the biradical obtained on the most substituted side of the furan ring is the more stable of the two.

The photochemical behavior of tertiary 2-furylcarbinols has been studied to help explain the observed stereoselectivity [98]. Irradiation of 1-methyl-1-phenyl-1-(2-furyl)methanol with benzaldehyde gives a mixture of two constitutionally isomeric products. The product of cycloaddition on the more substituted double bond is obtained in low yield, but shows complete diastereoselectivity. In contrast, the main adduct is a mixture of four diastereoisomeric products (Scheme 40).

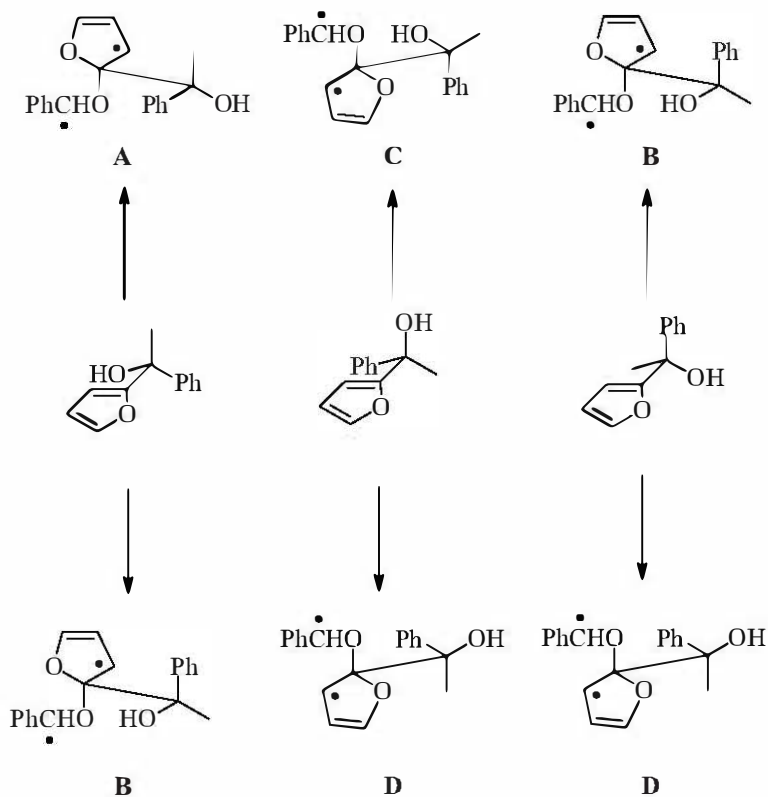


Scheme 40

The cycloaddition reaction of the same compound with benzophenone gives only the product deriving from attack on the more substituted double bond. This compound is obtained with 74:26 diastereoisomeric selectivity (Scheme 41).



Scheme 41



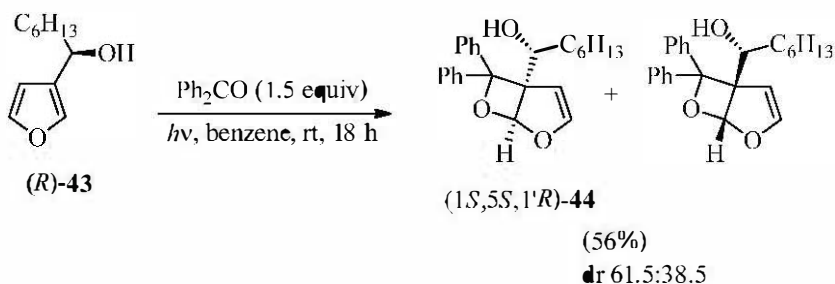
Scheme 42

The regioselectivity of the reaction reported in Scheme 41 is explained considering the relative stability of the biradical intermediates. In the reaction of 1-methyl-1-phenyl-1-(2-furyl)methanol with benzaldehyde (Scheme 40), the biradical obtained on the less substituted side of the substrate is calculated to be more stable than the other one by 18.03 kJ mol⁻¹. No relevant stereoselectivity is observed using 4,5,6,7-tetrahydrobenzofuran-7-ol derivatives, cyclic 2-furylcarbinol derivatives [99].

On the basis of these results, a rationale for the stereochemical behavior is proposed (Scheme 42) [84].

1-Methyl-1-phenyl-1-(2-furyl)methanol exists in three limiting conformations. The energies of all three conformers are in a range of 1.97 kJ mol⁻¹, and thus there is little conformational preference. The directing effect exerted by the hydroxyl group is attributed to the formation of a hydrogen bond between the hydroxyl group and the oxygen of the excited carbonyl compound, or to the formation of an exciplex. This type of interaction could favor the formation of a preferred conformation in the biradical intermediate in which the hydroxyl group and the oxygen of the carbonyl compound are in close proximity. These conformations could have different energies for different diastereoisomeric biradicals, providing an explanation of the observed behavior. In the case of 1-methyl-1-phenyl-1-(2-furyl)methanol, if the hydroxyl group directs the attack of the oxygen of the carbonyl group, the conformations of the biradical intermediate represented in Scheme 41 are obtained. When the hydroxyl group is perpendicular to the furan ring, only the conformers of the biradical intermediates derived by the attack of the carbonyl compound on the same side on the furan ring can be obtained. When the hydroxyl group is gauche to the furan ring, the attack of the carbonyl group can occur on both sides of the furan ring. Conformations **B** and **D** are preferred: calculations on these conformations show that there is an energy difference of 13.26 kJ mol⁻¹ between these two conformations. This difference accounts for the observed diastereoselectivity of the reaction. In the reaction of the same substrate with benzophenone, the corresponding conformers **B** and **D** show a difference energy of 7.79 kJ mol⁻¹; this difference is in agreement with the observed diastereoselectivity.

The same analysis can be used to rationalize the stereochemical behavior of the reaction of other furyl alcohols with benzophenone [100]. Thus, irradiation of (*R*)-**43** in the presence of benzophenone gives the (1*S*,5*S*,1'*R*)-isomer **44** as the major product (Scheme 43) [101].



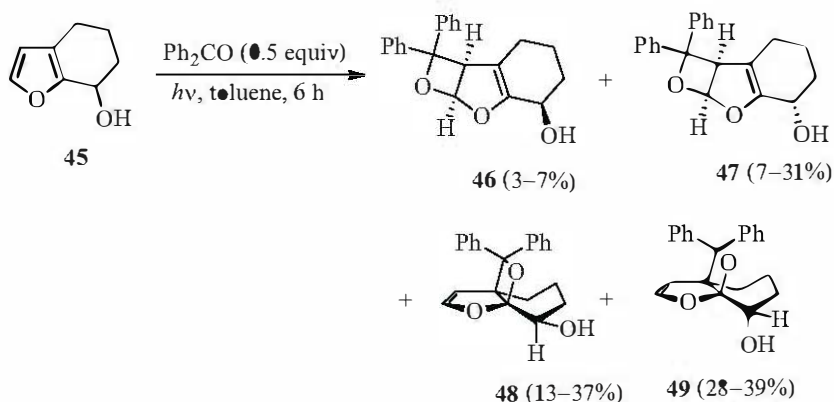
Scheme 43

Effects of Viscosity and Temperature. The *endo-exo* stereoselectivity in the Paternò–Büchi reaction between 2,3-dihydrofuran and some aldehydes has been studied in order to elucidate the effect of the change of both solvent viscosity and temperature [70]. An increase of viscosity induces a weak, but significant, increase in the *endo* selectivity. This result has been interpreted to be a consequence of the reduction in the diffusion rate in the triplet state. A study of the effect of the temperature on the *endo/exo* ratio plotted against $1/T$ gives curves showing inversion points. These results can justify that the cycloadduct is formed with low *exo* selectivity, assuming that the reaction occurs at room temperature under high concentration conditions. The *exo* selectivity increases when the temperature is decreased. After the inversion point, triplet reactivity induces an increased *endo* selectivity.

2,3-Dimethyl-2-butene reacts with chiral phenylglyoxylate esters to give the corresponding adduct with a dr of 83:17 when the reaction is performed at -66° , and a 60:40 ratio when the reaction is performed at 20° (Scheme 23) [78].

The effect of temperature on the stereoselectivity in the reaction of phenylglyoxylates with alkenes and furan has been studied [102]. The slope of the regression line obtained in this type of study is defined as the isoinversion temperature (T_i) and allows a description of the stereoselectivity of this reaction. In the high-temperature region ($T > T_{inv}$), mostly enthalpy-determined selection is observed. By contrast, in the low-temperature region ($T < T_{inv}$), entropy-determined selection is observed for the formation of the 1,4-biradical intermediate [102a]. This rule is important in explaining the observed stereochemical behavior at different temperatures.

More targeted studies can be found regarding temperature effects on the stereochemical course of benzophenone additions to alkenes. Among the four observed Paternò-Büchi products **46**–**49** in Scheme 44 using benzophenone and 2-hydroxycyclohexylfuran (**45**) [99a], isomers **46** and **48** are expected products resulting from the directing effects due to a benzophenone–OH hydrogen bond. Such hydrogen bonding is expected to be somewhat weak, having been evaluated by computational studies to be in the 2.1–3.2 kcal mol⁻¹ range between the $n \rightarrow \pi^*$ excited state of benzophenone and water [99b] and 4.5–6.0 kcal mol⁻¹ for the ground state. Because of the non-polar character of the solvent toluene, at low temperature extensive aggregation of the substrate **45** through OH---OH hydrogen bonds occurs. As a consequence, the yield of oxetane **48** is relatively low because of the “protection” of the OH group, and a higher yield of oxetane **47** results from benzophenone attack on the less-substituted side of the furan ring. At higher temperatures, aggregate formation is disfavored, and oxetane **47** becomes the predominant product.

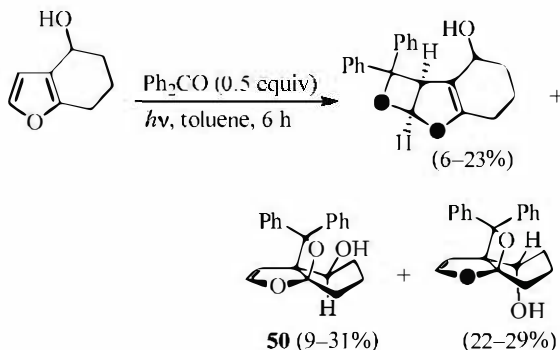


Scheme 44

The almost identical combined yield of the constitutional isomers **46** and **47** in comparison to **48** and **49** at -75° can be explained in the same way. Constitutional isomers **46** and **47** are derived from reactions of the furan ring not involved in aggregate formation. At higher temperature, in the absence of

strong aggregation, the normal preference on the more substituted furan double bond is again observed, so that **48** and **49** are preferred.

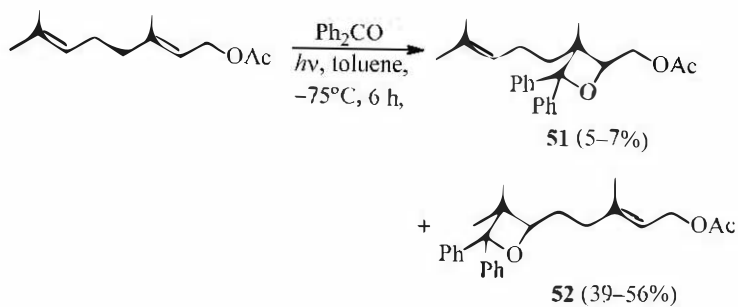
The same interpretation can be extended to the results obtained with 4-hydroxycyclohexylfuran (Scheme 45) [**99a**]. In this case, oxetane **50** is the result of the hydrogen bond-directed benzophenone cycloaddition, which is only possible when substrate aggregation is low (i.e. at higher temperature).



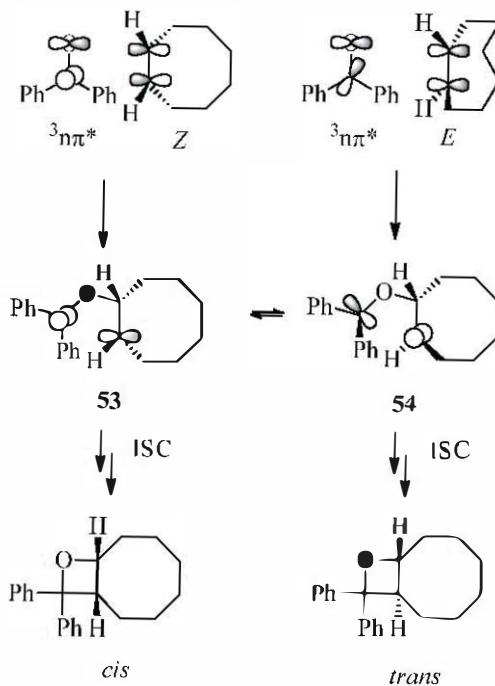
Scheme 45

Additional studies further support the aggregation effect discussed above (Scheme **39**) [**96**]. In this case, results at different substrate concentrations are compared with results at different temperatures. At higher concentrations, the substrate is expected to show a greater tendency towards aggregation. Thus, at -75° and 340 mM, the yield of the product **42** is more three-times that of the oxetane **41**. This result is probably due to the reaction on the double bond not involved in the aggregation. At 20° , the **41/42** ratio is significantly more favorable for **41**. At a concentration of 6.8 nM, aggregation is negligible, and similar yields of **41** and **42** are obtained, irrespective of the temperature.

When the substrate OH group is protected, as displayed in Scheme 46, the **51/52** ratio is constantly around $1/8$ both at 340 mM and at 6.8 nM, a fact that confirms the origin of the temperature dependence of the reaction regiochemistry [**96**].



Scheme 46



Scheme 47

Extensive studies have been carried out concerning the temperature dependence of the benzophenone photochemical cycloaddition to (*Z*)-cyclooctene [89b,103]. The diastereoisomeric ratio between *cis*- and *trans*-oxetanes shows a clear change going from low to high temperature. At low temperature, the *cis*-oxetane is observed almost exclusively. By increasing the temperature, an increase in the *trans*-oxetane fraction is observed.

In contrast, the reaction of (*E*)-cyclooctene with benzophenone shows little variation in stereochemical outcome versus temperature in analogous studies. The *trans*-oxetane is the only major stereoisomer produced in this case despite its lower stability compared to the *cis*-oxetane. These observations are explained on the basis of multiple reaction paths that can lead to interconversion of the biradical intermediates only at high temperature (Scheme 47) [103].

Starting from (*Z*)-cyclooctene and $n \rightarrow \pi^*$ -excited benzophenone (top-left of the scheme), two triplet-state biradical intermediates can be postulated using the correct orientation for a fast ISC (intersystem crossing) toward the oxetane ring as a guideline. Intermediate **53** is the first biradical produced. From **53**, an intersystem crossing process leads to the *cis*-oxetane isomer. The more stable triplet-state species **54** can be produced through internal rearrangement of **53**, but this process is kinetically disfavored at low temperature. At high temperature, **54** can be populated. Consequently, some *trans*-oxetane is formed. Starting from (*E*)-cyclooctene, the first-formed triplet-biradical intermediate is **54** and consequently the primary product is the *trans*-oxetane.

A very similar (although more detailed) explanation is proposed for the interpretation of related results obtained using (*E*)- and (*Z*)-1-methylcyclooctene [89b]. In this case, conformational equilibria in the biradical intermediates due to the presence of the methyl group at different temperatures explains the reported results.

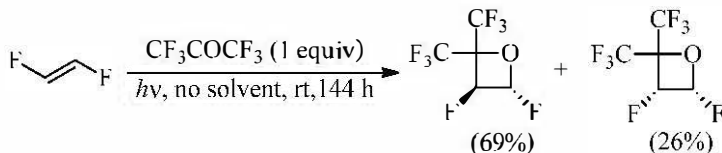
CHAPTER THREE

SCOPE AND LIMITATIONS

Intermolecular Reactions

Reactions with Electron-Poor Unsaturated Compounds. Although most of the work on the kinetic behavior of the alkenes when irradiated in the presence of carbonyl compounds have been performed on electron-poor alkenes, there is little data from a preparative point of view. Alkenes can be substituted with halogen atoms [104], cyano groups [23, 26a, 27, 32, 105], and carbonyl and carboxylic acid groups [23, 26a, 78c, 105k, 106]. In most of the cases, these compounds react only with aliphatic carbonyl compounds (Table 1). The reason for this behavior can be found in the interaction of the frontier orbitals: the HOMO of an electron-poor alkene shows a lower energy than an unsubstituted alkene, and it interacts better with the LUMO of the excited state of the carbonyl compound of an aliphatic carbonyl compound, which shows a lower energy than that of an aromatic carbonyl compound.

The observed yields in such Paternò-Büchi reactions are not very high. The reaction of tetrafluoroethene with acetaldehyde gives the corresponding oxetane in only 2.8% yield [104c]. However, (*E*)-1,2-difluoroethene reacts with hexafluoroacetone in good yields (Scheme 50) [104a]. The presence of halogen atoms on the alkene decreases the energy of the LUMO of the carbonyl compounds, allowing a better interaction. An oxetane is also obtained in the quenching of hexafluoroacetone by perfluoropropene [108].



Scheme 50

Table 1. Intermolecular reactions with electron-poor unsaturated compounds.


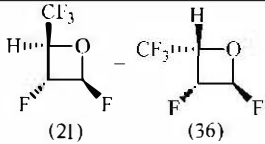

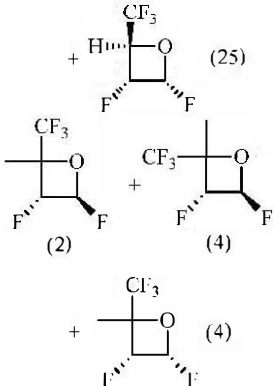
Alkene	Carbonyl compound	Product (yield %)	Ref.
	CF ₃ CHO (1 equiv)	 (21) (36)	104a
	CF ₃ COMe (0.99 equiv)	 (25) (2) (4)	104a

Table 1. *Continued*


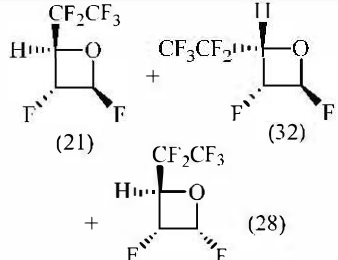

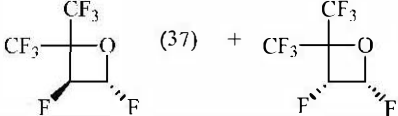
Alkene	Carbonyl compound	Product (yield %)	Ref.
	$\text{CF}_3\text{CF}_2\text{CHO}$ (1.01 equiv)	 (21) + (28) + (32)	104a
	CF_3COCF_3 (0.95 equiv)	 (37) + (38)	104a

Table 1. *Continued*


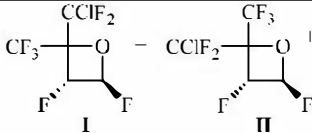
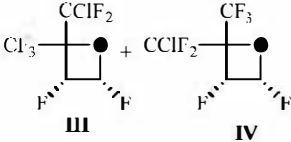

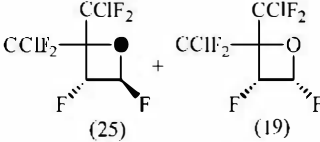

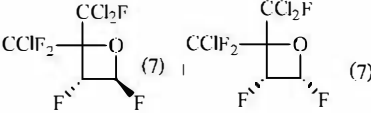
Alkene	Carbonyl compound	Product (yield %)	Ref.
	CClF ₂ COCF ₃ (1.04 equiv)	 I II	104a
		I + II (38), I/II = 1:1	
		 III IV	
		III + IV (38), III/IV = 1:1	
	CClF ₂ COCClF ₂ (1 equiv)	 (25) (19)	104a
	CCl ₂ FCOCClF ₂ (1.06 equiv)	 (7) (7)	104a
		1:1 1:1	

Table 1. *Continued*


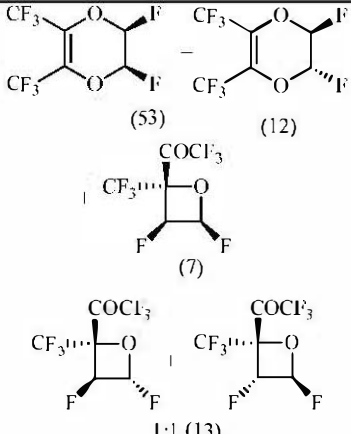

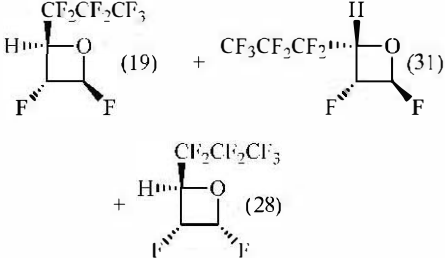
Alkene	Carbonyl compound	Product (yield %)	Ref.
	$\text{CF}_3\text{COCOCF}_3$ (0.99 equiv)		104b
	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CHO}$ (0.93 equiv)		104a

Table 1. *Continued*


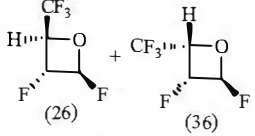
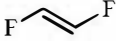
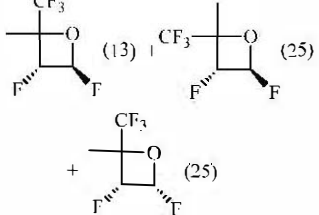
Alkene	Carbonyl compound	Product (yield %)	Ref.
	CF_3CHO (1.01 equiv)		104a
	CF_3COMe (1.01 equiv)		104a

Table 1. Continued


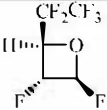
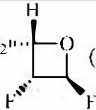
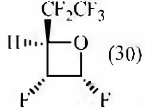
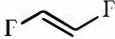
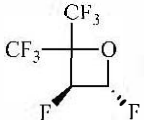
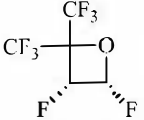
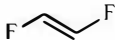
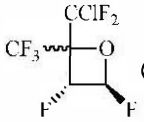
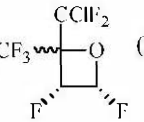

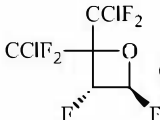
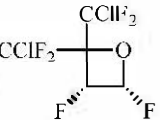
Alkene	Carbonyl compound	Product (yield %)	Ref.
	CF ₃ CF ₂ CHO (1.06 equiv)	 (23) +  (41)	104a
		+  (30)	
	CF ₃ COCF ₃ (1.0 equiv)	 (69) +  (26)	104a 108
	CClCF ₂ COCF ₃ (1.0 equiv)	 (62) +  (22)	104a
		1:1 1:1	
	CClF ₂ COCClF ₂ (1.0 equiv)	 (22) +  (7)	104a

Table 1. *Continued*

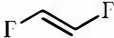
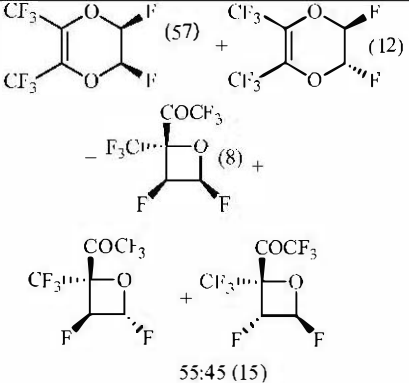
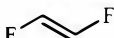
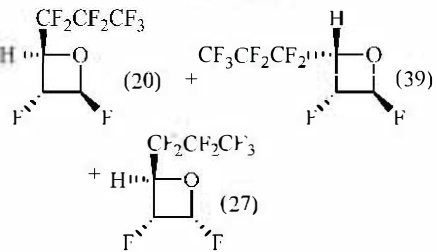
Alkene	Carbonyl compound	Product (yield %)	Ref.
	$\text{CF}_3\text{COCOCF}_3$ (0.99 equiv)		104b
	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CHO}$ (1.06 equiv)		104a

Table 1. *Continued*

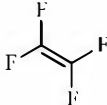
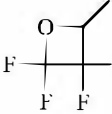
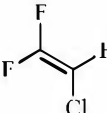
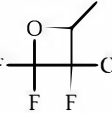
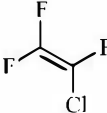
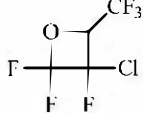
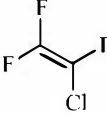
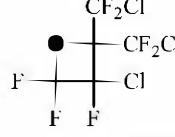
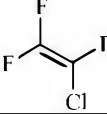
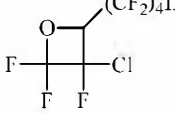
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCHO (1.0 equiv)	MeCOCF ₂ CF ₂ H (7.2) +  (2.8)	104c
	MeCHO (1.0 equiv)	MeCOCF ₂ CFClH (10) +  (4.1)	104c
	CF ₃ CHO (0.07 equiv)	 (14)	104d
	ClCF ₂ COCF ₂ Cl	 (11)	104d
	CHF ₂ (CF ₂) ₃ CHO (0.47 equiv)	 (15)	104d

Table 1. *Continued*


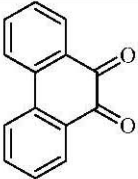
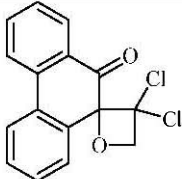


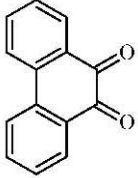
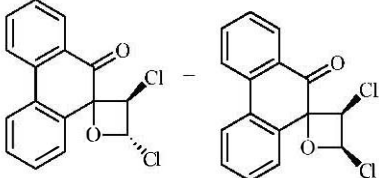


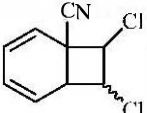
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.37 equiv)	 (31)	104e
	Ph ₂ CO	(—)	23
	 (0.008 equiv)	 (12) 1.6:1	104e
	MeCOCOMe (1 equiv)	(—)	105d
	PhCN (0.1 equiv)	 (27)	104f

Table 1. *Continued*

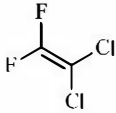
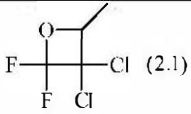
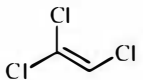
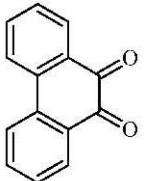
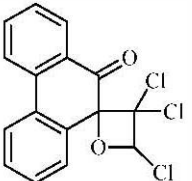
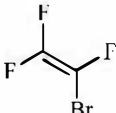
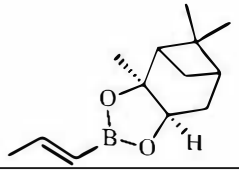
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCHO (1 equiv)	MeCOCF ₂ CCl ₂ II (5.5) –  (2.1)	104c
	 (0.009 equiv)	 (30)	104e
	MeCHO (1 equiv)	MeCOCF ₂ CFBrII (20.3)	104c
	Ph ₂ CO (3.7 equiv)	(—)	107

Table 1. *Continued*

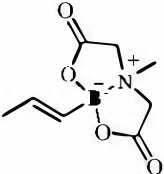
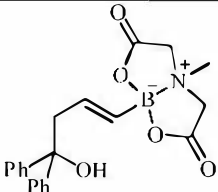

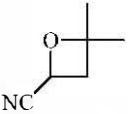

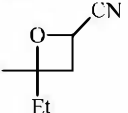

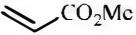
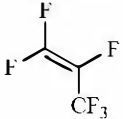
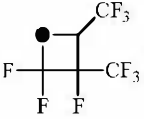
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO (3.7 equiv)	 (45)	107
	Me ₂ CO (0.9 equiv)	 (—)	27 105b 105c
	MeCOEt (0.9 equiv)	 (15)	105b
	MeCOCOMe (1 equiv)	(—)	105d
	Ph ₂ CO	(—)	23
	CF ₃ CHO (0.83 equiv)	 (32) 1:1 <i>cis-trans</i>	104d

Table 1. *Continued*

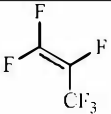
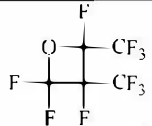
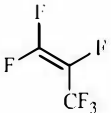
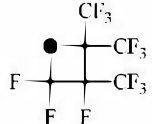
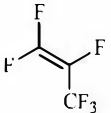
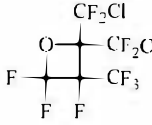
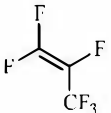
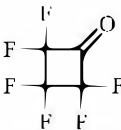
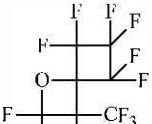
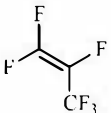
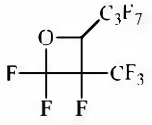
Alkene	Carbonyl compound	Product (yield %)	Ref.
	CF ₃ COF (0.76 equiv)	 (38) 65:35 <i>cis:trans</i>	104d
	CF ₃ COCF ₃ (0.82 equiv)	 (50)	104d
	ClCF ₂ COCF ₂ Cl (1.36 equiv)	 <u>irr. time</u> 7 days (39) 12 days (12)	104d
	 (0.57 equiv)	 (33)	104d
	C ₃ F ₇ CHO (0.73 equiv)	 (37)	104d

Table 1. *Continued*

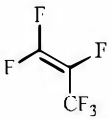
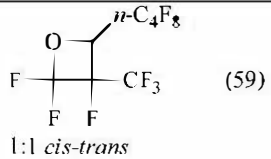
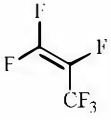
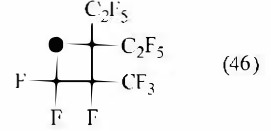
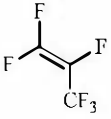
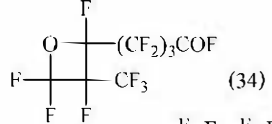
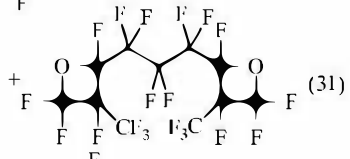
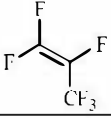
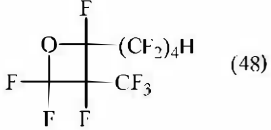
Alkene	Carbonyl compound	Product (yield %)	Ref.
	H(CF ₂) ₄ CHO (0.46 equiv)	 (59) 1:1 <i>cis-trans</i>	104d
	C ₂ F ₅ COC ₂ F ₅ (0.70 equiv)	 (46)	104d
	FCO(CF ₂) ₃ COF (0.7 equiv)	 (34)  (31)	104d
	H(CF ₂) ₄ COF (0.51 equiv)	 (48)	104d

Table 1. Continued

Alkene	Carbonyl compound	Product (yield %)	Ref.
	$C_3F_7COC_3F_7$ (0.49 equiv)	 (62)	104d
	$C_7F_{15}COF$ (0.29 equiv)	 (91)	104d
	Me_2CO (0.38 equiv)	 (42)	27 105b 105c
	$MeCOEt$ (0.35 equiv)	 (35)	105b
		 (34)	27 105b

Table 1. *Continued*


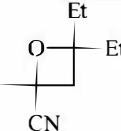

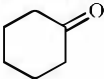
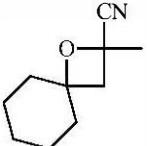

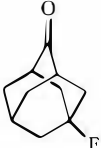
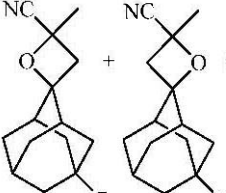
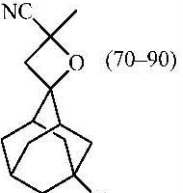
Alkene	Carbonyl compound	Product (yield %)	Ref.
	EtCOEt (0.35 equiv)	 (26)	27 105b
		 (55)	27 105b
	 (0.05 equiv)	 +  (70–90) 54:46	105e

Table 1. *Continued*


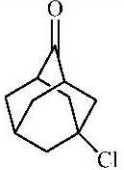
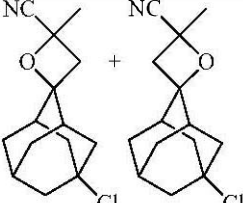

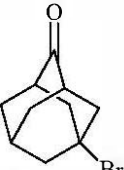
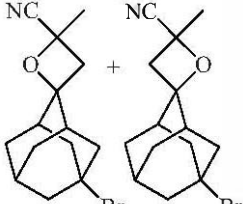
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.05 equiv)	 54:46 (70–90)	105e
	 (0.04 equiv)	 56:44 (70–90)	105e

Table 1. *Continued*


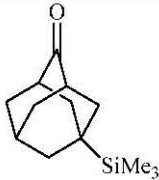
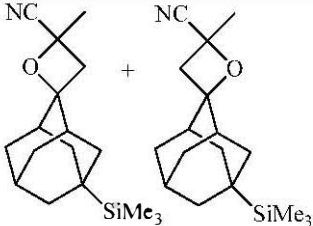

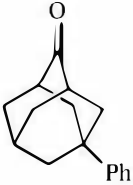
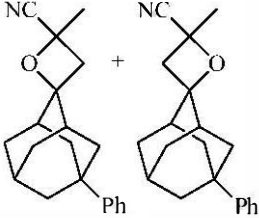
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 <p style="text-align: center;">52:48 (70-90)</p>	105e
		 <p style="text-align: center;">59:41 (70-90)</p>	105e

Table 1. Continued


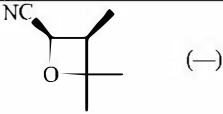

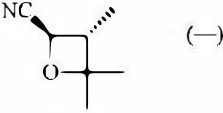

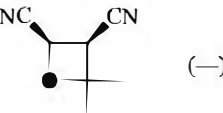
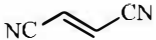
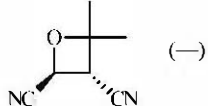
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (—)	105c
	Me ₂ CO	>98:2  (—)	105c
	Me ₂ CO	>98:2  (—)	105c
	Me ₂ CO	>99:1  (—)	26a

Table 1. *Continued*

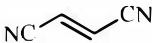
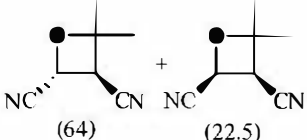

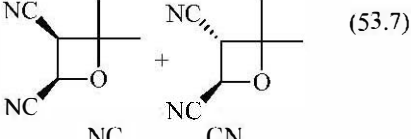
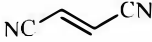
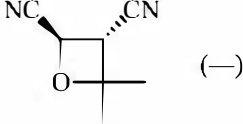
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (64) (22.5)	26a 105f
	Me ₂ CO (10 equiv)	 (53.7) (—)	105k
	Me ₂ CO	 (—) >99:1	105c

Table 1. Continued

Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (84) + (8)	105h
		 (70.2)	105k
		 (-)	26a
		 (53)	105k

Table 1. *Continued*

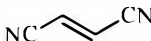
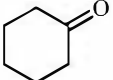
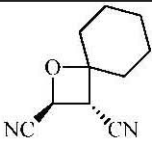
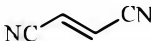
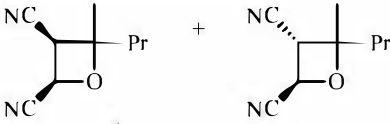
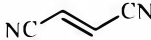
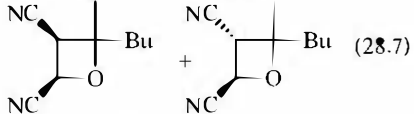
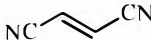

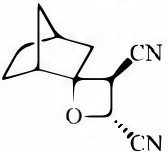
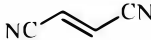
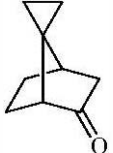
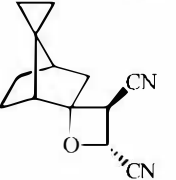
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (10 equiv)	 (—)	26a
	MeCOPr (10 equiv)	 (40)	105k
	MeCOBu (10 equiv)	 (28.7)	105k
		 (—)	32
		 (—)	32

Table 1. Continued

Alkene	Carbonyl compound	Product (yield %)	Ref.
			32
	Me ₂ CO		106a 26a 105k
			26a
			26a

Table 1. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO		106b
	Me ₂ CO		106b
			106c

Table 1. Continued

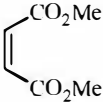
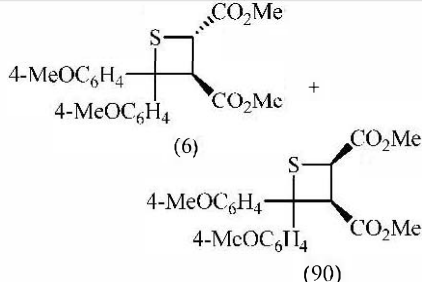
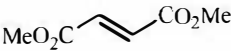
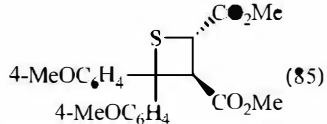
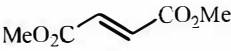
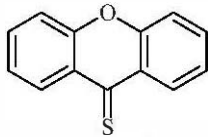
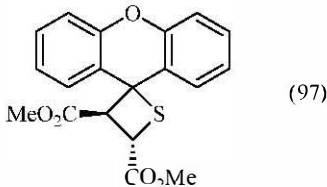
Alkene	Carbonyl compound	Product (yield %)	Ref.
	(4-MeOC ₆ H ₄) ₂ CS (0.12 equiv)	 (6) (90)	106c
	(4-MeOC ₆ H ₄) ₂ CS (0.25 equiv)	 (85)	106c
	 (0.2 equiv)	 (97)	106c

Table 1. *Continued*

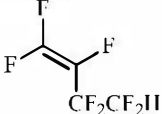
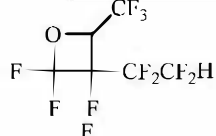
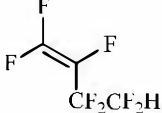
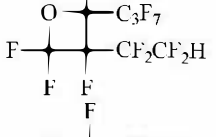
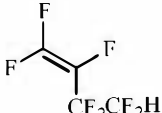
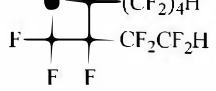
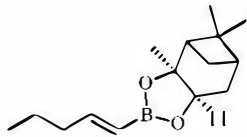
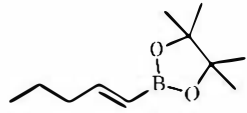
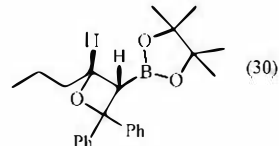
Alkene	Carbonyl compound	Product (yield %)	Ref.
	CF ₃ CHO	 (66)	104d
	C ₃ H ₇ COF (0.84 equiv)	 (35)	104d
	H(CF ₂) ₄ COF (0.51 equiv)	 (61)	104d
	Ph ₂ CO (3.7 equiv)	(—)	107
	Ph ₂ CO (3.7 equiv)	 (30)	107

Table 1. *Continued*

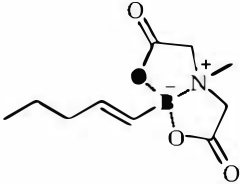
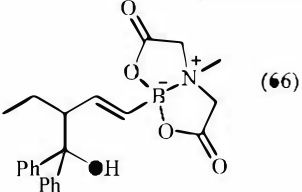
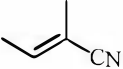
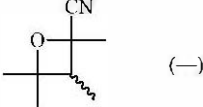
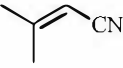
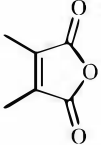
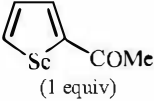
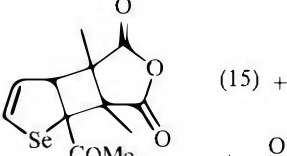
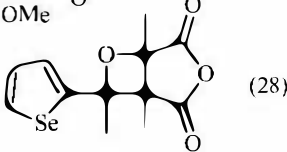
Alkene	Carbonyl compound	Product (yield %)	Ref.
	<p>Ph₂CO (3.7 equiv)</p>	 (66)	107
	<p>Me₂CO (10 equiv)</p>	 (—)	105b
	<p>Me₂CO (10 equiv)</p>	(—)	105b
	 <p>COMe (1 equiv)</p>	 (15) +	106d
		 (28)	

Table 1. *Continued*

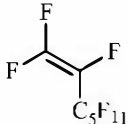
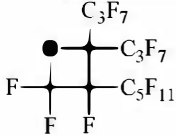
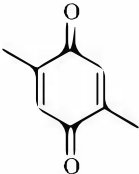
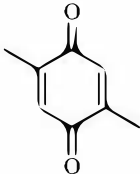
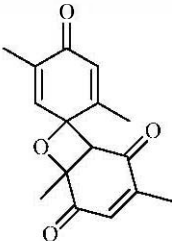
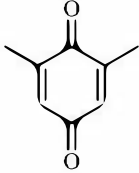
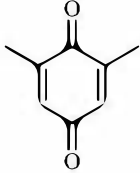
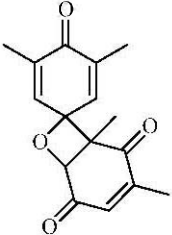
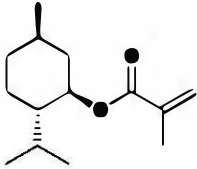
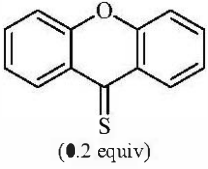
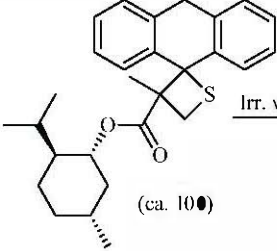
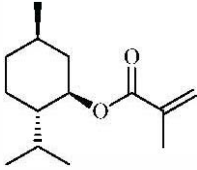
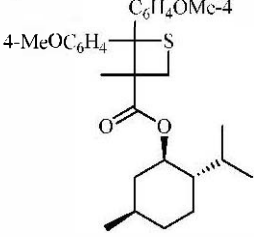
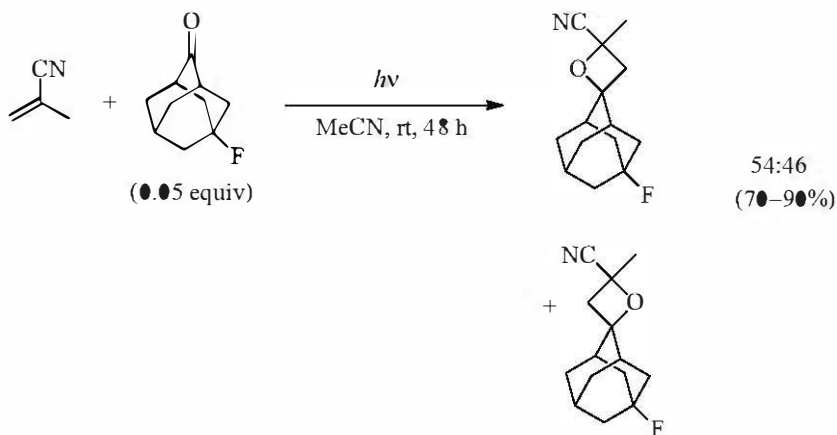
Alkene	Carbonyl compound	Product (yield %)	Ref.
	$\text{C}_3\text{F}_7\text{COC}_3\text{F}_7$ (1 equiv)	 (32)	104d
		 (—)	106e
		 (—)	106e

Table 1. Continued

Alkene	Carbonyl compound	Product (yield %)	Ref.						
	 (0.2 equiv)	 (ca. 100)	106f <table border="1"> <thead> <tr> <th>Irr. wavelength [nm]</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>589</td> <td>59:41</td> </tr> <tr> <td>400</td> <td>53:47</td> </tr> </tbody> </table>	Irr. wavelength [nm]	dr	589	59:41	400	53:47
Irr. wavelength [nm]	dr								
589	59:41								
400	53:47								
	(4-MeOC ₆ H ₄) ₂ CS (0.2 equiv)	 ()	106f <table border="1"> <thead> <tr> <th>Irr. wavelength [nm]</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>589</td> <td>59:41</td> </tr> <tr> <td>400</td> <td>53:47</td> </tr> </tbody> </table>	Irr. wavelength [nm]	dr	589	59:41	400	53:47
Irr. wavelength [nm]	dr								
589	59:41								
400	53:47								

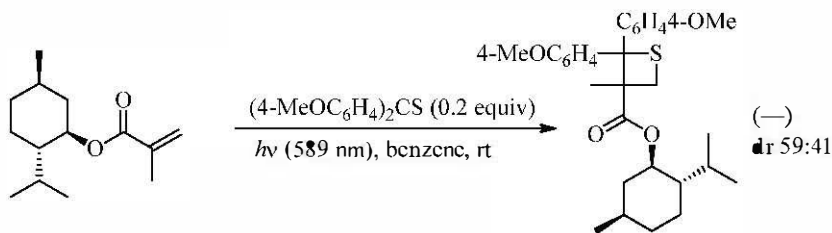
In some cases, the Paternò-Büchi reaction fails: for example, the reaction of (*E*)-1,2-dichloroethene with 2,3-butanedione does not give the oxetane [105d], and the same result is obtained in the reaction of (*Z*)-1,2-dichloroethene with benzophenone [23]. Acrylonitrile does not react with 2,3-butanedione [105d], and the reaction fails also in the reaction of 1-cyano-2,2-dimethylethene with acetone [105b].

As described above, in the reaction of electron-poor alkenes with aliphatic carbonyl compounds the reaction occurs through the first excited singlet state, and high stereoselectivity (see Scheme 50) is observed, in agreement with a concerted or quasi-concerted reaction. The presence of a methyl group, with its electron-donating properties, on electron-poor alkenes increases reactivity, allowing access to the corresponding oxetanes in very good yields (Scheme 51) [105e].



Scheme 51

Attempts to effect diastereoselective reactions using chiral, substituted acrylic esters in a Paternò-Büchi reaction with aromatic thioketones, such as 4,4'-dimethoxythiobenzophenone or xanthione, are not particularly successful (Scheme 52) [106f, 78c].



Scheme 52

Reactions with Electron-Rich Unsaturated Compounds. In this section we can find the interaction of carbonyl compounds with several types of double bond.

Reactions of Carbonyl Compounds with Alkenes, Dienes, and Alkynes. Alkyl- and aryl-substituted alkenes react well with aliphatic and aromatic carbonyl compounds. However, using acetone as the carbonyl substrate, very low yields of oxetanes are observed [109]. The regiochemistry of these reactions is in agreement with the formation of the most stable biradical intermediates [23, 110]. Sometimes the most hindered product is obtained [111], but this behavior is not general [112]. In some cases, a metathesis reaction product of the oxetane is prevalent [113]. Thus, the use of 2,3-dimethyl-2-butene as the alkene in the presence of acetone, 2,3-butanedione, or methyl glyoxylate furnishes products derived from the ring opening of the resulting oxetanes [105d, 114]. When acenaphthene is the alkene, ring enlargement products are obtained [115]. The Paternò-Büchi reaction can compete with a [2+2] alkene cycloaddition when the carbonyl compound contains an alkene (Table 2) [116].

The reaction of cyclopentadiene with acetaldehyde allows the stereoselective synthesis of the *exo* oxetane when acetaldehyde is the carbonyl compound and the *endo* oxetane when benzaldehyde is used (Scheme 53) [68d, 117]. The reaction of (*E*)- β -methylstyrene with acetaldehyde affords the corresponding oxetane with high stereoselectivity, probably via the singlet excited state (Scheme 54) [78c].

Table 2. Intermolecular reactions with electron-rich unsaturated compounds. A. Alkenes and dienes.


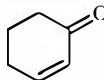
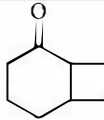
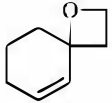

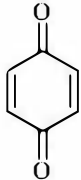

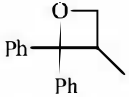



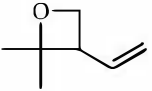
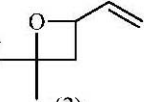

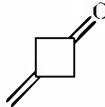
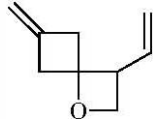
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (90) +  (—)	118
		No reaction	119
	Ph ₂ CO	 (5)	23
	Me ₂ CO	 (10)	109a
	Me ₂ CO	 (8) +  (2)	109c 120
	 (0.1 equiv)	 (17)	121

Table 2. *Continued*


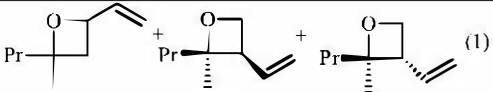

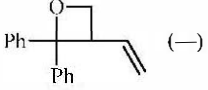

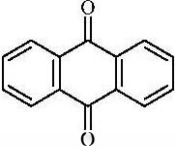




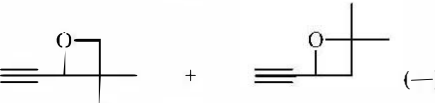

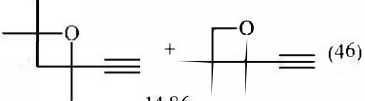
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCOPr	 (1)	109c
	Ph ₂ CO (0.36 equiv)	 (-)	122
		No reaction	123
	Me ₂ CO	 (-) 4.5:1	124
		 (-) 10:3.4	110a
	MeCOCCH	 (46) 14.86	110a 110b

Table 2. *Continued*


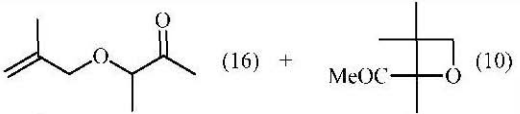

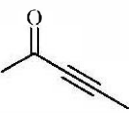
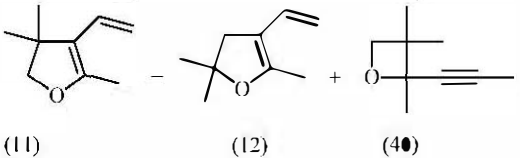


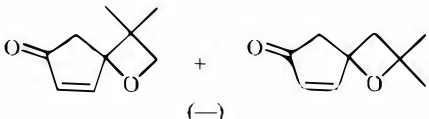

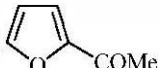
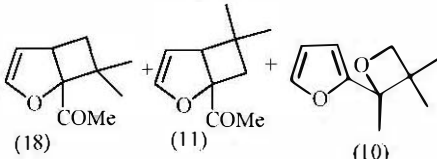


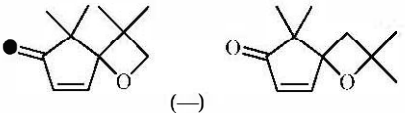
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCOCOMe		105d
			125
			126
	 (0.06 equiv)		127
			126

Table 2. Continued


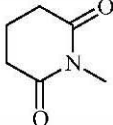
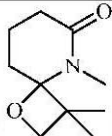

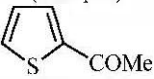
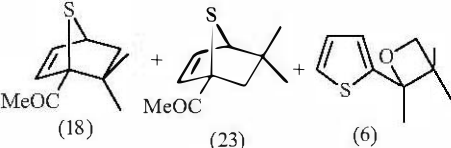

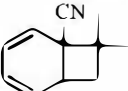

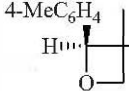

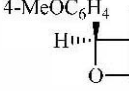

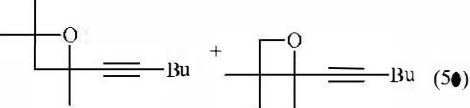
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.2 equiv)	 (71)	128
	 (0.06 equiv)	 (18) (23) (6)	127
	PhCN (0.1 equiv)	 (42)	105f
	4-MeC ₆ H ₄ CHO (0.24 equiv)	 (—)	129
	4-MeOC ₆ H ₄ CHO (0.24 equiv)	 (—)	129
	MeCOCCBu	 (50)	110b

Table 2. *Continued*


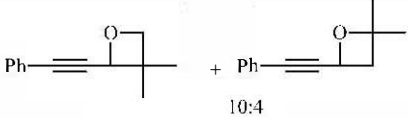

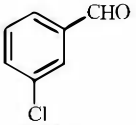
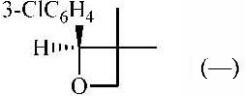

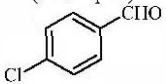
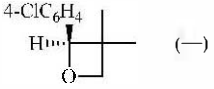

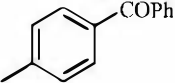
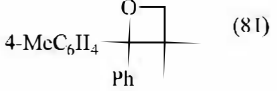

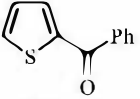
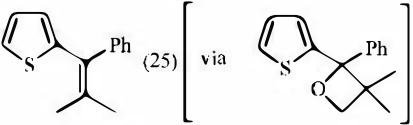

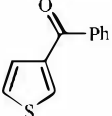
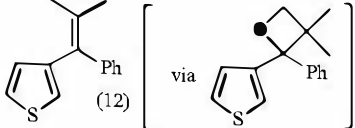
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph—C≡C—CHO		110a
	 (0.24 equiv)		129
	 (0.24 equiv)		129
			23
	 (0.01 equiv)		113a
			113a

Table 2. Continued


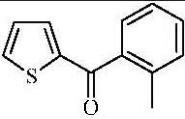
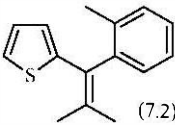
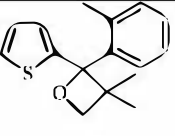

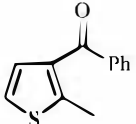
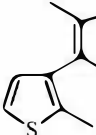
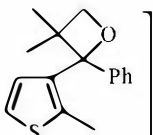

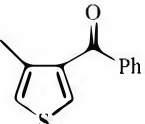
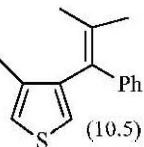
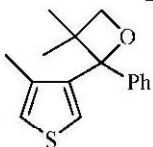

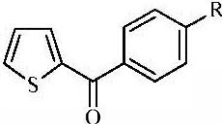
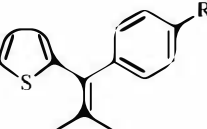
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (7.2) [via ]	130
		 (11.5) [via ]	113b
		 (10.5) [via ]	113b
		 R Temp CN rt (77) OMe 10 (5)	113a

Table 2. *Continued*


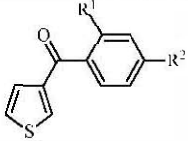
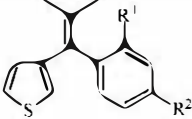

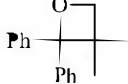


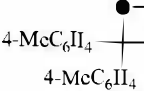

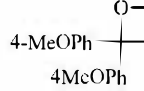

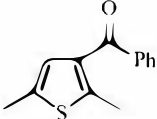
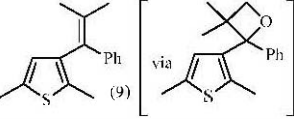
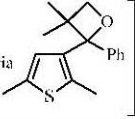
Alkene	Carbonyl compound	Product (yield %)	Ref.																
		 <table border="1" data-bbox="1027 232 1311 349"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Temp</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>CN</td> <td>10</td> <td>(90)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>rt</td> <td>(12)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>10</td> <td>(4.5)</td> </tr> </tbody> </table>	R ¹	R ²	Temp		H	CN	10	(90)	OMe	H	rt	(12)	H	OMe	10	(4.5)	<i>113a</i>
		R ¹	R ²	Temp															
		H	CN	10	(90)														
OMe	H	rt	(12)																
H	OMe	10	(4.5)																
			<i>113b</i>																
	Ph ₂ CO	 (93)	23																
	4-H ₂ NC ₆ H ₄ COPh	No reaction	23																
	(4-Me ₂ NC ₆ H ₄) ₂ CO	No reaction	23																
	(4-MeC ₆ H ₄) ₂ CO	 (74)	23																
	(4-MeOC ₆ H ₄) ₂ CO	 (80)	23																
		 (9) [via ]	<i>113b</i>																

Table 2. *Continued*


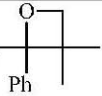

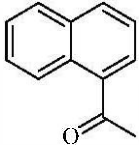

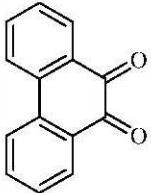
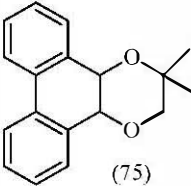
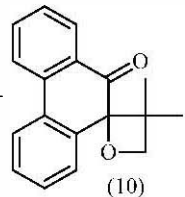

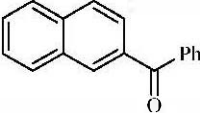

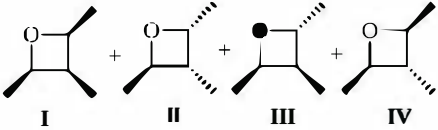
Alkene	Carbonyl compound	Product (yield %)	Ref.
	4-ClC ₆ H ₄ COPh	4-ClC ₆ H ₄  (76)	23
		No reaction	23
		 (75) +  (10)	131
		No reaction	23
	MeCHO		111
		(-) I:(II+III):IV 48.1:40.6:11.3	

Table 2. Continued.


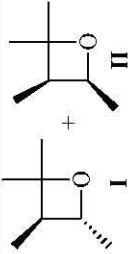

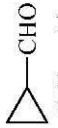
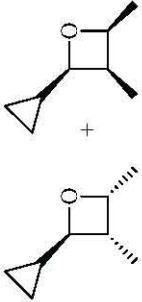

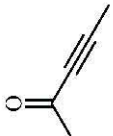
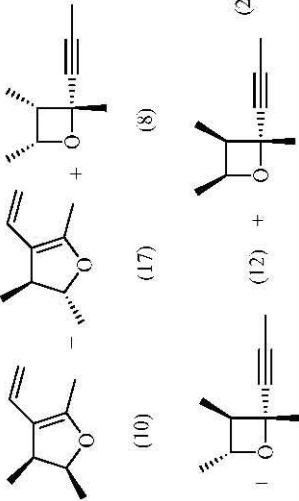
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO		124
	 (0.01 equiv)	(-), I/II = 1.61 	105h
			125

Table 2. Continued


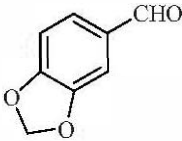
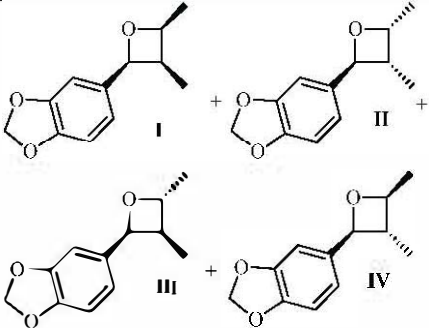

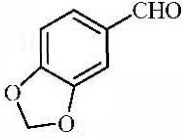
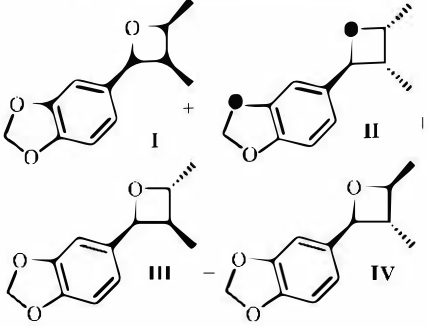
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 <p data-bbox="932 557 1232 576">(42) I:II:III:IV 41:22.8:10.7:25.5</p>	111
	 <p data-bbox="577 725 683 744">(0.02 equiv)</p>	 <p data-bbox="865 935 1171 954">(50) I:II:III:IV 36.6:24.1:7.9:31.4</p>	111

Table 2. *Continued*


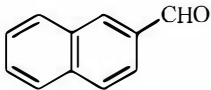
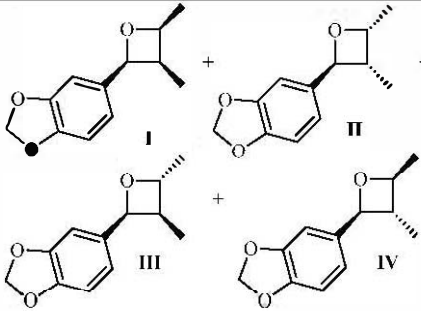

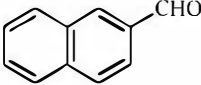
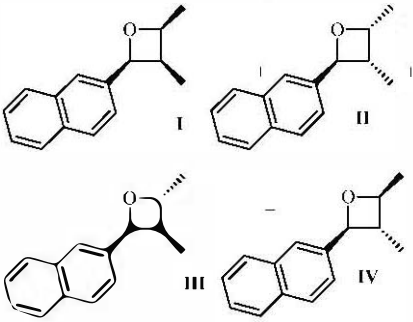
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 <p style="text-align: center;">(0.02 equiv)</p>	 <p style="text-align: center;">I:II:III:IV 36.6:24.1:7.9:31.4 (50)</p>	111
		 <p style="text-align: center;">I:II:III:IV 42.3:36.6:2.9:18.2 (57)</p>	111

Table 2. *Continued*


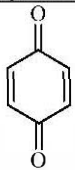
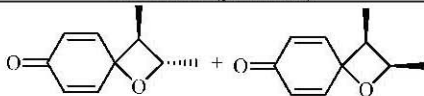

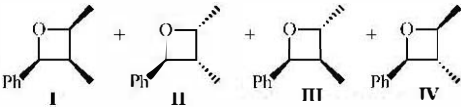

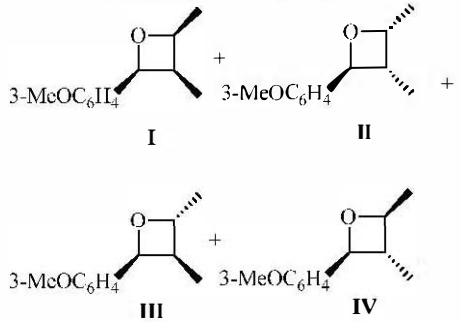
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 9:1 (-)	112
	PhCHO (0.4 equiv)	 I + II + III + IV I:II:III:IV 32.5:5:18.5:44 (64-68)	111
	3-MeOC ₆ H ₄ CHO	 I + II + III + IV I:II:III:IV 30:3.6:19.1:47.3 (59-63)	111

Table 2. *Continued*


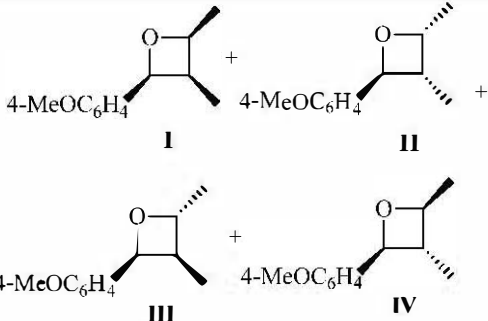

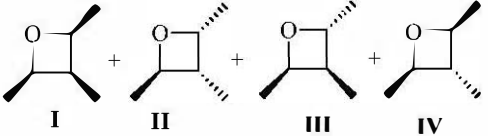

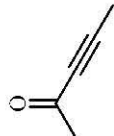
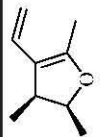
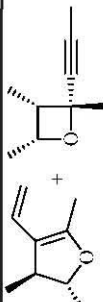
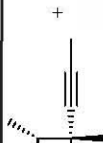

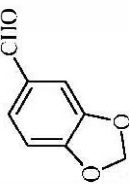
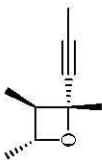
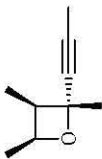
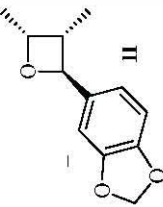
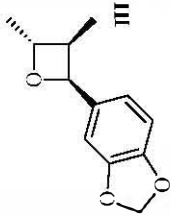
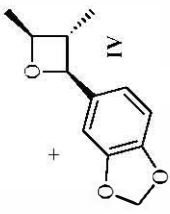
Alkene	Carbonyl compound	Product (yield %)	Ref.
	4-MeOC ₆ H ₄ CHO	 <p style="text-align: center;">I II</p> <p style="text-align: center;">III IV</p> <p style="text-align: center;">I:II:III:IV 28.2:4.9:17.2:49.7 (43-53)</p>	111
	MeCHO (0.12 equiv)	 <p style="text-align: center;">I II III IV</p> <p style="text-align: center;">I:(II+III):IV 4.6:42.2:53.4 (—)</p>	111

Table 2. Continued

Alkene	Carbonyl compound	Product (yield %)	Ref.
		 +  +  (7) (4) (2)	125
		 (19) +  (1) +  (II) +  (III) +  (IV)	111

I:II:III:IV 13:7:3:6:30.5:52.2 ()

Table 2. *Continued*


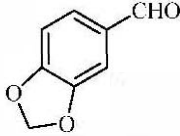
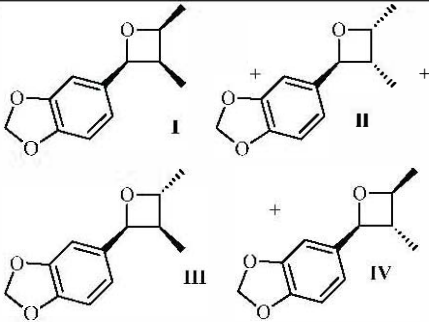

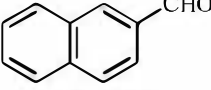
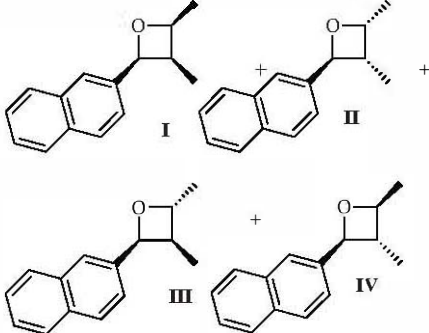
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 <p>(0.02 equiv)</p>	 <p>I:II:III:IV 15.1:5.5:28.2:51.2 (55)</p>	111
	 <p>(0.03 equiv)</p>	 <p>I:II:III:IV 3.2:3.2:36.2:57.4 (39)</p>	111

Table 2. Continued


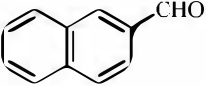
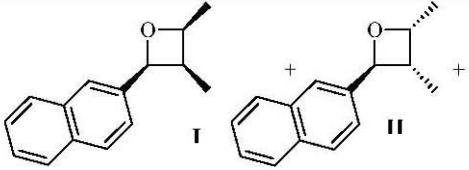
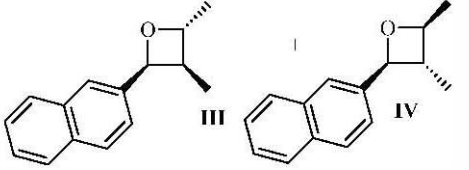

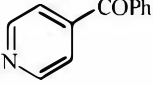
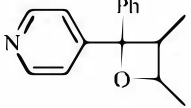

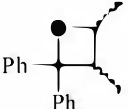

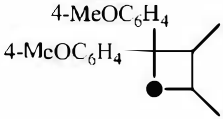
Alkene	Carbonyl compound	Product (yield %)	Ref.
		  I:II:III:IV 3.1:3.2:35.3:58.4 (64)	111
		 (—)	132
	Ph_2CO	 (79)	23 132
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CO}$	 (—)	132

Table 2. *Continued*

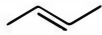
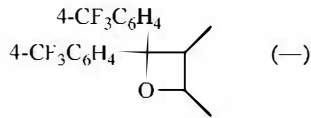
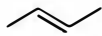
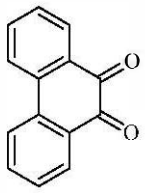
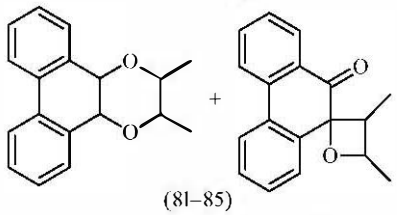
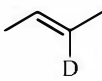
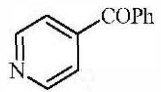
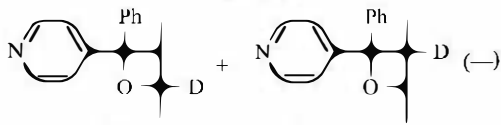
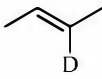
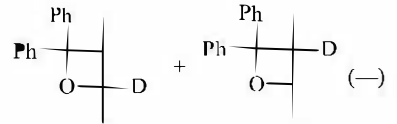
Alkene	Carbonyl compound	Product (yield %)	Ref.
	$(4F_3CC_6H_4)_2CO$		132
			131
			132
	Ph_2CO		132

Table 2. Continued

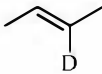
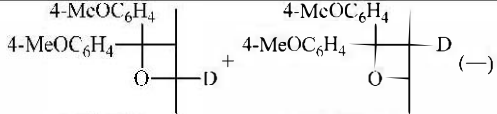
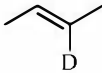
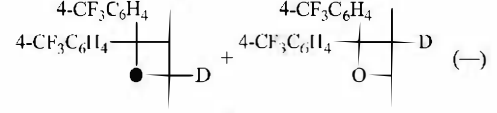
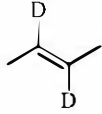
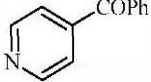
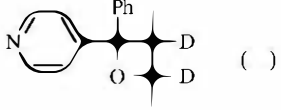
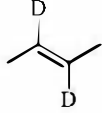
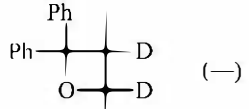
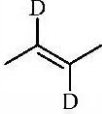
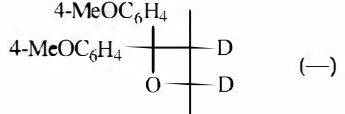
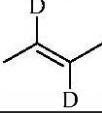
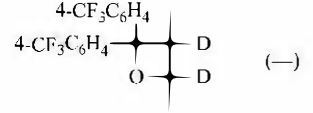
Alkene	Carbonyl compound	Product (yield %)	Ref.
	(4-MeOC ₆ H ₄) ₂ CO		132
	(4-F ₃ CC ₆ H ₄) ₂ CO		132
			132
	Ph ₂ CO		132
	(4-MeOC ₆ H ₄) ₂ CO		132
	(4-F ₃ CC ₆ H ₄) ₂ CO		132

Table 2. *Continued*

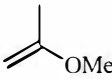
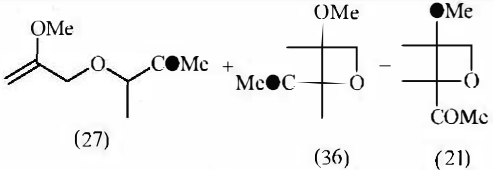

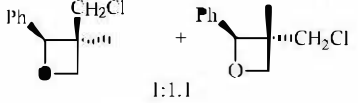

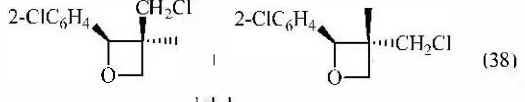

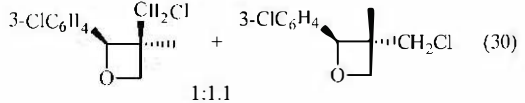

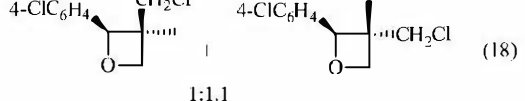
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCOCOMe	 (27) + (36) - (21)	114d
	PhCHO (0.5 equiv)	 (18)	133
	2-ClC ₆ H ₄ CHO (0.5 equiv)	 (38)	133
	3-ClC ₆ H ₄ CHO (0.5 equiv)	 (30)	133
	4-ClC ₆ H ₄ CHO (0.5 equiv)	 (18)	133

Table 2. Continued


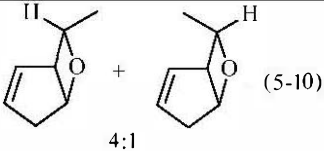



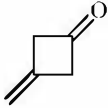
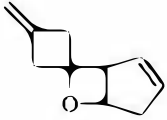

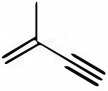
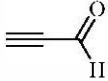
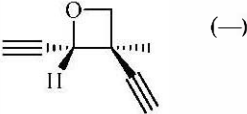
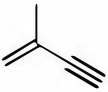
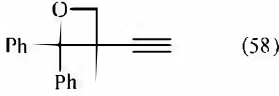
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCHO (1.75 equiv)		117
	Me ₂ CO (0.1 equiv)		134
			121
	Ph ₂ CO	No reaction	134
			110a
	Ph ₂ CO (1.08 equiv)		135

Table 2. *Continued*


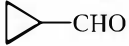
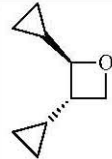

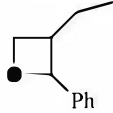
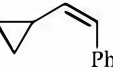

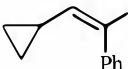
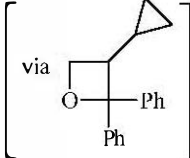
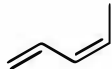
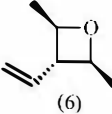
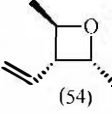
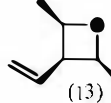

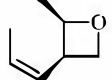
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 CHO	 (—)	105h
	PhCHO (1 equiv)	 (17.3) +  (0.7)	136
	Ph ₂ CO (1 equiv)	 (35) [via 	136
	MeCHO	 (6) +  (54) +  (13) +  (24) +  (4)	105h

Table 2. *Continued*

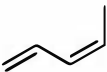
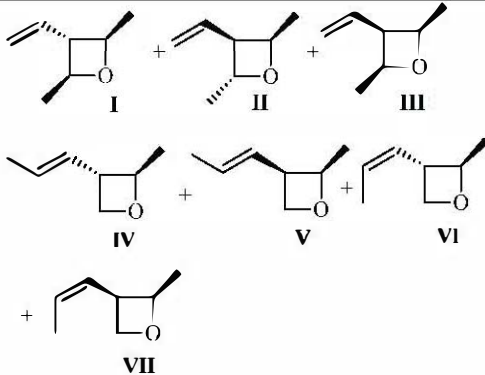
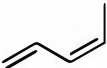
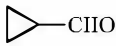
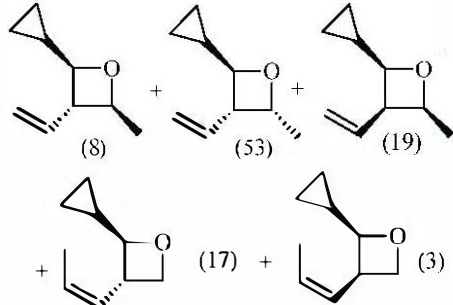
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCHO (1.8 equiv)	 <p style="text-align: center;"> $I:II:III:IV:V:VI:VII = 0.00:0.48:0.15:0.00:0.00:0.29:0.08$ </p>	137
			105h

Table 2. *Continued*

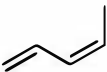
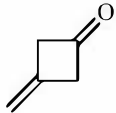
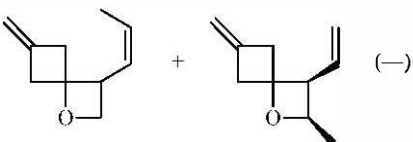
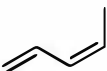
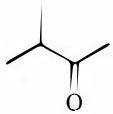
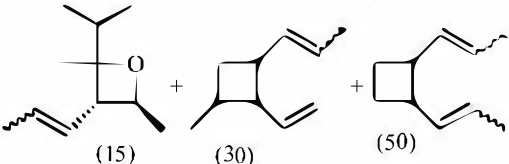
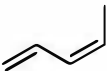
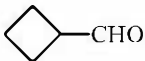
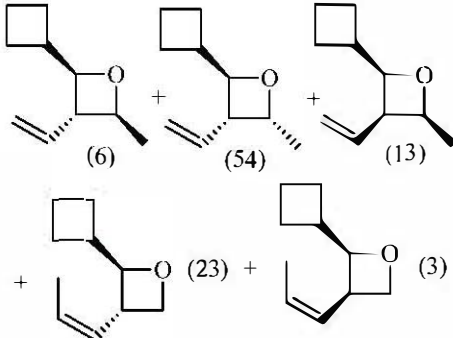
Alkene	Carbonyl compound	Product (yield %)	Ref.
			121
			105h
			105h

Table 2. Continued

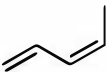
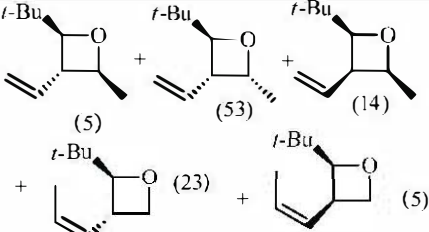
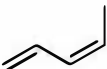
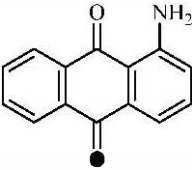

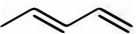
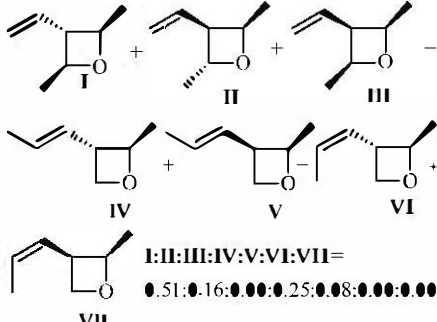
Alkene	Carbonyl compound	Product (yield %)	Ref.
	<p><i>t</i>-BuCHO</p>	 <p>(5) + (53) + (14) + (23) + (5)</p>	105h
		 (—)	138
	<p>MeCHO (1.8 equiv)</p>	 <p>I + II + III + IV + V + VI + VII = 0.51:0.16:0.00:0.25:0.08:0.00:0.00</p>	137

Table 2. *Continued*


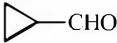
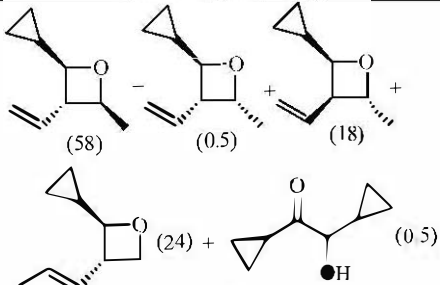

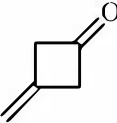
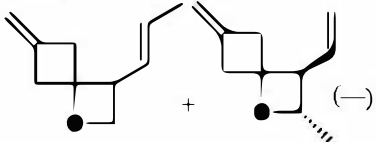

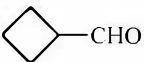
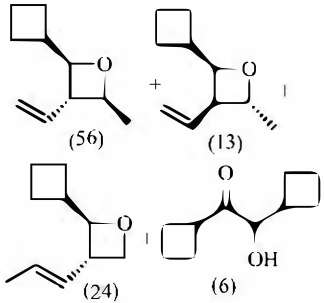
Alkene	Carbonyl compound	Product (yield %)	Ref.
			105h
			121
			105h

Table 2. Continued


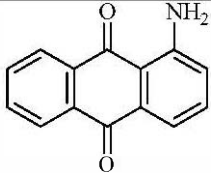
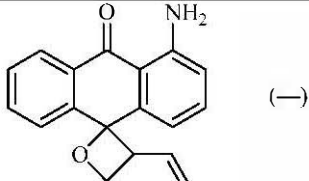
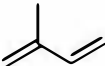
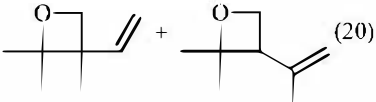
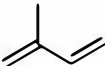
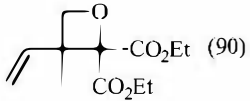
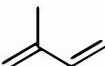
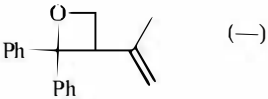

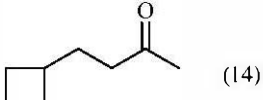

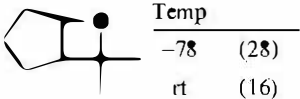
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (—)	138
	Me ₂ CO	 (20)	109c
	EtO ₂ CCOCO ₂ Et (0.5 equiv)	 (90)	139
	Ph ₂ CO (1 equiv)	 (—)	122
	Me ₂ CO	 (14)	140
	Me ₂ CO	 Temp -78 (28) rt (16)	134

Table 2. *Continued*


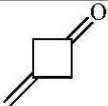
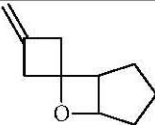

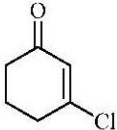
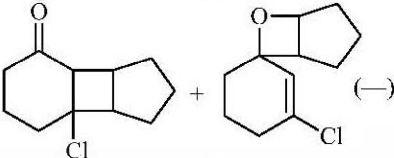

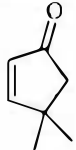
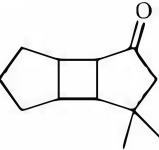

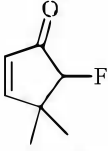
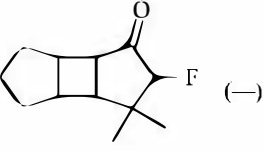

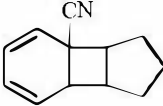
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (—)	121
	 (0.03 equiv)	 (—)	141
	 (0.1 equiv)	 (—)	116d
	 (0.1 equiv)	 (—)	116d
	PhCN (0.1 equiv)	 (3)	104f

Table 2. Continued


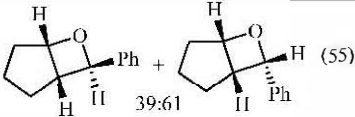

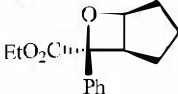

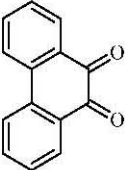
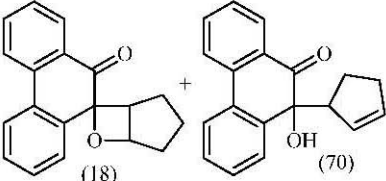


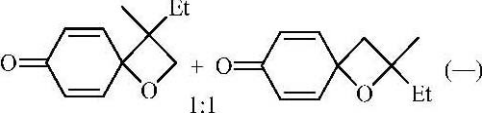


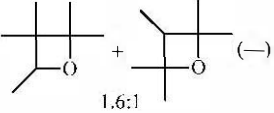
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO (0.03 equiv)	 (55) 39:61	68a 68c
	PhCOCO ₂ Et	 (65)	142
	 (0.3 equiv)	 (18) + (70)	143
	 (0.05 equiv)	 1:1	112
	(CO ₂ H) ₂	No reaction	144
	Me ₂ CO	 1,6:1	124

Table 2. *Continued*


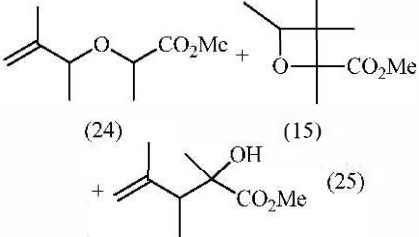

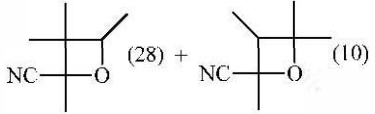

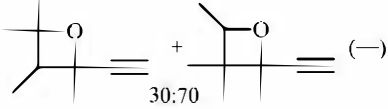

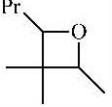

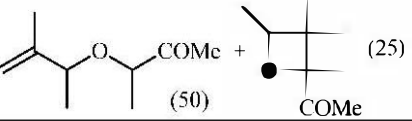
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCOCO ₂ Me (1 equiv)	 (24) (15) + (25)	114b
	MeCOCN (1 equiv)	 (28) + (10)	145
	MeCOCCH	 30:70 (-)	110b
	PrCHO (1.1 equiv)	 (6.5)	21
	MeCOCOMe (1 equiv)	 (50) (25) COMe	105d 114d 146

Table 2. *Continued*



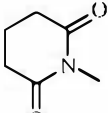
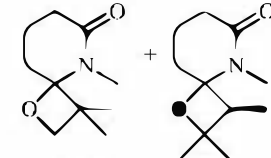

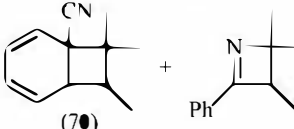

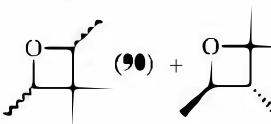


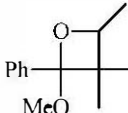
Alkene	Carbonyl compound	Product (yield %)	Ref.
	BuCHO	Decomposition ?	18
	 (0.2 equiv)	 (76)	128
	PhCN (0.1 equiv)	 (70) + (4)	147
	PhCHO (1.1 equiv)	 (90) + (10)	18 21 24 106a
	2-HOC ₄ H ₉ CHO	No reaction	144
	PhCO ₂ Me (0.18 equiv)	 (33–36)	148

Table 2. *Continued*


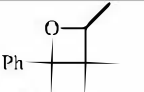

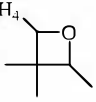


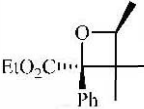


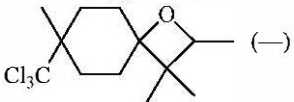

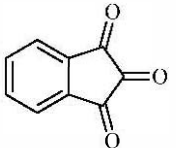
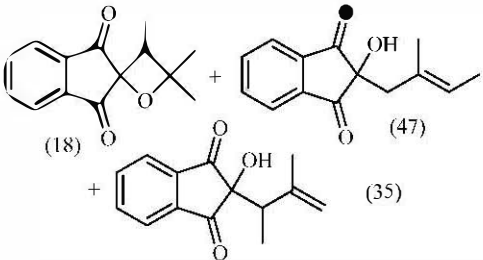
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOMe (0.8 equiv)	 (>90)	18 21 24
	4-MeC ₆ H ₄ CHO	 (—)	144
	4-MeOC ₆ H ₄ CHO	decomposition	18
	PhCOCO ₂ Et	 (70)	142
		 (—)	149
		 (18) + (47) + (35)	150

Table 2. *Continued*


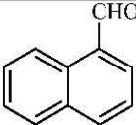
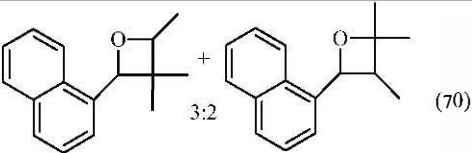

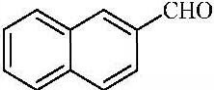
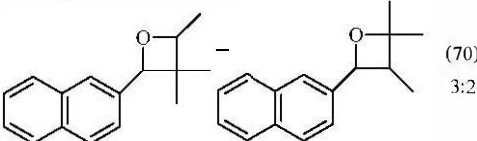

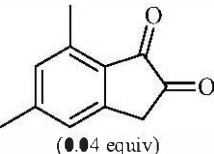
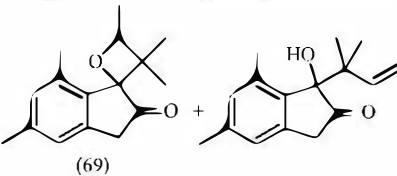

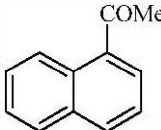

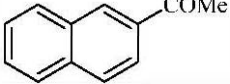
Alkene	Carbonyl compound	Product (yield %)	Ref.
			24
			24
			152
		No reaction	24
		No reaction	24

Table 2. *Continued*


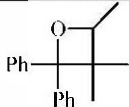

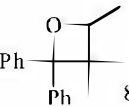
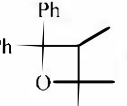

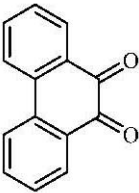
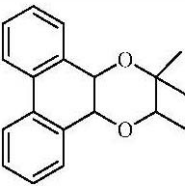
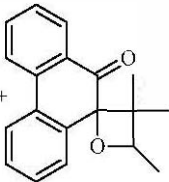

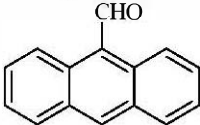
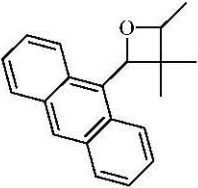

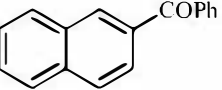
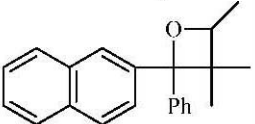

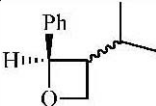


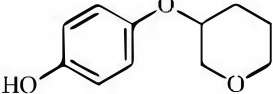
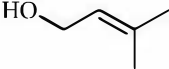
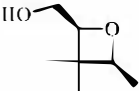
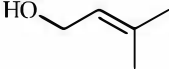
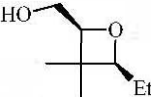
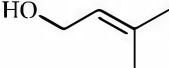

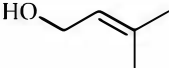
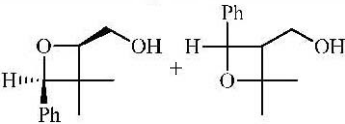
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO	 (50-90)	18 23 24
	Ph ₂ CO (0.5 equiv)	 +  (55) 84:16	92
		 +  (78)	131
		 (—)	24
		 (62)	24

Table 2. Continued

Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO (0.24 equiv)	 (69)	129
		 (20)	152
	MeCHO	 (—) dr 81:19	93
	EtCHO	 (—) dr 86:14	93
	<i>t</i> -BuCHO	 (—) dr 83:17	93
	PhCHO (0.5 equiv)	 (72) 65:35	92

cis:trans >95:5

Table 2. *Continued*

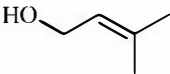
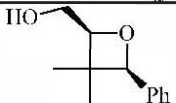
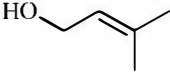
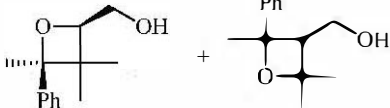
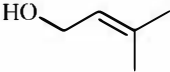
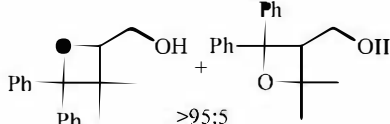
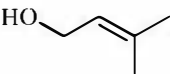
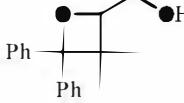
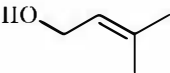
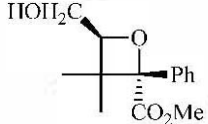
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO	 (—) dr >97:3	93
	PhCOMe (1 equiv)	 (91) <i>cis:trans</i> >95:5 >95:5	92
	Ph ₂ CO (0.5 equiv)	 (57) >95:5	92
	Ph ₂ CO (0.5 equiv, flux)	 (91)	153
	PhCOCO ₂ Me	 (62) dr 79:21	154

Table 2. *Continued*

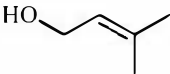
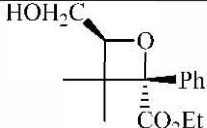
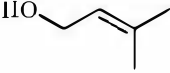
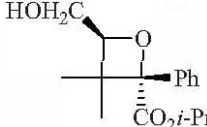
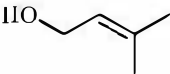
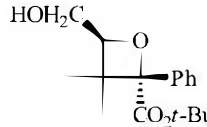
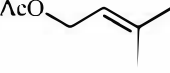
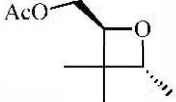
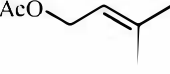
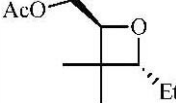
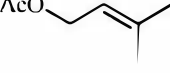
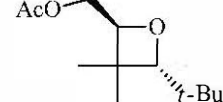
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOCO ₂ Et (1 equiv)	 (58) dr 77:23	154
	PhCOCO ₂ <i>i</i> -Pr (1 equiv)	 (55) dr 71:29	154
	PhCOCO ₂ <i>t</i> -Bu (1 equiv)	 (67) dr 67:33	154
	MeCHO	 (—) dr 77:23	93
	EtCHO	 (—) dr 81:19	93
	<i>t</i> -BuCHO	 (—) dr 80:20	93

Table 2. *Continued*

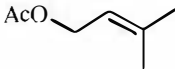
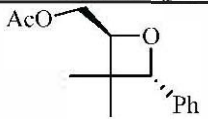

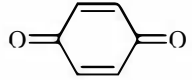
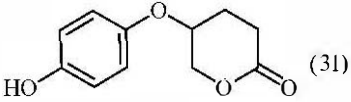
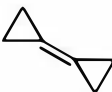
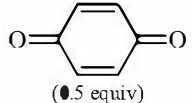
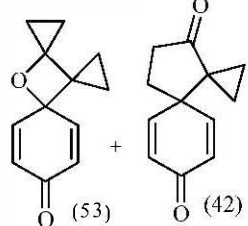

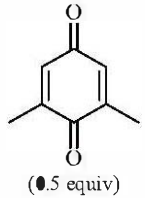
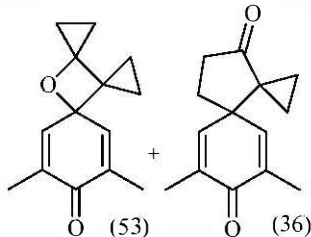
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO	 (—) dr 93:7	93
		 (31)	152
	 (0.5 equiv)	 (53) + (42)	155
	 (0.5 equiv)	 (53) + (36)	155

Table 2. Continued

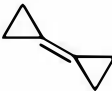
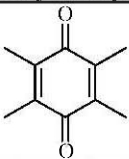

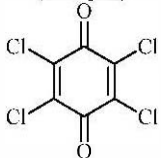
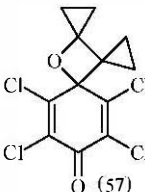
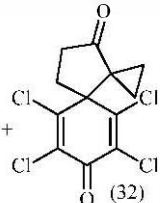

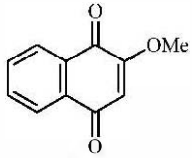
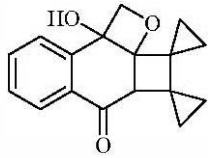

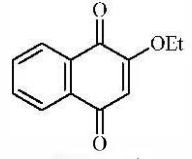
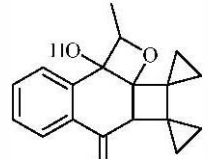
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)	No reaction	155
	 (0.5 equiv)	 (57) +  (32)	155
	 (0.5 equiv)	 (85)	155
	 (0.5 equiv)	 (88)	155

Table 2. *Continued*


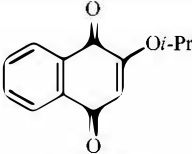
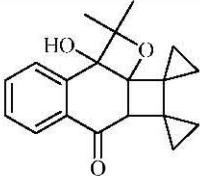

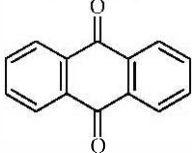
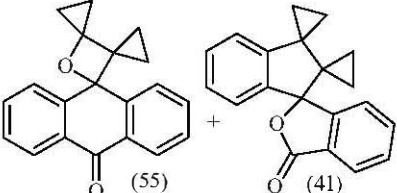

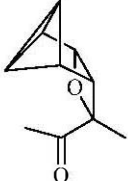

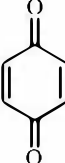
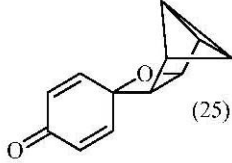
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)	 (54)	155
	 (0.5 equiv)	 (55) + (41)	155
	MeCOCOMe	 (19)	156
		 (25)	156

Table 2. *Continued*


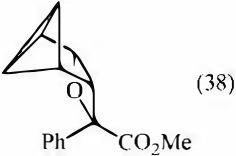

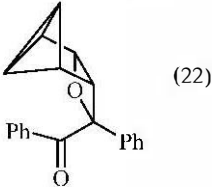

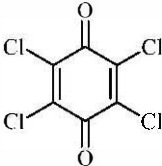
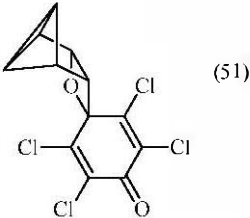

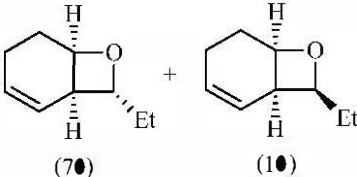
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOCO ₂ Me	 (38)	156
	PhCOCOPh	 (22)	156
		 (51)	156
	EtCHO (1 equiv)	 (70) + (10)	157 158 159

Table 2. *Continued*


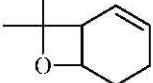

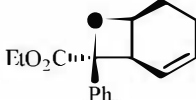

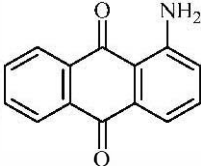


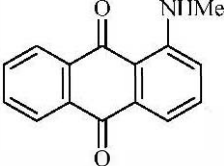

Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me_2CO (7.2 equiv)	 (—)	31j
	PhCOCO_2Et	 (81)	142
		 (91.8)	138
		 (17.9)	138

Table 2. Continued


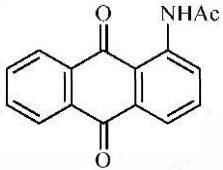
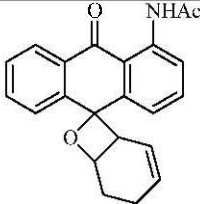

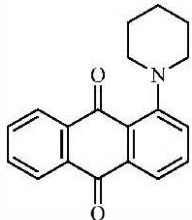

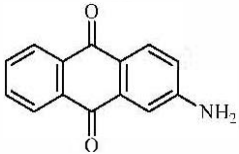
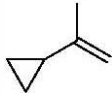
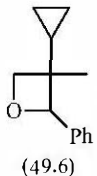
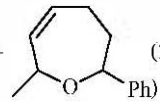
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (63.5)	138
		No reaction	138
		No reaction	138
	PhCHO (1 equiv)	 +  (2,3) (49.6)	160

Table 2. *Continued*

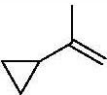
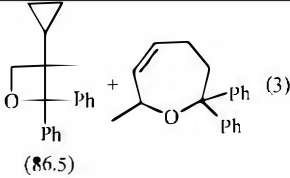

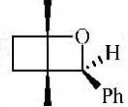

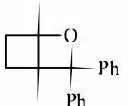

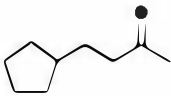

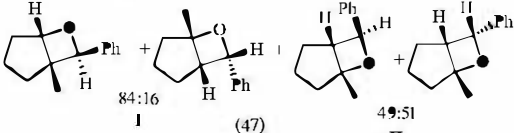
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO (1 equiv)	 (86.5) + (3)	160
	PhCHO	 (48)	68a
	Ph ₂ CO (1.25 equiv)	 (48)	161
	Me ₂ CO	 (12)	140
	PhCHO (2 equiv)	 (47) I:II 49:51	68c

Table 2. *Continued*


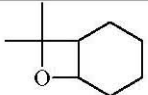

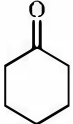
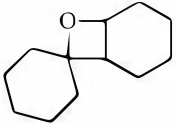

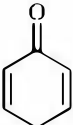
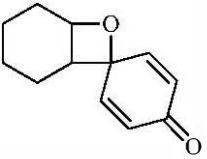

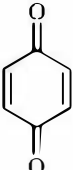
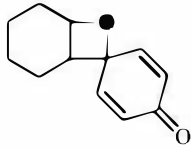

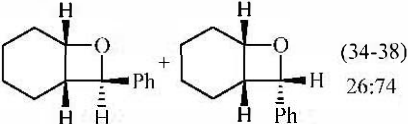
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (8)	162 163
		 (—)	164
		 (>90)	165
		 (10)	119
	PhCHO (0.09 equiv)	 (34-38) 26:74	68a 68c 158 162

Table 2. *Continued*


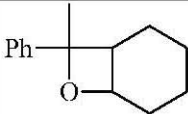

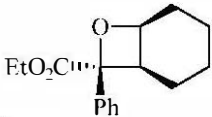

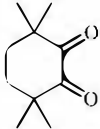
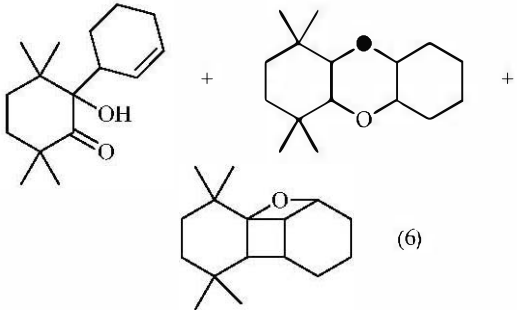

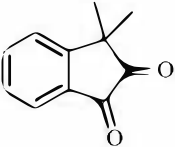
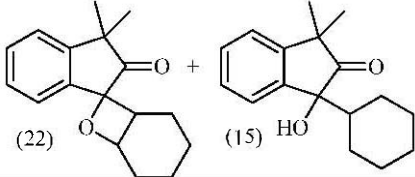
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOMe	 (15)	162
	PhCOCO ₂ Et	 (76)	142
		 (6)	166
		 (22) (15) HO	166

Table 2. *Continued*


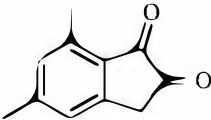
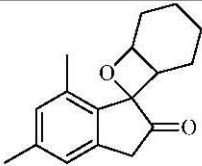

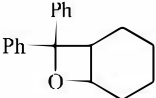

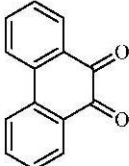
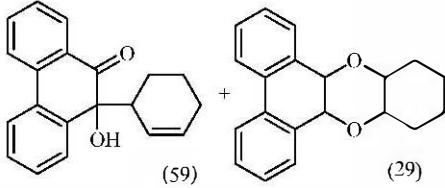

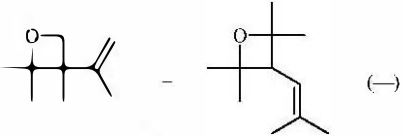

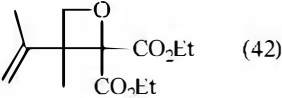
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.7 equiv) Ph ₂ CO	 (—)	151
	Ph ₂ CO	 (13)	162
	 (0.3 equiv) Me ₂ CO	 (59) + (29)	143
	Me ₂ CO	 (—)	109
	EtO ₂ CCOCO ₂ Et	 (42)	139

Table 2. *Continued*



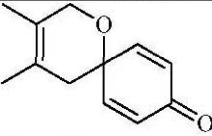

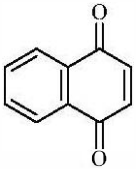
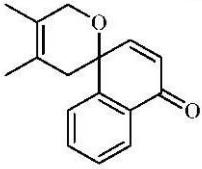

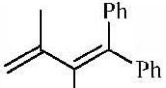

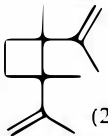
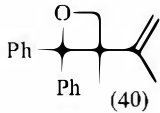

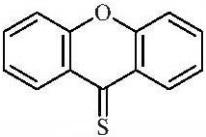
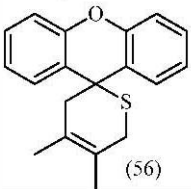
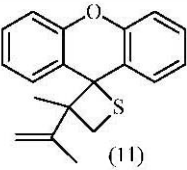
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (33)	167
		 (1.5)	168
	Ph ₂ CO (2 equiv)	 (28)	161
	Ph ₂ CO	 (21) +  (40)	122
	 (0.35 equiv)	 (56) +  (11)	106c

Table 2. Continued


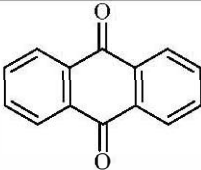
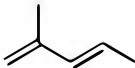
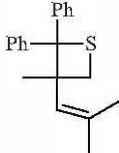
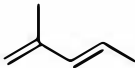
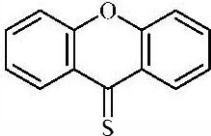
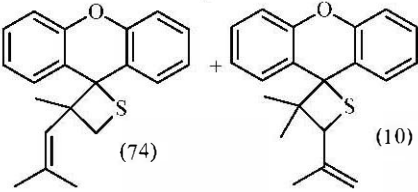

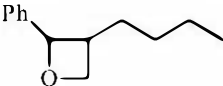

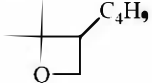
Alkene	Carbonyl compound	Product (yield %)	Ref.
		No reaction	123
	Ph ₂ CS (0.32 equiv)	 (69)	106c
	 (0.48 equiv)	 (74) + (10)	106c
	PhCHO	 (30)	162
	Ph ₂ CO	 (20)	18 162

Table 2. *Continued*

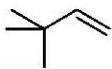
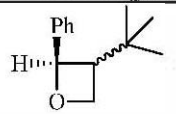
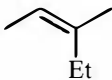
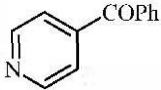
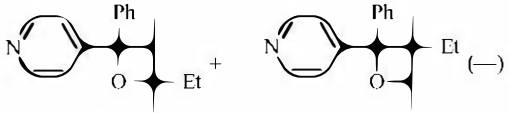
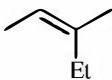
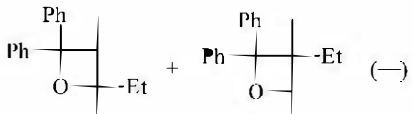
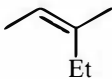
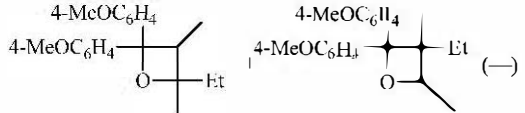
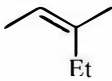
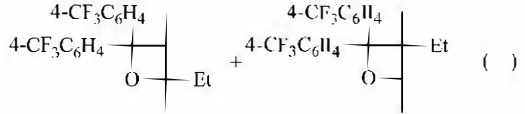
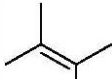

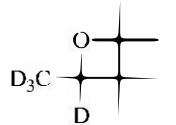
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO (1 equiv)	 (43)	128
		 (—)	132
	Ph ₂ CO	 (—)	132
	(4-MeOC ₆ H ₄) ₂ CO	 (—)	132
	(4-F ₃ CC ₆ H ₄) ₂ CO	 ()	132
		 (—)	169

Table 2. *Continued*

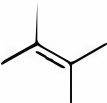
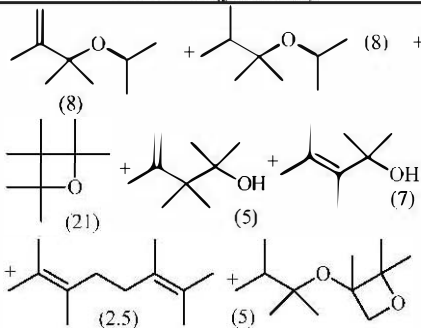
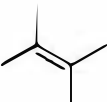
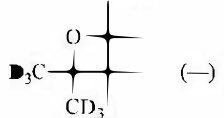
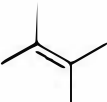
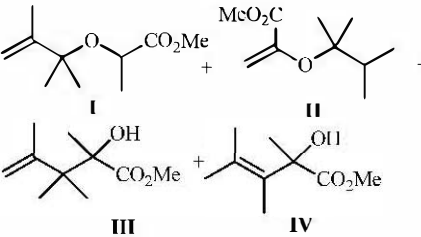
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (8) + (5) + (7) + (2.5) + (5)	114a
	CD ₃ COC ₂ CD ₃	 (-)	169
	MeOCO ₂ Me (1 equiv)	 I + II + III + IV	114b 114c
		I/II/III/IV-22:15:26:37 (-)	

Table 2. *Continued*

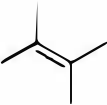
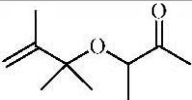
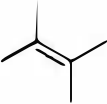
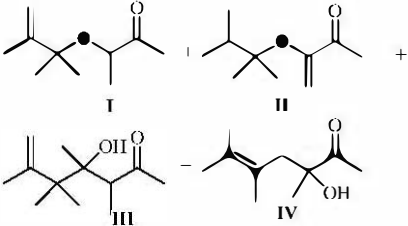
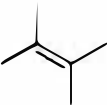
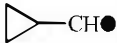
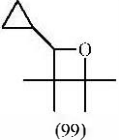
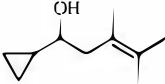
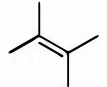
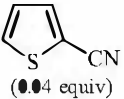
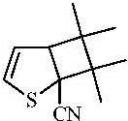
Alkene	Carbonyl compound	Product (yield %)	Ref.																				
	MeCOCOMe	 (70)	105d 114d																				
	MeCOCOMe	 <table border="1" data-bbox="890 580 1214 695"> <thead> <tr> <th>Solvent</th> <th>I</th> <th>II</th> <th>III</th> <th>IV</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>(56)</td> <td>(35)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>benzene</td> <td>(41)</td> <td>(22)</td> <td>(15)</td> <td>(22)</td> </tr> <tr> <td>hexane</td> <td>(33)</td> <td>(3)</td> <td>(23)</td> <td>(41)</td> </tr> </tbody> </table>	Solvent	I	II	III	IV	MeCN	(56)	(35)	(0)	(0)	benzene	(41)	(22)	(15)	(22)	hexane	(33)	(3)	(23)	(41)	114e
Solvent	I	II	III	IV																			
MeCN	(56)	(35)	(0)	(0)																			
benzene	(41)	(22)	(15)	(22)																			
hexane	(33)	(3)	(23)	(41)																			
		 (99) +  (1)	105h																				
	 (0.04 equiv)	 (24)	105f																				

Table 2. Continued


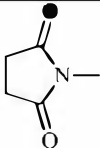
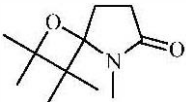

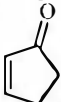
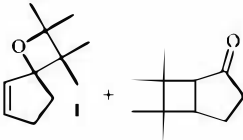

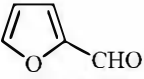
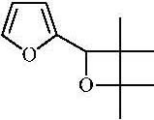

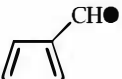
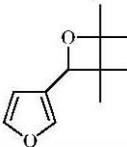

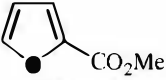
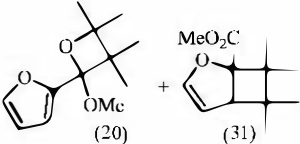
Alkene	Carbonyl compound	Product (yield %)	Ref.									
	 (0.2 equiv)	 (71)	123									
	 (0.1 equiv)		116d									
		<table border="1" data-bbox="1123 456 1326 542"> <thead> <tr> <th>Solvent</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>cyclohexane</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>MeCN</td> <td>(0)</td> <td>(100)</td> </tr> </tbody> </table>	Solvent	I	II	cyclohexane	(0)	(100)	MeCN	(0)	(100)	
Solvent	I	II										
cyclohexane	(0)	(100)										
MeCN	(0)	(100)										
	 (0.05 equiv)	 (—)	116b									
	 (0.05 equiv)	 (53)	116b									
	 (0.07 equiv)		116a									

Table 2. *Continued*


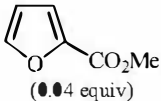
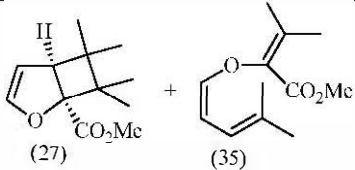

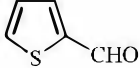
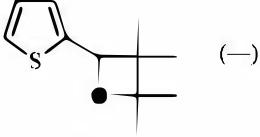

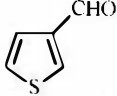
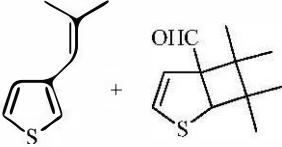

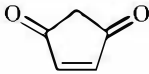
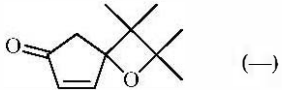
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.04 equiv)	 (27) (35)	170
	 CHO	 (—)	116b
	 CHO (0.05 equiv)	 (46) (9)	116b
		 (—)	126

Table 2. *Continued*


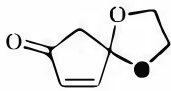
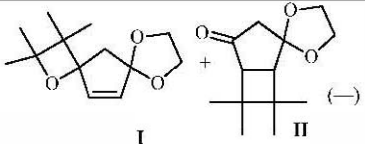

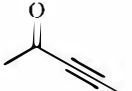
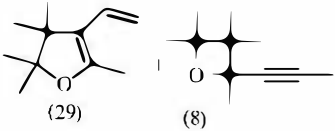

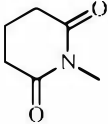
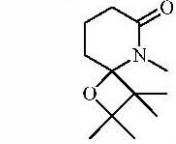

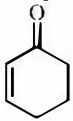
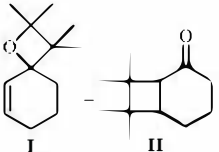
Alkene	Carbonyl compound	Product (yield %)	Ref.										
		 I + II (1:1)	116g										
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>I/II</th> </tr> </thead> <tbody> <tr> <td>no solvent</td> <td>1:1</td> </tr> <tr> <td>cyclohexane</td> <td>76:34</td> </tr> <tr> <td>chloroform</td> <td>63:37</td> </tr> <tr> <td>MeCN</td> <td>62:38</td> </tr> </tbody> </table>	Solvent	I/II	no solvent	1:1	cyclohexane	76:34	chloroform	63:37	MeCN	62:38	
Solvent	I/II												
no solvent	1:1												
cyclohexane	76:34												
chloroform	63:37												
MeCN	62:38												
	 (0.5 equiv)	 I (29) + II (8)	125 171										
	 (0.2 equiv)	 I (65)	128										
	 (1 equiv)	 I + II	<table border="1"> <thead> <tr> <th>Solvent</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>isooctane</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>MeCN</td> <td>(0)</td> <td>(100)</td> </tr> </tbody> </table>	Solvent	I	II	isooctane	(0)	(100)	MeCN	(0)	(100)	116c 116d
Solvent	I	II											
isooctane	(0)	(100)											
MeCN	(0)	(100)											

Table 2. *Continued*


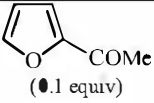
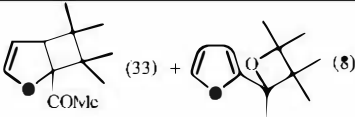

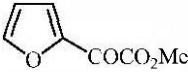
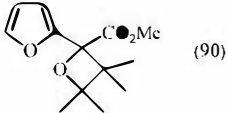

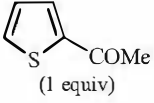
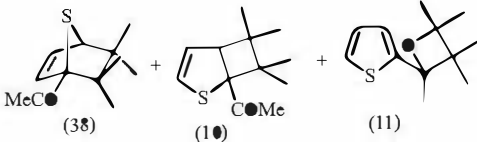

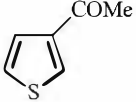
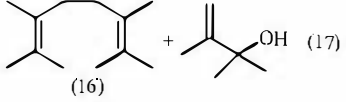

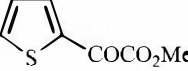
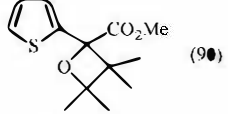

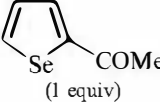
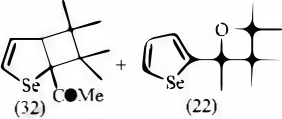
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.1 equiv)	 (33) + (8)	127
		 (90)	172
	 (1 equiv)	 (38) + (10) + (11)	127
		 (16) + (17)	116b
		 (90)	172
	 (1 equiv)	 (32) + (22)	106d

Table 2. *Continued*


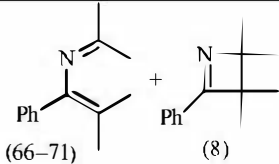



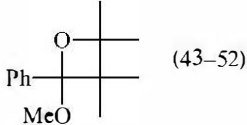

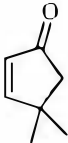
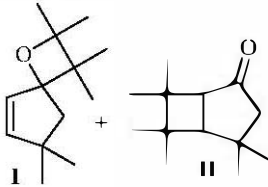
Alkene	Carbonyl compound	Product (yield %)	Ref.									
	PhCN (0.17 equiv)		147 173									
	PhCHO (1 equiv)		174									
	PhCO ₂ Me		148 170									
			116d 116g									
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>cyclohexane</td> <td>56</td> <td>47</td> </tr> <tr> <td>MeCN</td> <td>47</td> <td>71</td> </tr> </tbody> </table>	Solvent	I	II	cyclohexane	56	47	MeCN	47	71	
Solvent	I	II										
cyclohexane	56	47										
MeCN	47	71										

Table 2. *Continued*


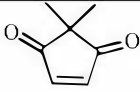


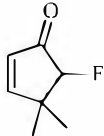
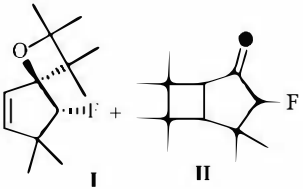

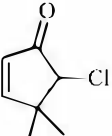
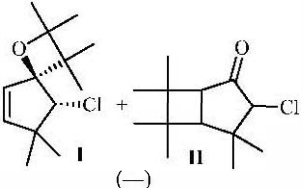

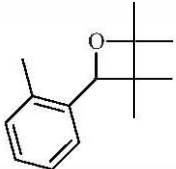
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (—)	126
		 I + II	116d 116f
		Solvent I:II cyclohexane 100:0 MeCN 75:25	
		()	
	 (0.1 equiv)	 I + II	116f
		Solvent I:II cyclohexane 96:4 MeCN 0:100	
		(—)	
	2-MeC ₆ H ₄ CHO (1 equiv)	 (94)	174

Table 2. *Continued*


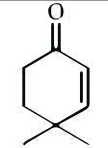
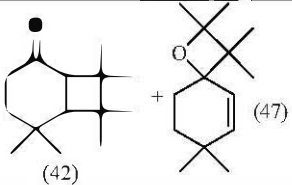

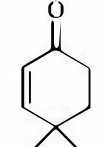
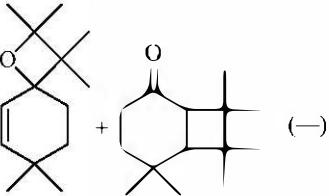

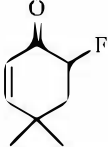
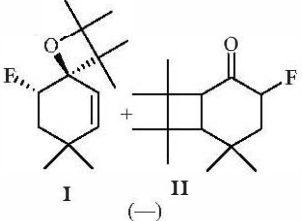
Alkene	Carbonyl compound	Product (yield %)	Ref.						
	 (0.17 equiv)	 (42) + (47)	116e						
	 (0.1 equiv)	 52:48 (—)	116c 116d						
	 (0.1 equiv)	 I II (—)	116c 116d 116f						
		<table border="1"> <tr> <td>Solvent</td> <td>I:II</td> </tr> <tr> <td>isooctane</td> <td>90:10</td> </tr> <tr> <td>MeCN</td> <td>15:85</td> </tr> </table>	Solvent	I:II	isooctane	90:10	MeCN	15:85	
Solvent	I:II								
isooctane	90:10								
MeCN	15:85								

Table 2. *Continued*


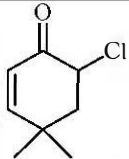
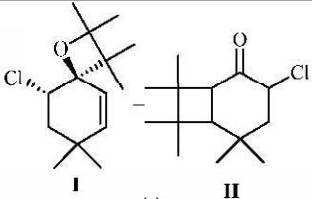

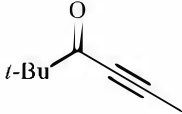
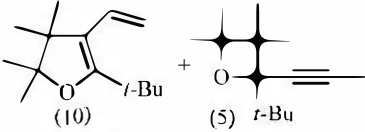

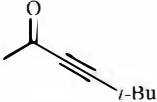
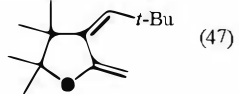

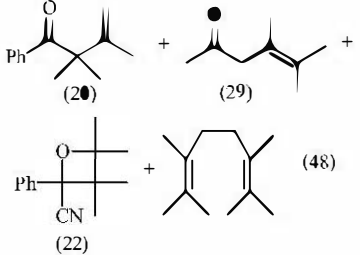
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.08 equiv)	 I (-) II	116f Solvent: cyclohexane 10:90 MeCN 0:100
	 <i>t</i> -Bu	 (10) (5) <i>t</i> -Bu	171
	 (0.5 equiv)	 (47)	125
	PhCOCN	 (20) (29) (22)	175

Table 2. *Continued*


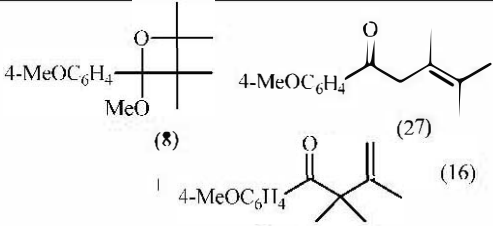

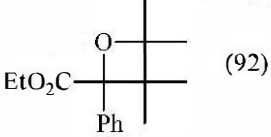

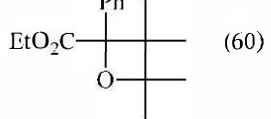
Alkene	Carbonyl compound	Product (yield %)	Ref.
	4-MeOC ₆ H ₄ CO ₂ Me		148
	PhCOCO ₂ Et		142
	PhCOCO ₂ Et (0.5 equiv; flux)		176

Table 2. *Continued*


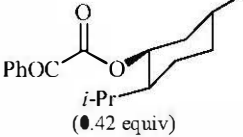
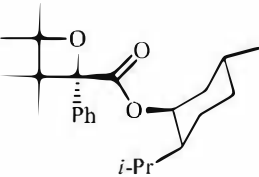

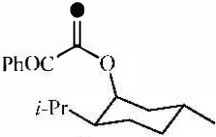
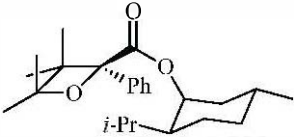

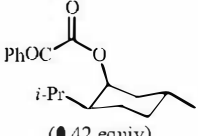
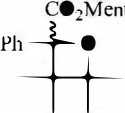
Alkene	Carbonyl compound	Product (yield %)	Temp	dr	Ref.
	 <i>i</i> -Pr (0.42 equiv)		-72	80:20	78a
			-66	83:17	78b
			-57	82.5:17.5	
			-50	81.5:18.5	
			-46	80:20	
			-28	73.5:26.5	
			-15	69:31	
			-3	65.5:34.5	
			+20	60:40	
			+35	56.5:43.5	
+55	52.5:47.5				
	 <i>i</i> -Pr		(43)	dr 57.5:42.5	78a
	 <i>i</i> -Pr (0.42 equiv)	 C ₂ Menthyl(-) Ph	(90)	23.7:76.3 <i>dr</i>	78c

Table 2. *Continued*


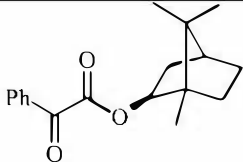
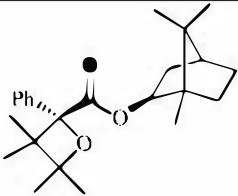

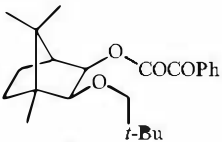

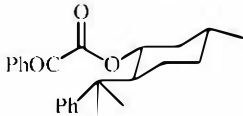
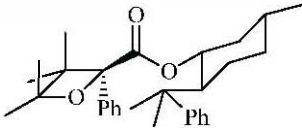

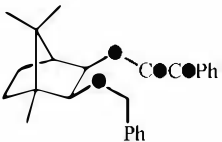
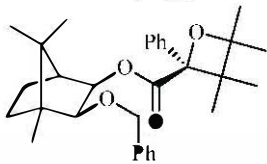

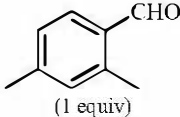
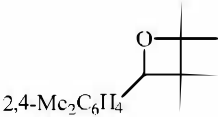
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (59) dr 58:42	78a
		No reaction	78a
		 (42) dr >98:2	78a
		 (25) dr 65:35	78a
		 2,4-Me ₂ C ₆ H ₄	174

Table 2. *Continued*


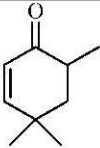
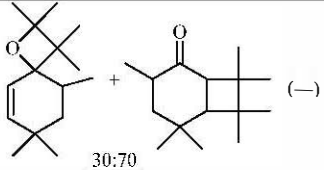

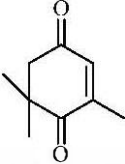
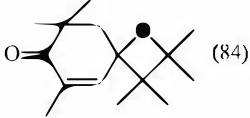

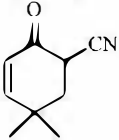

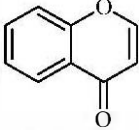
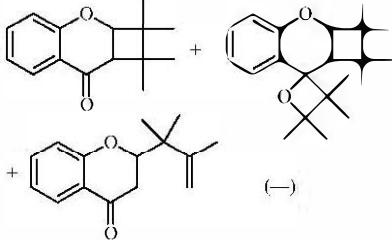
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (—) 30:70	116c
	 (0.23 equiv)	 (84)	177
	 (0.23 equiv)	No reaction	116c
	 (0.1 equiv)	 (—)	178

Table 2. *Continued*


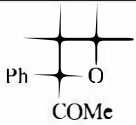

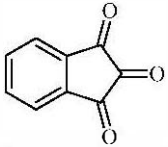
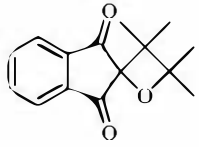

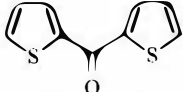
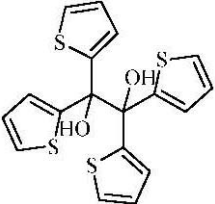

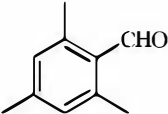
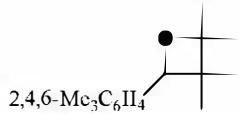

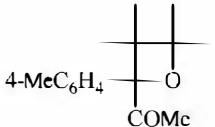
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOCOMe (0.7 equiv)	 (75)	179
		 (29.4)	180
	 (0.01 equiv)	 (—)	116b 127
	 (1 equiv)	 2,4,6-Me ₃ C ₆ H ₄	174
	4-MeC ₆ H ₄ COCOMe (0.7 equiv)	 (89)	179

Table 2. *Continued*


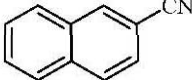
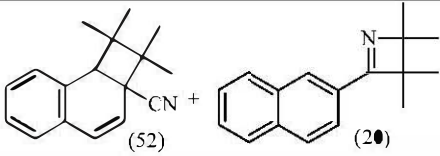

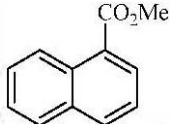
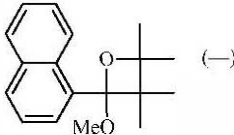

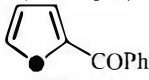
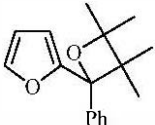

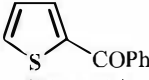
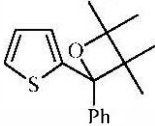

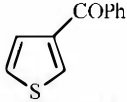
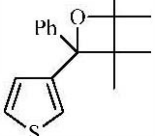
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.05 equiv)	 (52) + (20)	147
	 (0.006 equiv)	 (—)	170
	 (0.02 equiv)	 (27)	127
	 (0.04 equiv)	 (76)	127
	 (0.03 equiv)	 (28)	127

Table 2. Continued


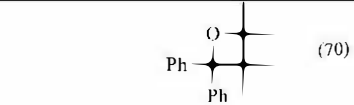

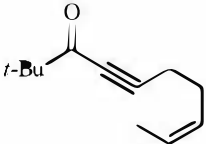
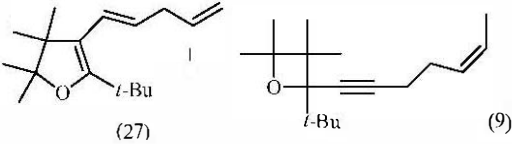

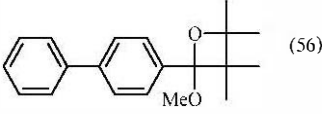

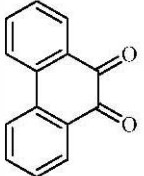
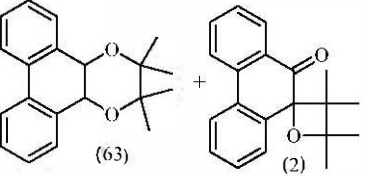

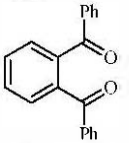
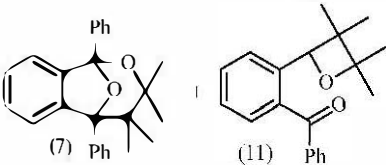
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO	 (70)	23
	 (0.14 equiv)	 (9)	171
	4-PhC ₆ H ₄ CO ₂ Me	 (56)	170
		 (63) + (2)	131
	 (0.2 equiv)	 (7) + (11)	181

Table 2. *Continued*

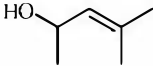
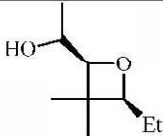
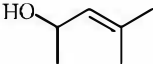
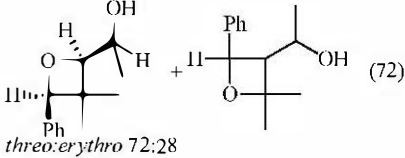
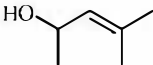
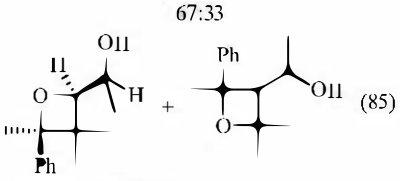
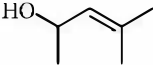
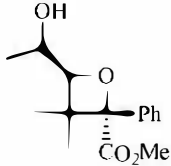
Alkene	Carbonyl compound	Product (yield %)	Ref.
	EtCHO	 (—) dr >95:5	93
	PhCHO (1 equiv)	 threo:erythro 72:28	92
	PhCOMe (1 equiv)	 threo:erythro 82:18	92
	PhCOCO ₂ Me (1 equiv)	 (64) dr >95:5	154

Table 2. *Continued*

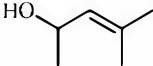
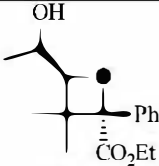
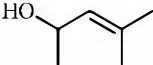
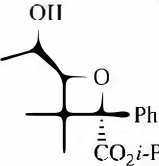
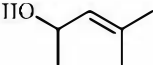
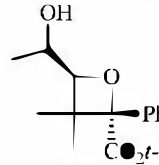
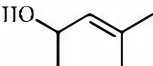
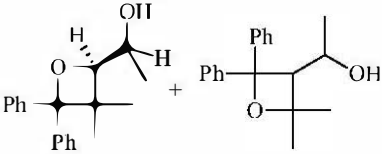
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOCO ₂ Et (1 equiv)	 (57) dr >95:5	154
	PhCOCO ₂ <i>i</i> -Pr (1 equiv)	 (48) dr >95:5	154
	PhCOCO ₂ <i>t</i> -Bu (1 equiv)	 (65) dr >95:5	154
	Ph ₂ CO (1 equiv)	 (90) <i>threo:erythro</i> 90:10 >95:5	89a 92

Table 2. *Continued*

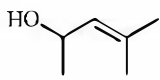
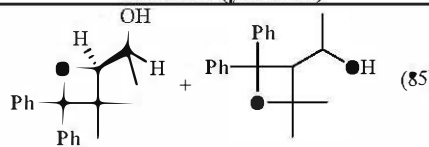
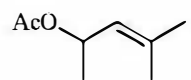
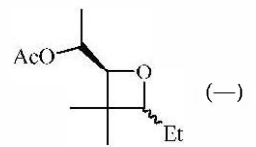
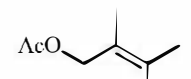
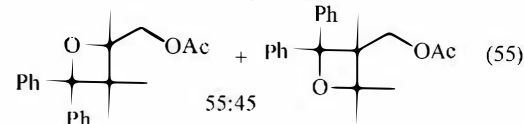
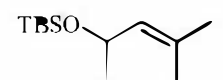
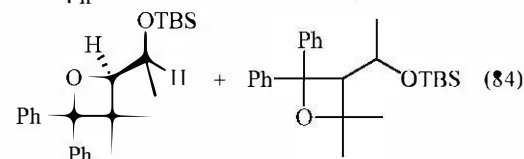
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO (1 equiv; C ₂ D ₂ -C ₂ D ₂ O ₂)		92
		<i>threo:erythro</i> 69:31	
	EtCHO		93
	Ph ₂ CO (1 equiv)		92
		<i>threo:erythro</i> 55:45	
	Ph ₂ CO (1 equiv)		89a 92
		<i>threo:erythro</i> 52:48	
		83:17	

Table 2. *Continued*


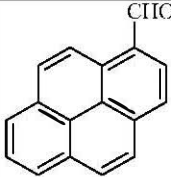
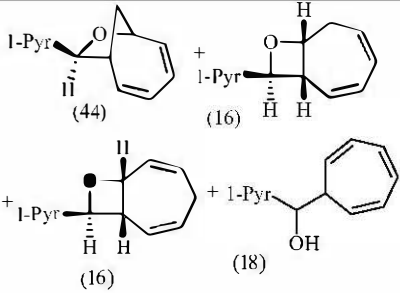

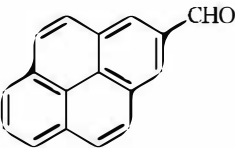
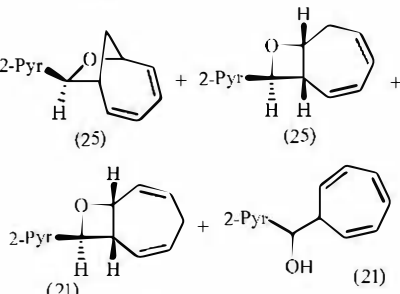

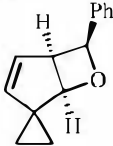
Alkene	Carbonyl compound	Product (yield %)	Ref.
			182
			182
	PhCHO (0.1 equiv)	 (<20) dr 3.5:1	68d

Table 2. *Continued*


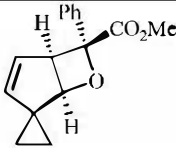

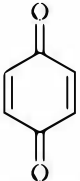
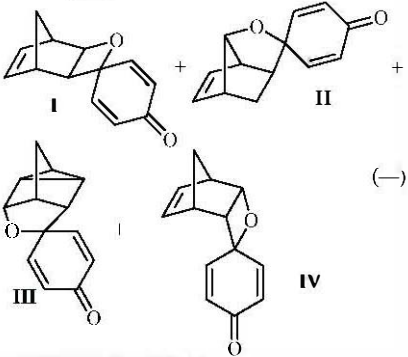

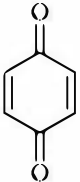
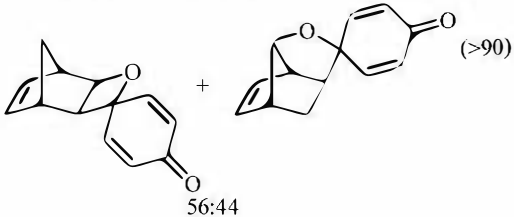
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOCO ₂ Me (0.1 equiv)	 (50) dr >19:1	68d
	 (0.06 equiv)	 I:III:IV=48:16:21:15	119 183
	 (0.06 equiv)	 (>90) 56:44	165 183

Table 2. *Continued*


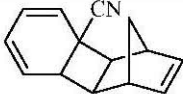

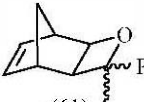
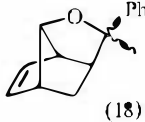

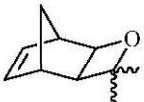
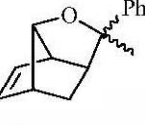

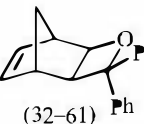
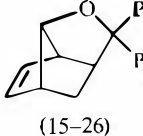
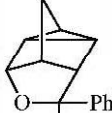

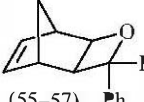
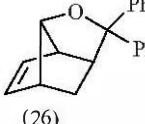
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCN (0.1 equiv)	 (41)	147
	PhCOMe (0.3 equiv)	 (61) +  (18)	184
	PhCOMe (0.3 equiv)	 (57) +  (21)	184
	Ph ₂ CO (0.6 equiv)	 (32-61) +  (15-26) +  (3)	184 185 186
	Ph ₂ CO (0.6 equiv)	 (55-57) +  (26)	184 186

Table 2. *Continued*


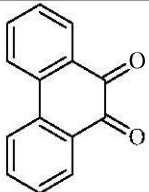
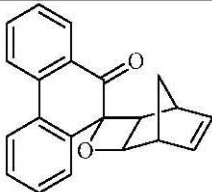

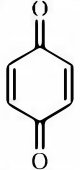
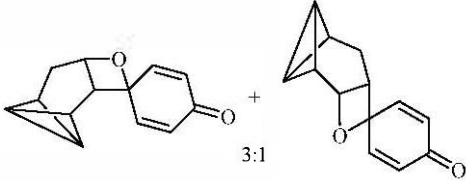

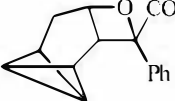

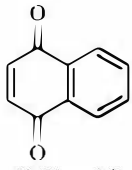
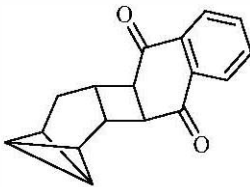
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.3 equiv)	 (60)	143
	 (0.67 equiv)	 + 3:1 (22)	187
	PhCOCO ₂ Me (0.67 equiv)	 (70)	187
	 (0.67 equiv)	 (21)	187

Table 2. *Continued*


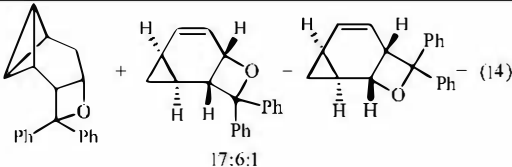

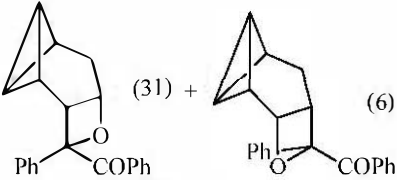

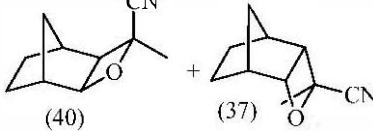

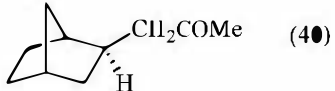
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO (0.67 equiv)	 17:6:1 (14)	187
	PhCOCOPh (0.67 equiv)	 (31) + (6)	187
	MeCOCN (1 equiv)	 (40) + (37)	145
	Me ₂ CO	 (40)	188

Table 2. *Continued*




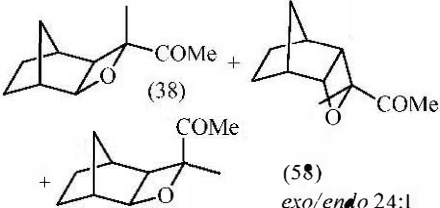

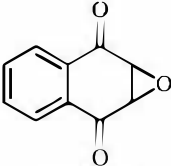
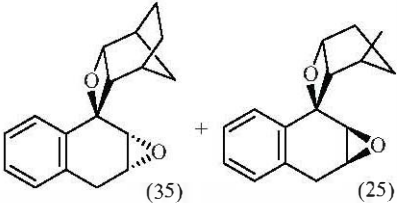

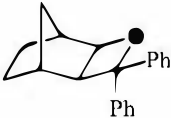
Alkene	Carbonyl compound	Product (yield %)	Ref.
	EtO ₂ CCOCO ₂ Et (0.5 equiv)	 (97)	139
	MeCOCOMe (0.13 equiv)	 (38) (58) <i>exo/endo</i> 24:1	189
	 (0.33 equiv)	 (35) + (25)	190
	Ph ₂ CO (1 equiv)	 (50–80)	23 184 191 192

Table 2. *Continued*


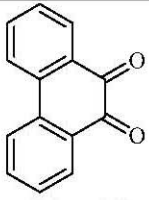
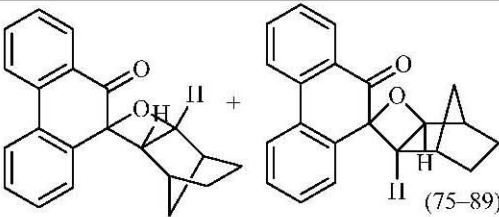

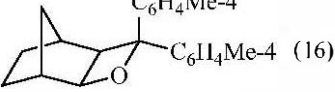

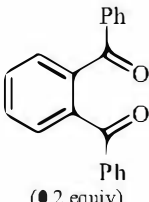
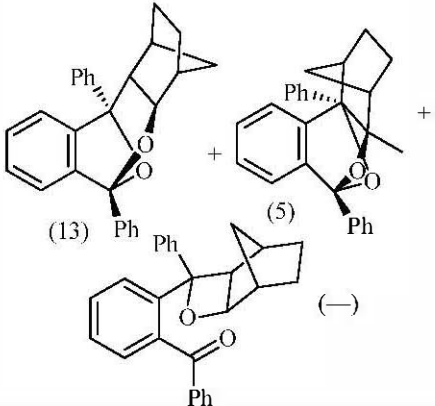
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.3 equiv)	 (75–89)	143 193 194
	(4-MeC ₆ H ₄) ₂ CO	 C ₆ H ₄ Me-4 C ₆ H ₄ Me-4 (16)	23
	 (0.2 equiv)	 (13) (5) (—)	181

Table 2. *Continued*

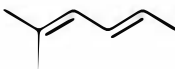
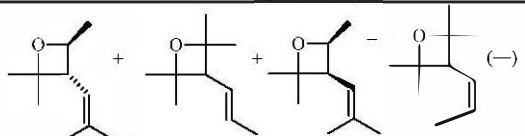
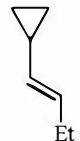
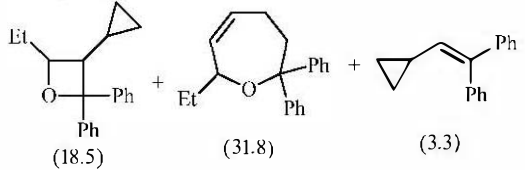

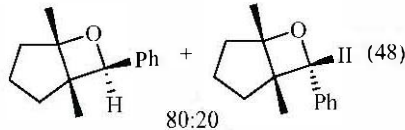
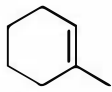
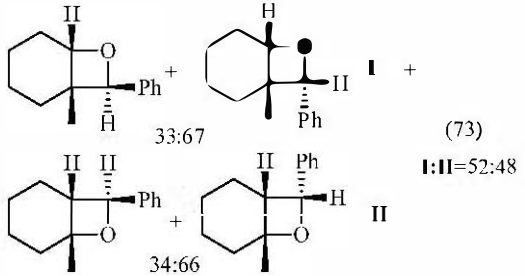
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (→)	195
	Ph ₂ CO (1 equiv)		160
	PhCHO (0.9 equiv)		68c
	PhCHO (0.5 equiv)		68c

Table 2. *Continued*

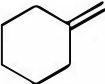
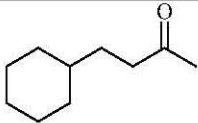

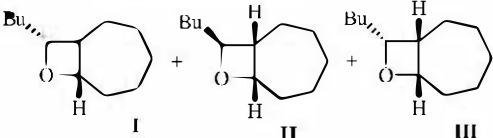

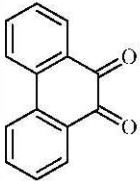
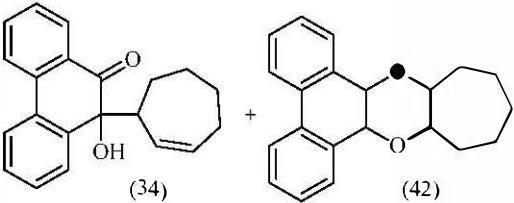

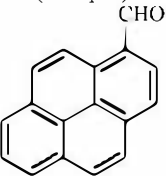
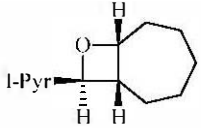
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (60)	140
	BuCHO	 I + II + III Solvent I:II:III MeCN 0:26:27 (30) no solvent 0:42.5:52.9 (41)	196
	 (0.3 equiv)	 (34) + (42)	143
		 (—)	182

Table 2. *Continued*


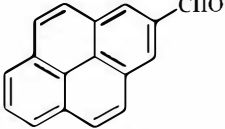
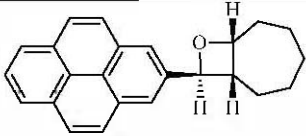

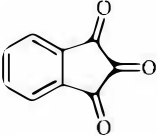
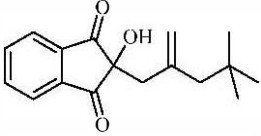

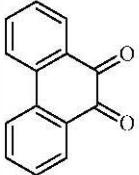
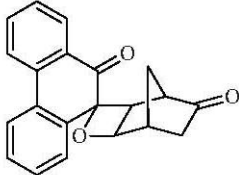
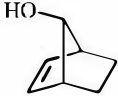
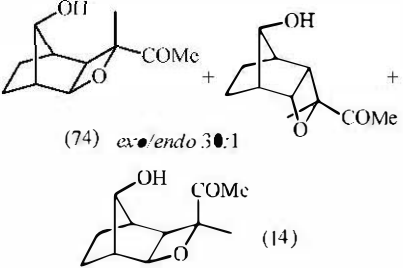
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (—)	182
		 ()	150
	 <p>(0.3 equiv)</p>	 (83)	143
	<p>MeCOCOMe (0.13 equiv)</p>	 <p>(74) <i>exo/endo</i> 30:1</p> <p>(14)</p>	189

Table 2. Continued

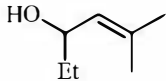
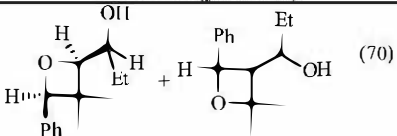
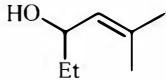
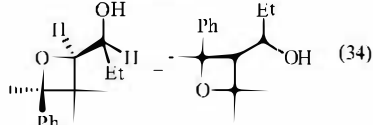
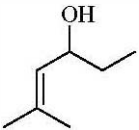
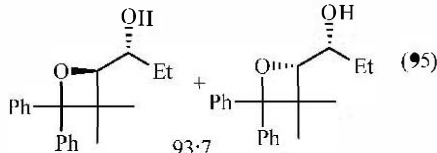
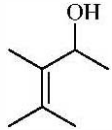
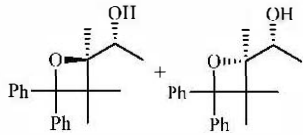
Alkene	Carbonyl compound	Product (yield %)	Ref.															
	PhCHO (1 equiv)	 (70)	92															
		<i>threo:erythro</i> 81:19 65:35																
	PhCOMe (1 equiv)	 (34)	92															
		<i>threo:erythro</i> 88:12 >95:5																
	Ph ₂ CO (1 equiv)	 (95)	89a 92															
	Ph ₂ CO		99b															
		<table border="1"> <thead> <tr> <th>Temp</th> <th><i>threo</i></th> <th><i>erythro</i></th> </tr> </thead> <tbody> <tr> <td>60</td> <td>54</td> <td>4</td> </tr> <tr> <td>20</td> <td>67</td> <td>7</td> </tr> <tr> <td>25</td> <td>70</td> <td>14</td> </tr> <tr> <td>-75</td> <td>72</td> <td>3</td> </tr> </tbody> </table>	Temp	<i>threo</i>	<i>erythro</i>	60	54	4	20	67	7	25	70	14	-75	72	3	
Temp	<i>threo</i>	<i>erythro</i>																
60	54	4																
20	67	7																
25	70	14																
-75	72	3																

Table 2. *Continued*

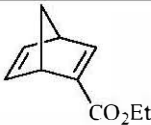
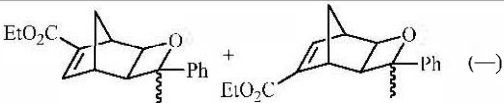
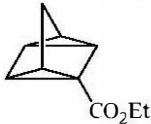
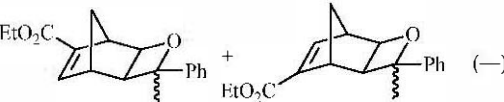
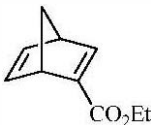
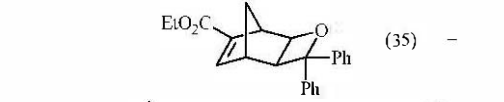
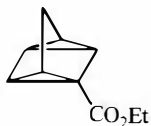
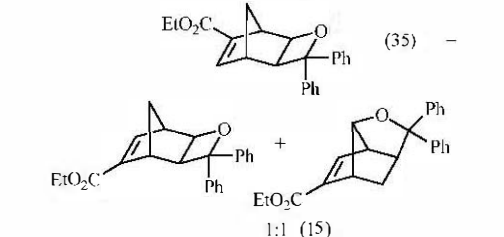
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOMe (6 equiv)	 (—)	184
	PhCOMe (17 equiv)	 (—)	184
	Ph ₂ CO (0.5 equiv)	 (35) —	184
	Ph ₂ CO (0.5 equiv)	 (35) — 1:1 (15)	184

Table 2. *Continued*



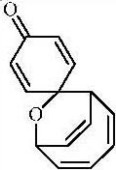

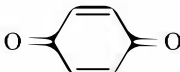
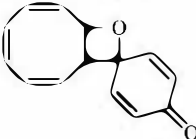

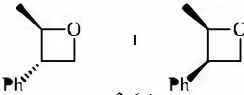

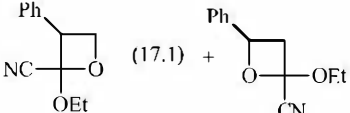

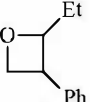

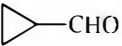
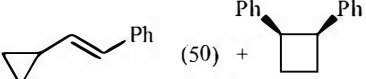
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.25 equiv)	 (77)	197
		 (10-30)	119 165
	MeCHO (1 equiv)	 (49)	198
	NCCO ₂ Et (5 equiv)	 (17.1) + (8.5)	199
	EtCHO (1 equiv)	 (38.5)	198
		 (50) + (50)	105h

Table 2. *Continued*




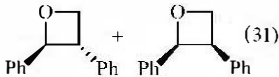

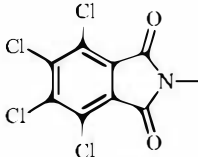
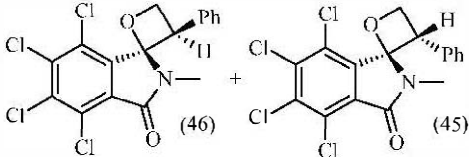

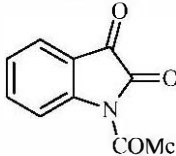
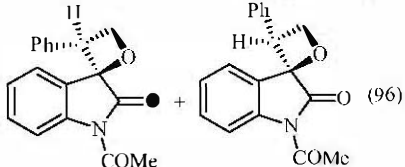


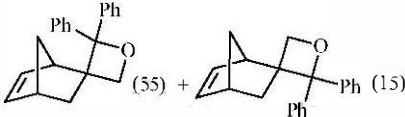
Alkene	Carbonyl compound	Product (yield %)	Ref.
		No reaction	119
	PhCHO (0.1 equiv)	 (31) 3:1 to 1:1	200
		 (46) (45)	201
	 (0.1 equiv)	 (96) 1.42:1	202
	Ph ₂ CO	No reaction	18 23
	Ph ₂ CO (0.5 equiv)	 (55) (15)	191

Table 2. *Continued*

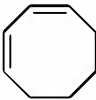
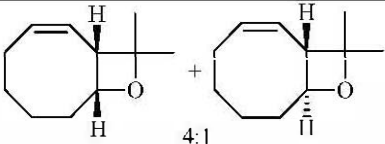

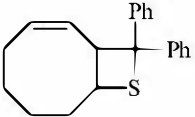

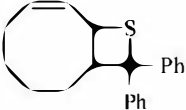

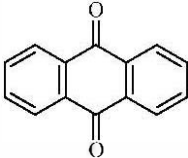
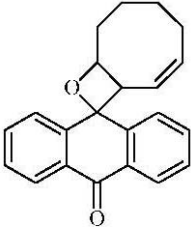
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO (1.2 equiv)	 4:1	203
	Ph ₂ CS (0.8 equiv)	 (41)	204
	Ph ₂ CS	 (—)	205
		 (ca. 100)	123

Table 2. Continued

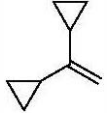
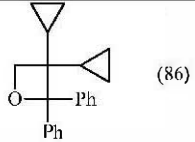
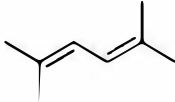
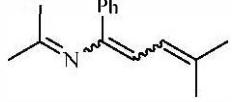
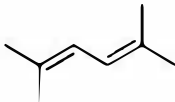
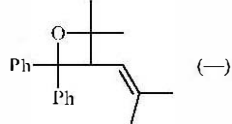
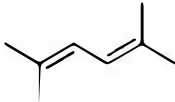
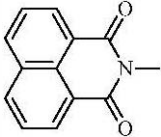
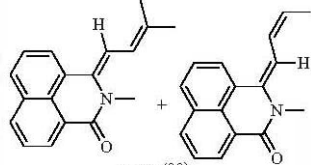
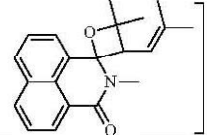
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO (1 equiv)	 (86)	160
	PhCN (0.17 equiv)	 (54)	147
	Ph ₂ CO (1 equiv)	 (—)	122
		 (90) 2.6:1 (90) via 	113c

Table 2. *Continued*

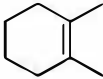
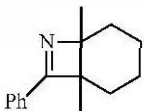
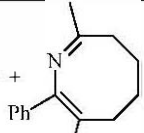
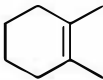
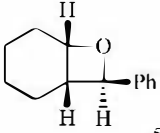
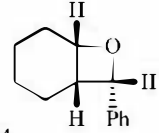
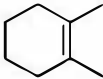
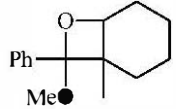
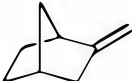
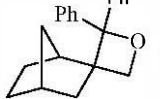
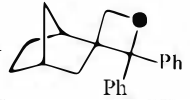
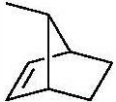
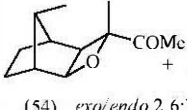
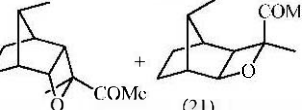
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCN (0.15 equiv)	 (17) +  (26)	147
	PhCHO (0.15 equiv)	 +  (60) 56:44	68c
	PhCO ₂ Me (0.25 equiv)	 (48)	170
	Ph ₂ CO (0.14 equiv)	 (57) +  (10)	191
	MeCOCOMe (0.13 equiv)	 (54) <i>exo/endo</i> 2.6:1 +  (21)	189

Table 2. Continued


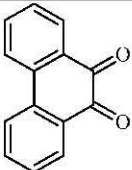
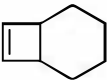
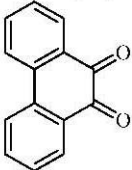
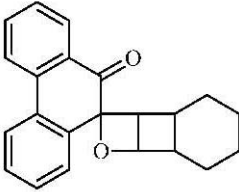

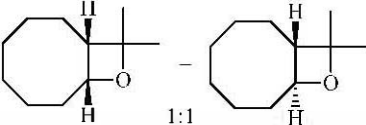
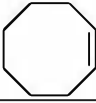
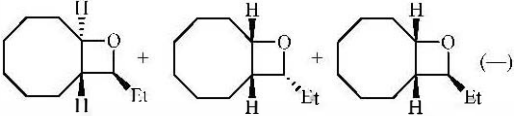
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.3 equiv)	No reaction	143
	 (0.3 equiv)	 (21)	143
	Me ₂ CO (1 equiv)	 (1:1)	203
	EtCHO	 (—)	206

Table 2. *Continued*

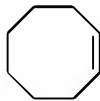
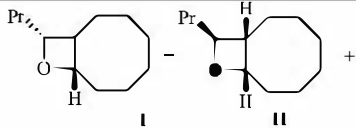
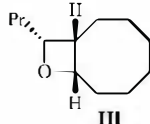
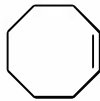

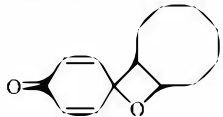


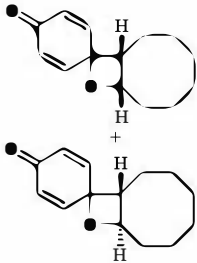
Alkene	Carbonyl compound	Product (yield %)	Ref.																								
	PrCHO	  <table border="1" data-bbox="1013 364 1284 448"> <thead> <tr> <th>Solvent</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>65:17:18 (34)</td> </tr> <tr> <td>no solvent</td> <td>2.8:47.5:49.7 (43)</td> </tr> </tbody> </table>	Solvent	I:II:III	MeCN	65:17:18 (34)	no solvent	2.8:47.5:49.7 (43)	196																		
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MeCN	65:17:18 (34)																										
no solvent	2.8:47.5:49.7 (43)																										
		 (88)	112 119																								
	 (0.3 equiv)	 <table border="1" data-bbox="1114 605 1233 952"> <thead> <tr> <th>Temp</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>-80</td> <td>92:8</td> </tr> <tr> <td>-60</td> <td>81:19</td> </tr> <tr> <td>-40</td> <td>70:30</td> </tr> <tr> <td>-20</td> <td>51:48</td> </tr> <tr> <td>0</td> <td>42:58</td> </tr> <tr> <td>29</td> <td>35:65</td> </tr> <tr> <td>40</td> <td>28:71</td> </tr> <tr> <td>60</td> <td>28:72</td> </tr> <tr> <td>80</td> <td>24:76</td> </tr> <tr> <td>100</td> <td>22:78</td> </tr> <tr> <td>110</td> <td>21:79</td> </tr> </tbody> </table>	Temp	dr	-80	92:8	-60	81:19	-40	70:30	-20	51:48	0	42:58	29	35:65	40	28:71	60	28:72	80	24:76	100	22:78	110	21:79	89b
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Table 2. *Continued*


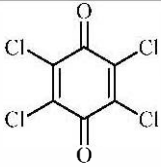
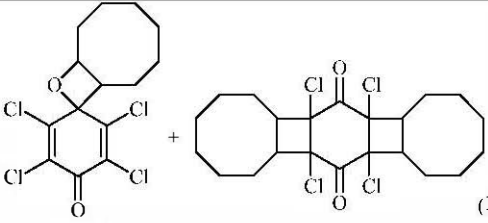

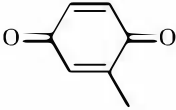
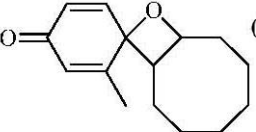

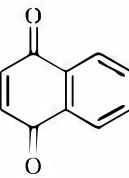
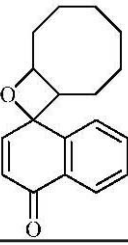
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 <p>(16->90) (10)</p>	165 207
		 <p>(>90)</p>	165
		 <p>(>90)</p>	165

Table 2. *Continued*


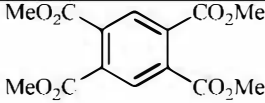
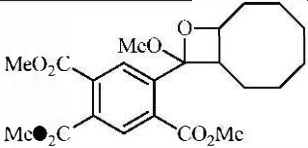

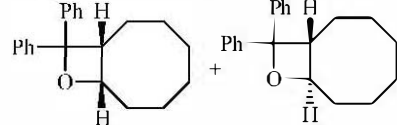
Alkene	Carbonyl compound	Product (yield %)	Ref.																																																				
	 (0.3 equiv)	 (16)	203																																																				
	Ph_2CO (0.3 equiv)		89b 103																																																				
		<table border="1"> <thead> <tr> <th>Temp</th> <th>time (min.)</th> <th>conv.</th> <th>dr</th> </tr> </thead> <tbody> <tr><td>-95</td><td>10</td><td>11</td><td>98:2</td></tr> <tr><td>-80</td><td>10</td><td>19</td><td>88:12</td></tr> <tr><td>-60</td><td>10</td><td>28</td><td>76:24</td></tr> <tr><td>-40</td><td>10</td><td>30</td><td>59:41</td></tr> <tr><td>-20</td><td>10</td><td>33</td><td>45:55</td></tr> <tr><td>0</td><td>10</td><td>37</td><td>36:64</td></tr> <tr><td>20</td><td>10</td><td>45</td><td>27:73</td></tr> <tr><td>40</td><td>10</td><td>46</td><td>25:75</td></tr> <tr><td>60</td><td>10</td><td>48</td><td>23:77</td></tr> <tr><td>80</td><td>5</td><td>28</td><td>21:79</td></tr> <tr><td>100</td><td>5</td><td>33</td><td>20:80</td></tr> <tr><td>110</td><td>5</td><td>32</td><td>20:80</td></tr> </tbody> </table>	Temp	time (min.)	conv.	dr	-95	10	11	98:2	-80	10	19	88:12	-60	10	28	76:24	-40	10	30	59:41	-20	10	33	45:55	0	10	37	36:64	20	10	45	27:73	40	10	46	25:75	60	10	48	23:77	80	5	28	21:79	100	5	33	20:80	110	5	32	20:80	
Temp	time (min.)	conv.	dr																																																				
-95	10	11	98:2																																																				
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100	5	33	20:80																																																				
110	5	32	20:80																																																				

Table 2. *Continued*


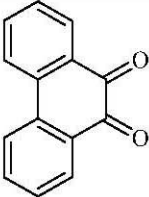
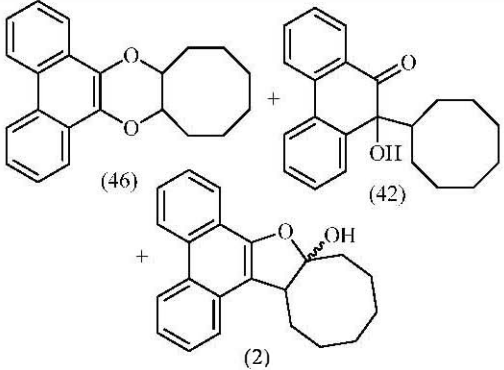

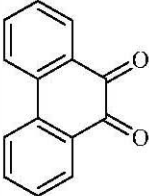
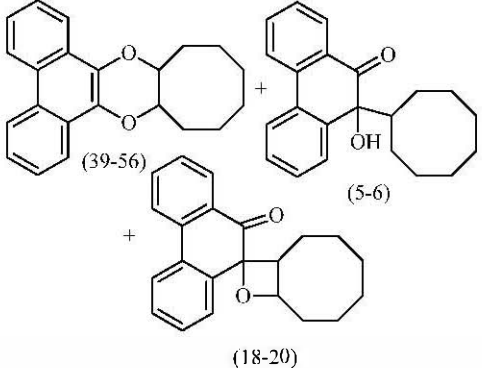
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)	 (46) + (42) + (2)	193
	 (0.5 equiv)	 (39-56) + (5-6) + (18-20)	143 193

Table 2. *Continued*


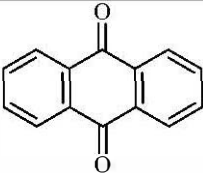
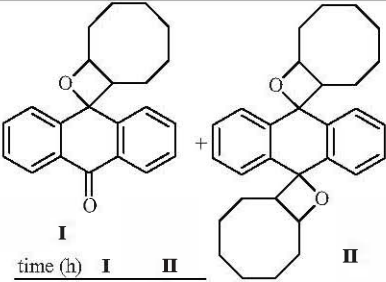

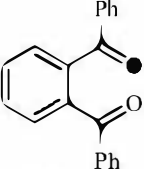
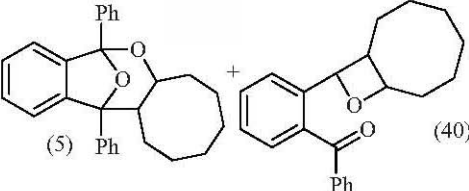
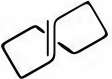
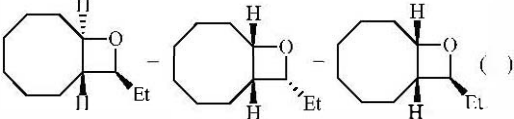
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 I II time (h) I II 12 (40) (10) 60 (0) (90)	123
	 (0.2 equiv) EtCHO	 (5) (40)	181
		 36:30:34	206
<i>cis/trans</i> 15:85			

Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)				Ref.	
		Temp	dr				
	 (0.2 equiv)		80	<5:95		89b	
			60	<5:95			
			40	<5:95			
			20	<5:95			
			0	<5:95			
			20	<5:95			
			40	<5:95			
			60	<5:95			
			80	<5:95			
			100	<5:95			
	Ph ₂ CO (0.3 equiv)		Temp	time (min.)	conv.	dr	89b 103
			-80	10	22	4:96	
			-60	10	32	3:97	
			-40	10	43	1:99	
			-20	10	44	2:98	
			0	10	37	2:98	
			20	10	39	2:98	
			40	5	39	2:98	
			60	5	39	4:96	
			80	3	35	6:94	
100	3	48	8:92				
	110	3	58	10:90			

Table 2. *Continued*


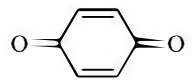
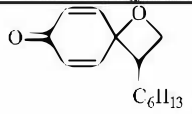
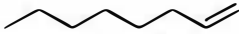
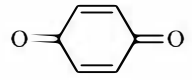
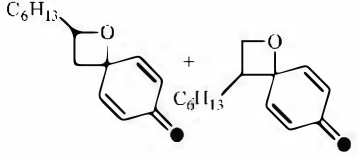



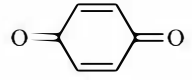
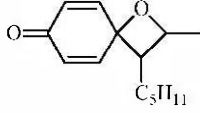
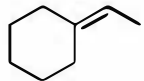
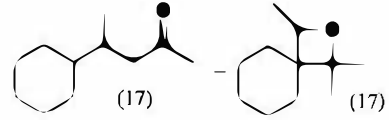
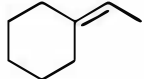
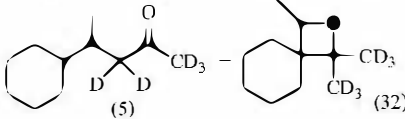
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (>90)	165
		 (15)	119
	PhCHO	Adduct (—)	18
	Ph ₂ CO	Adduct (—)	18
		 (>90)	165
	Me ₂ CO	 (17) - (17)	140
	(CD ₃) ₂ CO	 (5) - (32)	140

Table 2. *Continued*

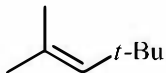
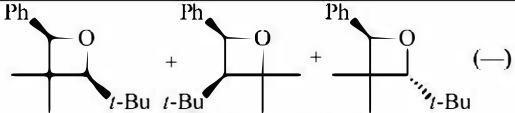
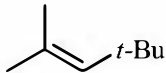
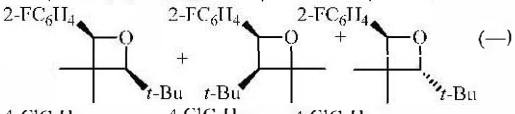
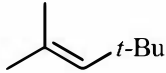
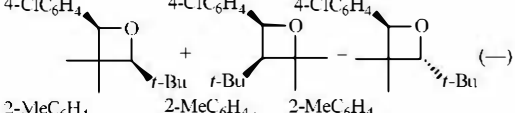
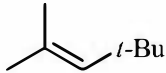
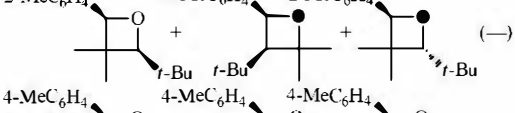
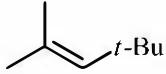
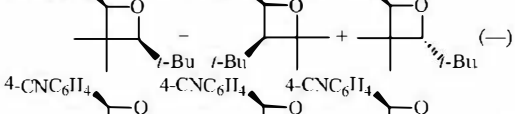
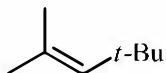
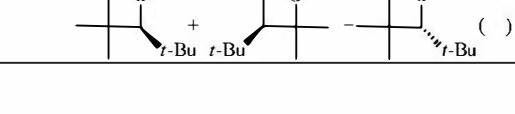
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO	 (—)	209
	2-FC ₆ H ₄ CHO	 (—)	209
	4-ClC ₆ H ₄ CHO	 (—)	209
	2-MeC ₆ H ₄ CHO	 (—)	209
	4-MeC ₆ H ₄ CHO	 (—)	209
	4-CNC ₆ H ₄ CHO	 ()	209

Table 2. *Continued*

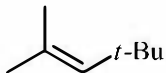
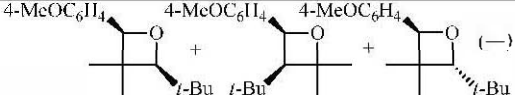
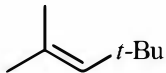
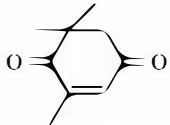

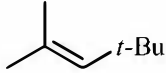
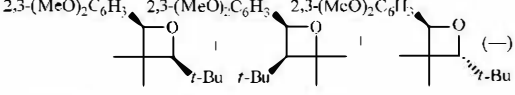
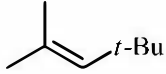
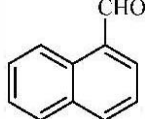
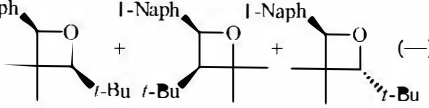
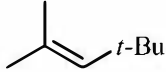
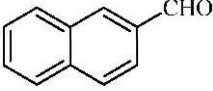
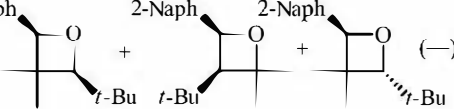
Alkene	Carbonyl compound	Product (yield %)	Ref.
	4-MeOC ₆ H ₄ CHO	 (—)	209
	 (0.23 equiv)	 (63)	177
	2,3-(MeO) ₂ C ₆ H ₃ CHO	 (—)	209
		 (—)	209
		 (—)	209

Table 2. Continued

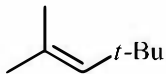
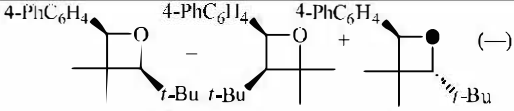
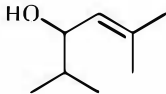
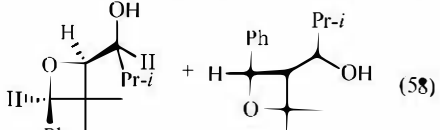
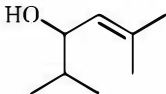
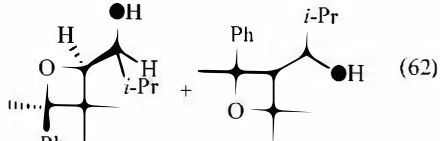
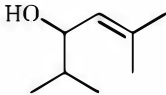
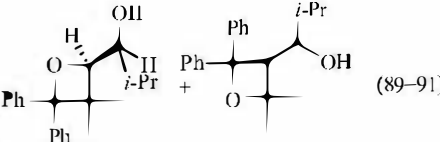
Alkene	Carbonyl compound	Product (yield %)	Ref.
	4-PhC ₆ H ₄ CHO		209
	PhCHO (1 equiv)		92
		<p><i>threo:erythro</i> 91:9 60:40</p>	
	PhCOMe (1 equiv)		92
		<p><i>threo:erythro</i> 92:8 >95:5</p>	
	Ph ₂ CO (1 equiv)		89a 92
		<p><i>threo:erythro</i> 95:5 >95:5</p>	

Table 2. *Continued*

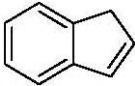
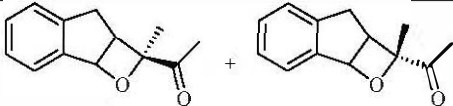
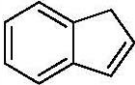
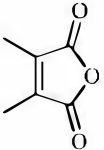
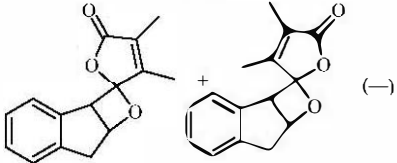
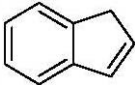

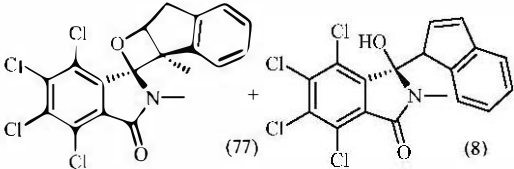
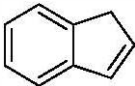
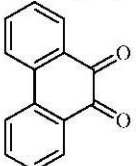
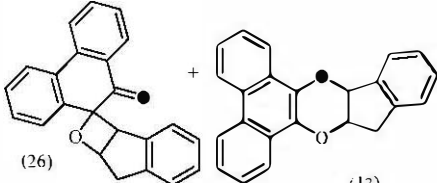
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCOCOMe (1 equiv)	 2:1 (60)	105d 146
		 8:2	210
	 (0.17 equiv)	 (77) (8)	201
	 (0.1 equiv)	 (26) (13)	211

Table 2. *Continued*


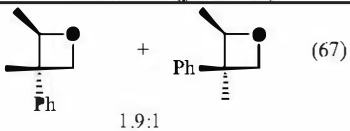

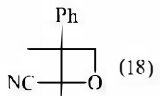

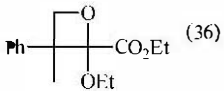

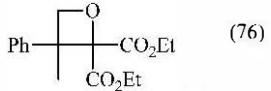

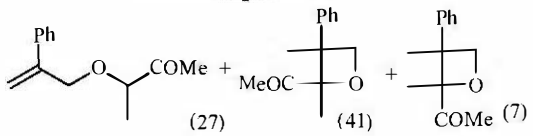
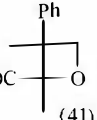
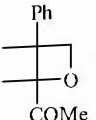

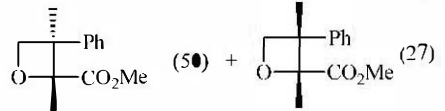
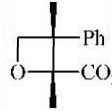
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCHO (4 equiv)	 (67) 1.9:1	200
	MeCOCN (1 equiv)	 (18)	145
	EtO ₂ CCO ₂ Et (0.5 equiv)	 (36)	139
	EtO ₂ CCOCO ₂ Et (0.5 equiv)	 (76)	139
	MeCOCOMe (1 equiv)	 (27) +  (41) +  (7)	114d 146
	MeCOCO ₂ Me (0.5 equiv)	 (50) +  (27)	114b

Table 2. *Continued*


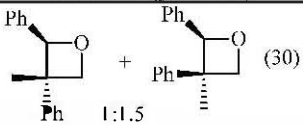

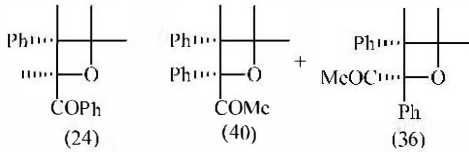

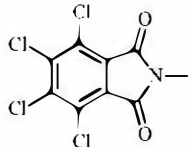
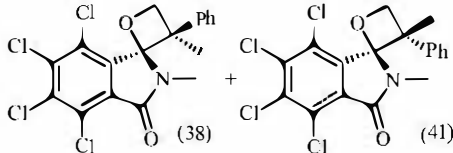

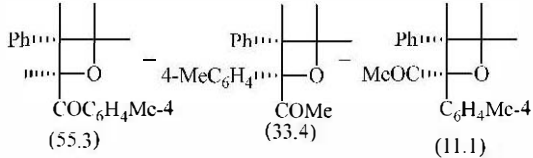
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCHO (4 equiv)	 (30) 1:1.5	200
	PhCOCOMe (0.7 equiv)	 (24) (40) (36)	179
	 (0.18 equiv)	 (38) (41)	201
	4-MeC ₆ H ₄ COCOMe (0.07 equiv)	 (55.3) (33.4) (11.1)	179

Table 2. Continued


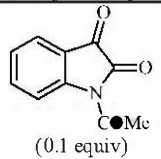
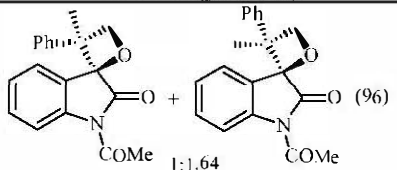

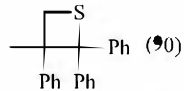
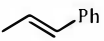
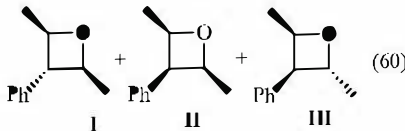
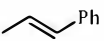
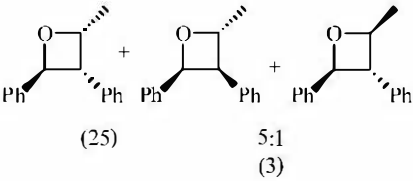
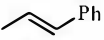
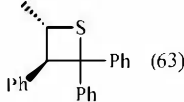
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.1 equiv)	 1:1.64 (96)	202
	Ph ₂ CS	 Ph Ph (90)	205
	MeCHO	 I II III (60) I:II:III=0.78:0.20:0.02	78c
	PhCHO	 (25) 5:1 (3)	212
	Ph ₂ CS	 Ph Ph (63)	205

Table 2. *Continued*


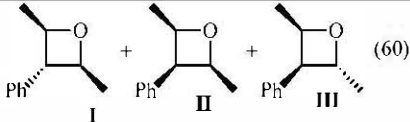

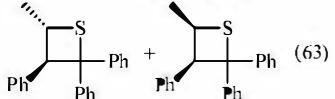
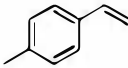
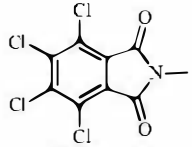
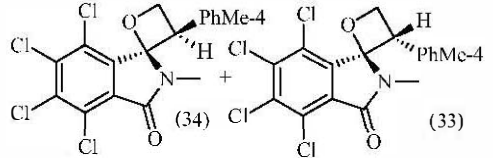
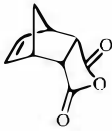
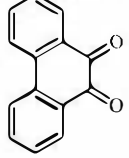
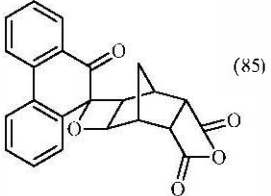
Alkene	Carbonyl compound	Product (yield %)	Ref.
	MeCHO	 <p style="text-align: center;">I:II:III=0.05:0.57:0.38</p>	78c
	Ph ₂ CS	 <p style="text-align: center;">79:21</p>	205
	 (0.17 equiv)		201
			143

Table 2. *Continued*

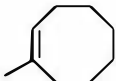
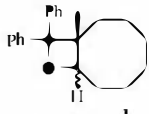

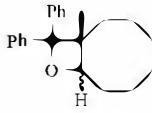
Alkene	Carbonyl compound	Product	Product (yield %)			Ref.
			Temp	<i>cis/trans</i> I	<i>cis/trans</i> II	
	Ph ₂ CO (0.83 equiv)		-95	>98:2	>95:5	89b
			80	>98:2	>95:5	
			-60	>98:2	>95:5	
			40	>98:2	>95:5	
			20	>98:2	>95:5	
			0	88:12	95:5	
			20	77:23	90:10	
			40	64:36	87:13	
			60	57:43	83:17	
			80	50:50	80:20	
			100	45:55	77:23	
			110	44:56	76:24	
	Ph ₂ CO (0.83 equiv)		-95	35:65	54:46	89b
			80	16:84	25:75	
			-60	9:91	11:89	
			-40	<2:98	4:96	
			-20	<2:98	8:92	
			0	<2:98	13:87	
			20	<2:98	20:80	
			40	<2:98	20:80	
			60	<2:98	27:73	
			80	<2:98	42:58	
			100	5:95	51:49	
			110	6:94	51:49	

Table 2. *Continued*


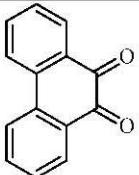
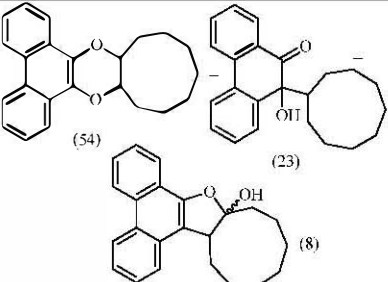

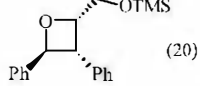
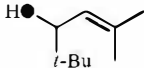
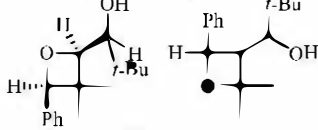
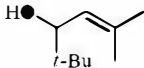
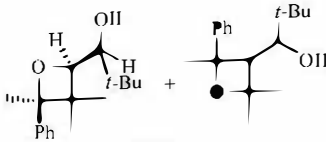
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)	 (54) (23) (8)	193
	PhCHO	 (20)	212
	PhCHO (1 equiv)	 (52) <i>threo:erythro</i> >95:5 59:41	92
	PhCOMe (1 equiv)	 (76) <i>threo:erythro</i> >95:5 >95:5	92

Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.
			105h
	Me ₂ CO		215
	PhCHO		215
	Ph ₂ CO		215

Table 2. *Continued*


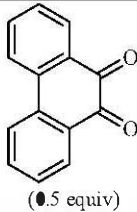
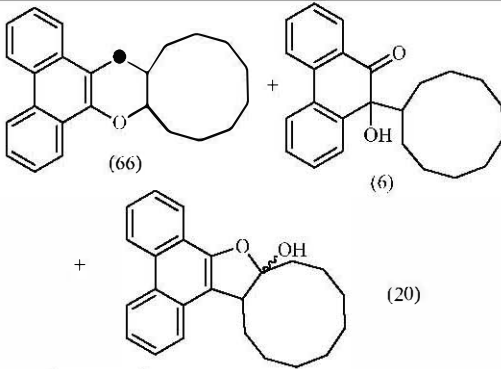

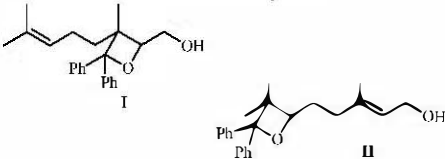

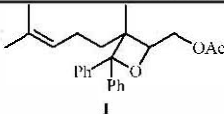
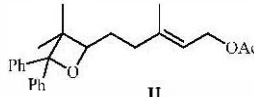
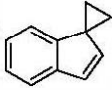
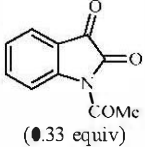
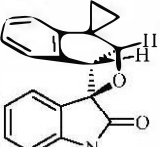
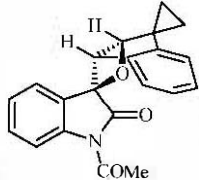
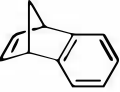
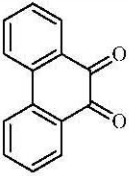
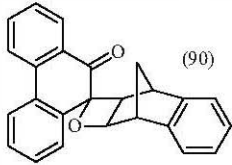
Alkene	Carbonyl compound	Product (yield %)	Ref.																																								
	 (0.5 equiv)	 (66) + (6) + (20)	193																																								
	Ph ₂ CO	 I + II	96																																								
		<table border="1"> <thead> <tr> <th>Solv</th> <th>Temp</th> <th>Conc [mM]</th> <th>I</th> <th>II</th> <th>Conc [nM]</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Toluene</td> <td>-75</td> <td>340</td> <td>(13)</td> <td>(44)</td> <td>6.8</td> <td>(27)</td> <td>(28)</td> </tr> <tr> <td>Toluene</td> <td>-40</td> <td>340</td> <td>(14)</td> <td>(38)</td> <td>6.8</td> <td>(18)</td> <td>(20)</td> </tr> <tr> <td>Toluene</td> <td>2</td> <td>340</td> <td>(16)</td> <td>(26)</td> <td>6.8</td> <td>(10)</td> <td>(12)</td> </tr> <tr> <td>Benzene</td> <td>20</td> <td>340</td> <td>(15)</td> <td>(29)</td> <td>6.8</td> <td>(20)</td> <td>(26)</td> </tr> </tbody> </table>	Solv	Temp	Conc [mM]	I	II	Conc [nM]	I	II	Toluene	-75	340	(13)	(44)	6.8	(27)	(28)	Toluene	-40	340	(14)	(38)	6.8	(18)	(20)	Toluene	2	340	(16)	(26)	6.8	(10)	(12)	Benzene	20	340	(15)	(29)	6.8	(20)	(26)	
Solv	Temp	Conc [mM]	I	II	Conc [nM]	I	II																																				
Toluene	-75	340	(13)	(44)	6.8	(27)	(28)																																				
Toluene	-40	340	(14)	(38)	6.8	(18)	(20)																																				
Toluene	2	340	(16)	(26)	6.8	(10)	(12)																																				
Benzene	20	340	(15)	(29)	6.8	(20)	(26)																																				

Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO	 + 	96
	 (0.33 equiv)	 -  (90) 6:1	202
	 (0.33 equiv)	 (90)	143

Solv	Temp	Cone [m.M]	I	II	Cone [nM]	I	II
Toluene	75	340	(7)	(56)	6.8	(5)	(39)

Table 2. Continued

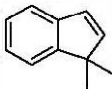
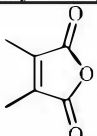
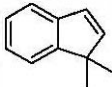
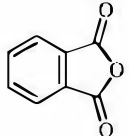
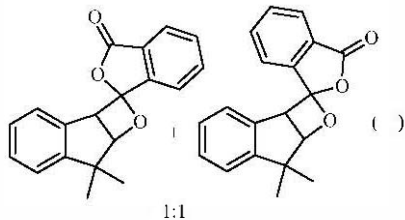
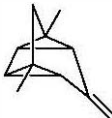
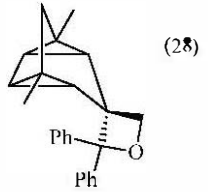
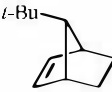
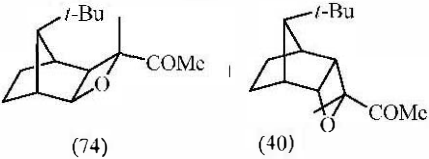
Alkene	Carbonyl compound	Product (yield %)	Ref.
		No reaction	210
		 1:1	210
	Ph ₂ CO (1 equiv)	 (28)	216
	MeCOCOMe (8 equiv)	 (74) (40) <i>exo/endo</i> 1:30	189

Table 2. *Continued*


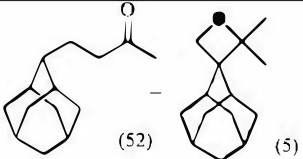
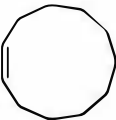
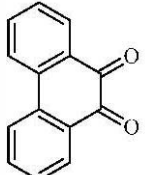
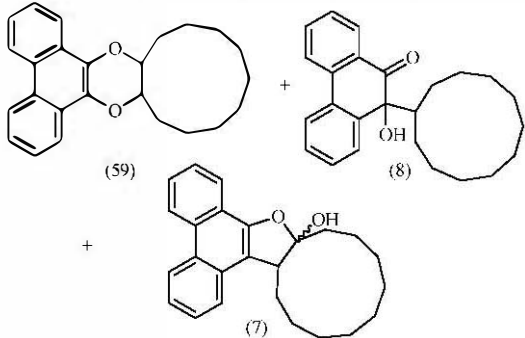
Alkene	Carbonyl compound	Product (yield %)	Ref.
	Me ₂ CO	 (52) (5)	140
	 (0.5 equiv)	 (59) (8) (7)	193

Table 2. Continued

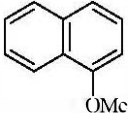
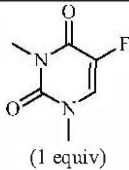
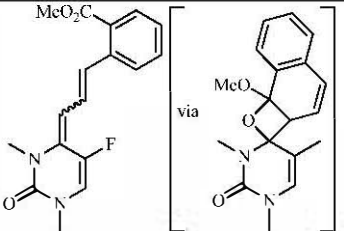

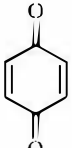
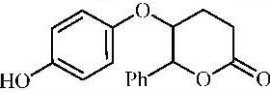


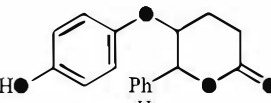


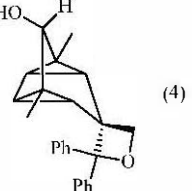
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (1 equiv)	 Solvent cyclohexane (38-43) benzene (62) toluene (45) MeCN (0) MeOH (0)	113d
		 (39)	152
	 Ph ₂ CO (1 equiv)	 (52)	152
	 Ph ₂ CO (1 equiv)	 (4)	216

Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.
	Ph ₂ CO	 I II	96
		No reaction	119
		 (19)	115

Solv	Temp	Conc [mM]	I	II	Conc [nM]	I	II
Toluene	-75	340	(6)	(33)	6.8	(5)	(29)

Table 2. Continued

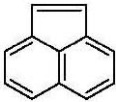
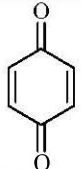
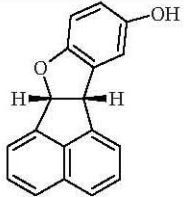
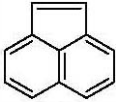
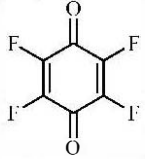
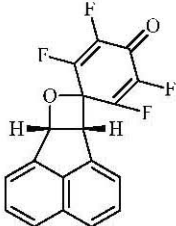
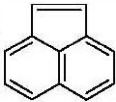
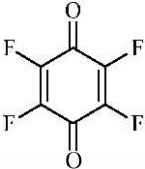
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (1 equiv, 500 nm)	 (32)	115
	 (1 equiv, 420 nm)	 (11)	115
	 (1 equiv, 500 nm)	No reaction	115

Table 2. *Continued*

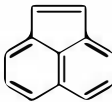
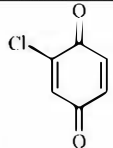
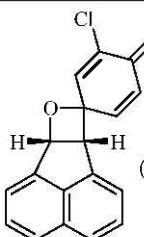
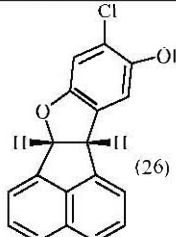
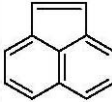
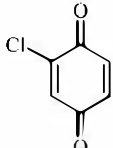
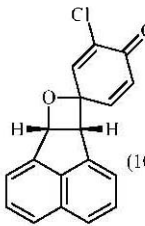
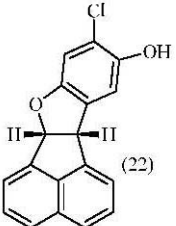
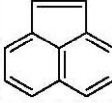
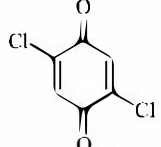
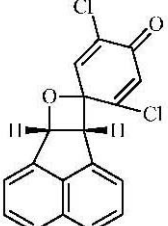
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (1 equiv, 420 nm)	 (9) -  (26)	115
	 (1 equiv, 500 nm)	 (10) +  (22)	115
	 (1 equiv, 420 nm)	 (25)	115

Table 2. *Continued*

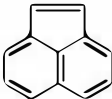
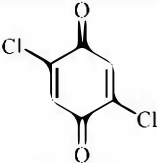
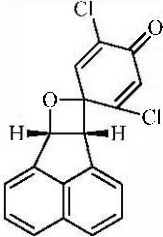
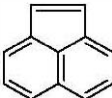
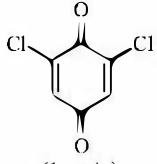
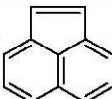
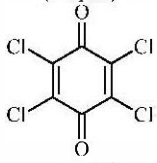
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 <p data-bbox="552 412 708 437">(1 equiv, 500 nm)</p>	 <p data-bbox="1161 339 1198 365">(24)</p>	115
	 <p data-bbox="588 645 671 670">(1 equiv)</p>	No reaction	115
	 <p data-bbox="588 824 671 850">(1 equiv)</p>	No reaction	115

Table 2. *Continued*

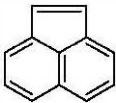
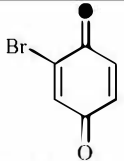
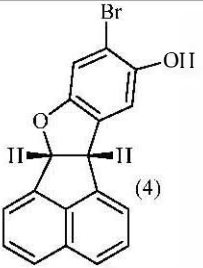
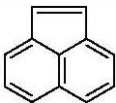
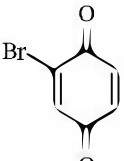
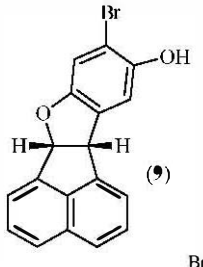
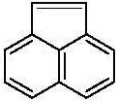
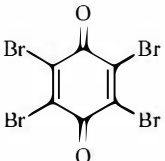
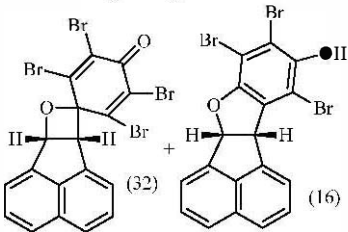
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (1 equiv, 420 nm)	 (4)	115
	 (1 equiv, 500 nm)	 (9)	115
	 (1 equiv, 420 nm)	 (32) + (16)	115

Table 2. Continued

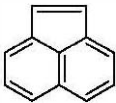
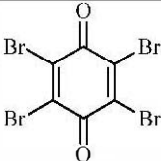
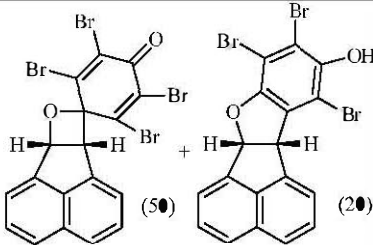
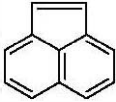
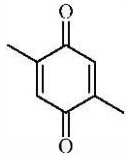
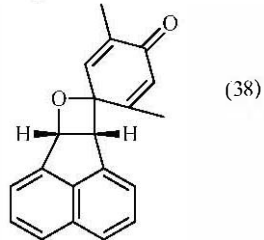
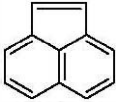
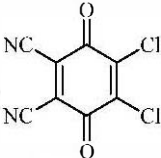
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (1 equiv, 500 nm)	 (50) (20)	115
	 (1 equiv)	 (38)	115
	 (1 equiv)	No reaction	115

Table 2. *Continued*

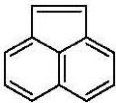
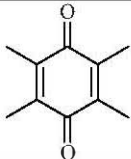
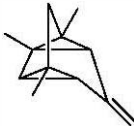
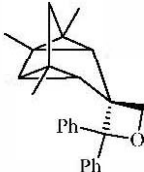

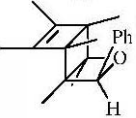

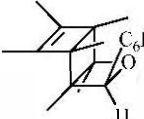


Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (1 equiv)	No reaction	115
	Ph ₂ CO	 (26)	216
	PhCHO	 (29)	217
	4-MeC ₆ H ₄ CHO	 (29)	217
	4-MeOC ₆ H ₄ CHO	 (20)	217

Table 2. *Continued*

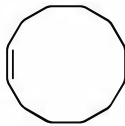
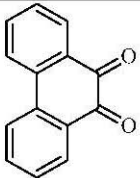
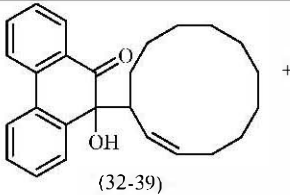
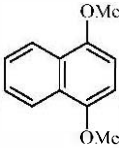
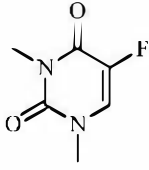
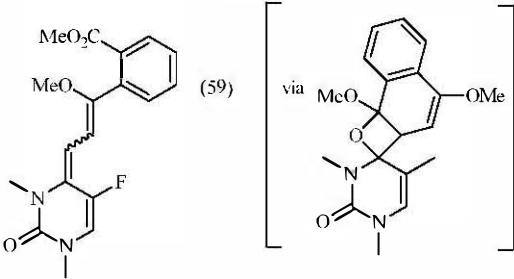
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)	 (32-39)	143 193
	 (1 equiv)	 (59)	113d

Table 2. *Continued*

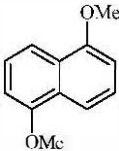
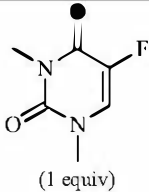
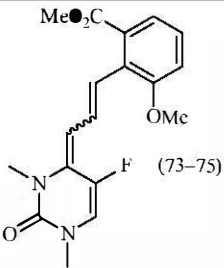
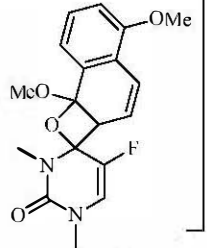
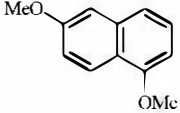
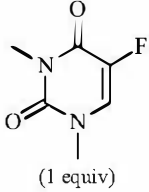
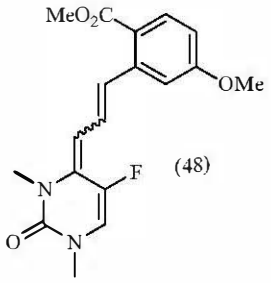
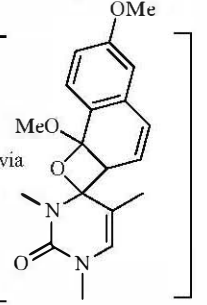
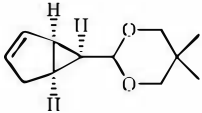
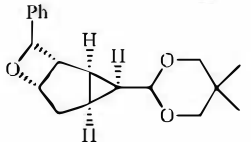
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 <p>(1 equiv)</p>	 <p>(73–75)</p> <p>via </p>	113d 113e
	 <p>(1 equiv)</p>	 <p>(48)</p> <p>via </p>	113d
	<p>PhCHO (0.3 equiv)</p>	 <p>(47)</p>	218

Table 2. *Continued*

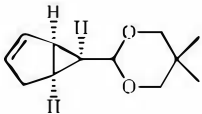
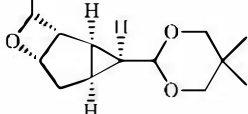
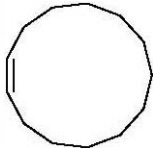
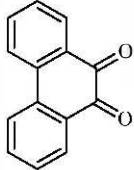
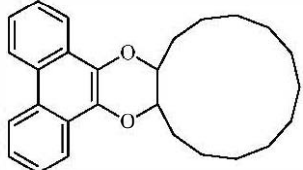


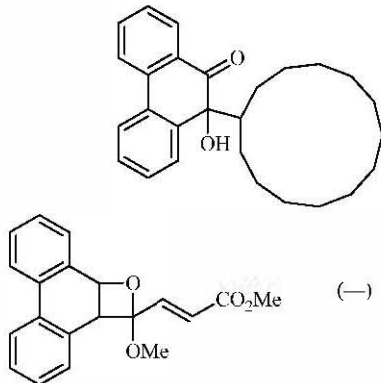
Alkene	Carbonyl compound	Product (yield %)	Ref.
	3-AcOC ₆ H ₄ CHO (0.3 equiv)	 (33)	218
	 (0.5 equiv)	 (35)	193
	 (1 equiv)	 (—)	219

Table 2. *Continued*


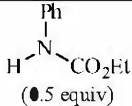
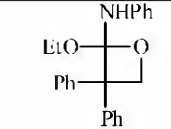


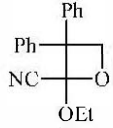

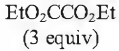
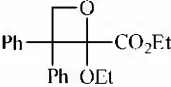


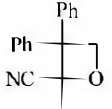

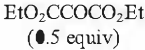
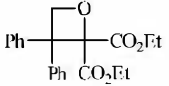

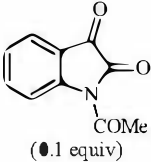
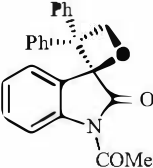

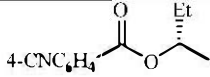
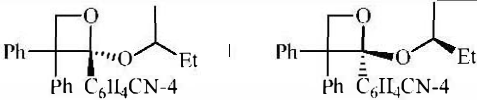
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (52)	220
		 (24.1)	199
		 (15.7)	221
		 (52)	145
		 (64)	139
		 (98)	202

Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.																																																	
			79b																																																	
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>wavelength</th> <th>time (h)</th> <th>Temp</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td rowspan="6">THF</td> <td rowspan="3">290</td> <td rowspan="3">3</td> <td>50 (9)</td> <td>78.5:21.5</td> </tr> <tr> <td>25 (18)</td> <td>77:23</td> </tr> <tr> <td>-50 (4)</td> <td>66:34</td> </tr> <tr> <td rowspan="3">330</td> <td rowspan="3">5</td> <td>50 (4)</td> <td>44:56</td> </tr> <tr> <td>25 (5)</td> <td>46:54</td> </tr> <tr> <td>-50 (4)</td> <td>56:44</td> </tr> <tr> <td rowspan="6">MeCN</td> <td rowspan="3">290</td> <td rowspan="3">3</td> <td>50 (4)</td> <td>43.5:56.5</td> </tr> <tr> <td>25 (4)</td> <td>44:56</td> </tr> <tr> <td>-20 (5)</td> <td>44.5:55.5</td> </tr> <tr> <td rowspan="3">330</td> <td rowspan="3">7</td> <td>-40 (6)</td> <td>44.5:55.5</td> </tr> <tr> <td>50 (11)</td> <td>48.5:51.5</td> </tr> <tr> <td>25 (15)</td> <td>46:54</td> </tr> <tr> <td></td> <td></td> <td></td> <td>20 (15)</td> <td>45:55</td> </tr> <tr> <td></td> <td></td> <td></td> <td>40 (14)</td> <td>44.5:55.5</td> </tr> </tbody> </table>	Solvent	wavelength	time (h)	Temp	dr	THF	290	3	50 (9)	78.5:21.5	25 (18)	77:23	-50 (4)	66:34	330	5	50 (4)	44:56	25 (5)	46:54	-50 (4)	56:44	MeCN	290	3	50 (4)	43.5:56.5	25 (4)	44:56	-20 (5)	44.5:55.5	330	7	-40 (6)	44.5:55.5	50 (11)	48.5:51.5	25 (15)	46:54				20 (15)	45:55				40 (14)	44.5:55.5	
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	330	5	50 (4)	44:56																																																
			25 (5)	46:54																																																
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MeCN	290	3	50 (4)	43.5:56.5																																																
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			20 (15)	45:55																																																
			40 (14)	44.5:55.5																																																

Solvent	wavelength	time (h)	Temp	dr	
methylcyclohexane	290	3	50	(12)	88.5:11.5
			25	(12)	82:18
			0	(11)	81.5:18.5
			-25	(11)	71.5:28.5
			-50	(9)	67:33
	330	10	50	(5)	51.5:48.5
			25	(4)	52:48
			0	(4)	51.5:48.5
			-25	(4)	62:38
			-50	(6)	63:37
toluene	290	3	50	(12)	87:13
			25	(13)	82:18
			0	(9)	84:16
			25	(10)	77:23
			-50	(10)	68.5:31.5
	330	6	50	(4)	44.5:55.5
			25	(4)	48:52
			0	(5)	48:52
			-25	(4)	53.47
			-50	(5)	61:39

Table 2. Continued


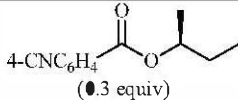
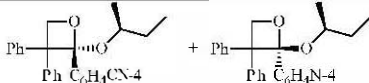


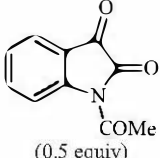
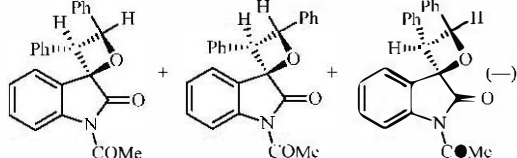
Alkene	Carbonyl compound	Product (yield %)	Ref.																																																																		
		 Ph C_6H_4CN-4	79a																																																																		
		<table border="1"> <thead> <tr> <th>wavelength</th> <th>time (h)</th> <th>dr</th> <th>Temp</th> <th>wavelength</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>254</td> <td>5</td> <td>(12) 82.5:17.5</td> <td>50</td> <td>290</td> <td>88.5:11.5</td> </tr> <tr> <td>290</td> <td>5</td> <td>(13) 82.5:17.5</td> <td></td> <td>330</td> <td>51.5:48.5</td> </tr> <tr> <td>300</td> <td>1</td> <td>(9) 78:22</td> <td>25</td> <td>290</td> <td>82:18</td> </tr> <tr> <td>310</td> <td>1</td> <td>(8) 71.5:28.5</td> <td></td> <td>330</td> <td>52:48</td> </tr> <tr> <td>320</td> <td>1</td> <td>(3) 73:27</td> <td>0</td> <td>290</td> <td>81.5:18.5</td> </tr> <tr> <td>330</td> <td>6</td> <td>(4) 48:52</td> <td></td> <td>330</td> <td>51.5:48.5</td> </tr> <tr> <td></td> <td></td> <td></td> <td>-25</td> <td>290</td> <td>71.5:28.5</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> <td>330</td> <td>62.5:37.5</td> </tr> <tr> <td></td> <td></td> <td></td> <td>-50</td> <td>290</td> <td>67:33</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> <td>330</td> <td>63:37</td> </tr> </tbody> </table>	wavelength	time (h)	dr	Temp	wavelength	dr	254	5	(12) 82.5:17.5	50	290	88.5:11.5	290	5	(13) 82.5:17.5		330	51.5:48.5	300	1	(9) 78:22	25	290	82:18	310	1	(8) 71.5:28.5		330	52:48	320	1	(3) 73:27	0	290	81.5:18.5	330	6	(4) 48:52		330	51.5:48.5				-25	290	71.5:28.5					330	62.5:37.5				-50	290	67:33					330	63:37	
wavelength	time (h)	dr	Temp	wavelength	dr																																																																
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				330	63:37																																																																
	Ph_2CO	No reaction	23																																																																		
		 (0.5 equiv)	202																																																																		

Table 2. *Continued*

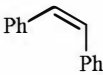
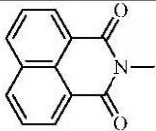
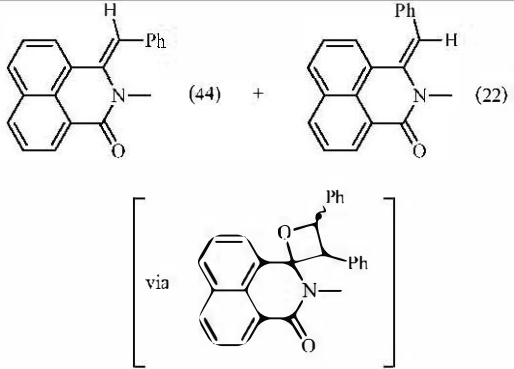
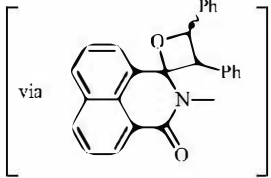
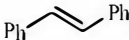

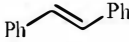
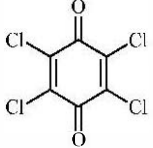
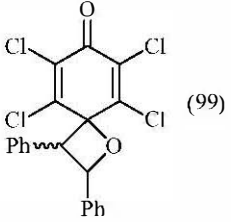
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 <p>(44) + (22)</p> <p>via </p>	113c
		No reaction	119
	 <p>(0.5 equiv)</p>	 <p>(99)</p>	222 223

Table 2. Continued

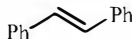
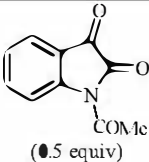
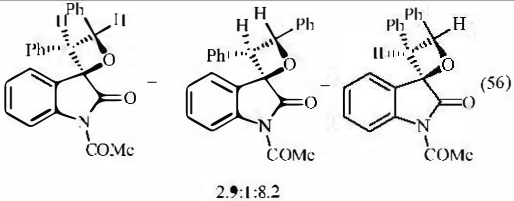
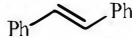
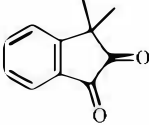
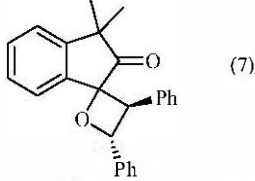
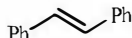
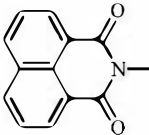
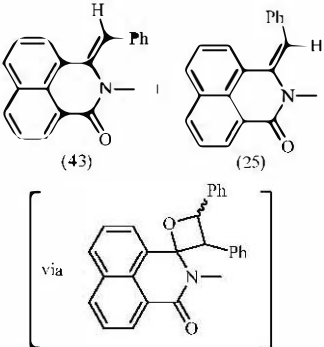
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)	 2.9:1:8.2 (56)	202
		 (7)	166
	 (25)	 (43) (25) via	113c

Table 2. *Continued*

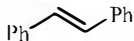
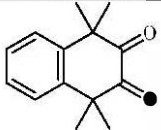
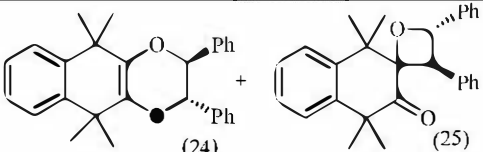
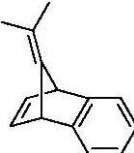

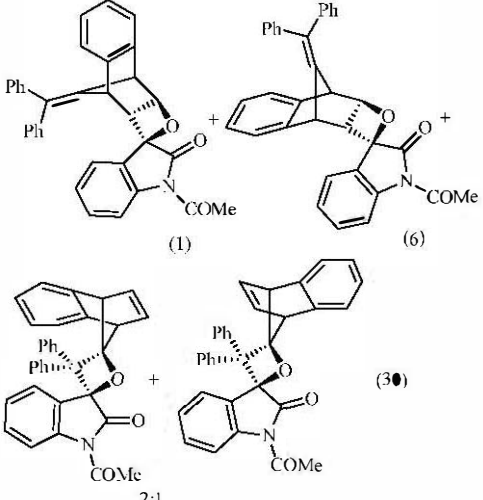
Alkene	Carbonyl compound	Product (yield %)	Ref.
		 <p>(24) + (25)</p>	166
	 <p>(0.5 equiv)</p>	 <p>(1) + (6) + (30)</p> <p>2:1</p>	202

Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.
			222
			222
			222
			222

Table 2. *Continued*

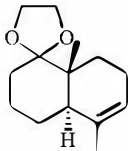
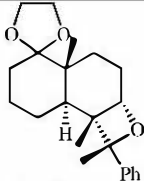
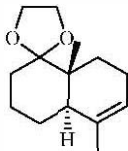
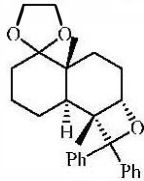
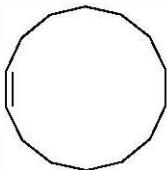
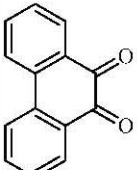
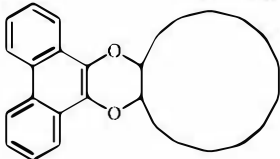
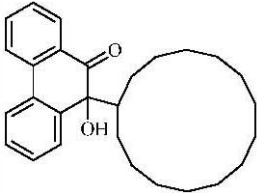
Alkene	Carbonyl compound	Product (yield %)	Ref.
	PhCOMe (1.04 equiv)	 (3)	224
	Ph ₂ CO (1.14 equiv)	 (20)	224
	 (0.5 equiv)	 (42) +  (40)	193

Table 2. *Continued*

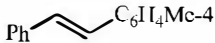
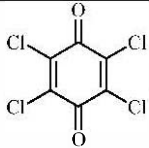
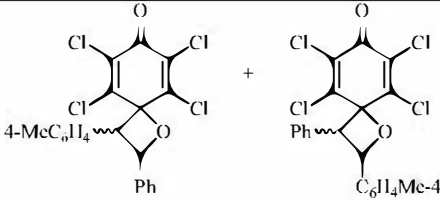
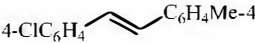
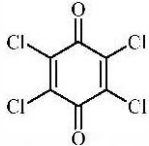
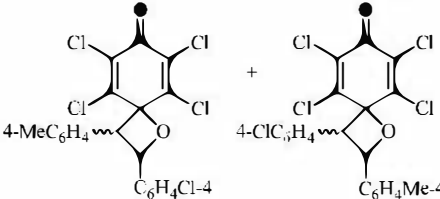
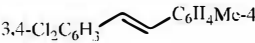

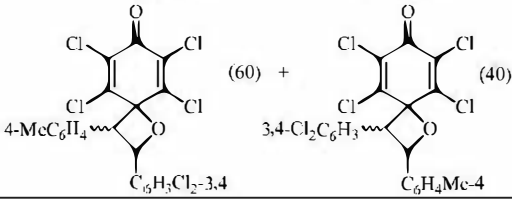
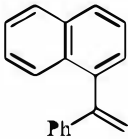
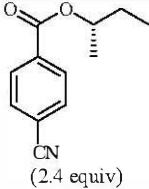
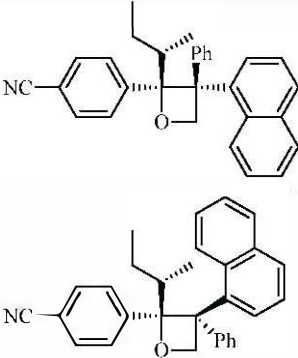
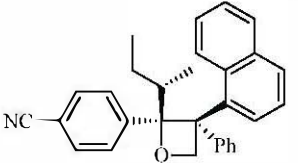
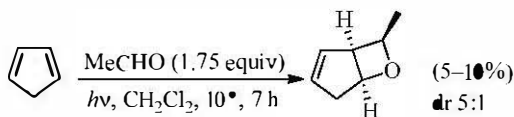
Alkene	Carbonyl compound	Product (yield %)	Ref.
	 (0.5 equiv)		222 (—)
	 (0.5 equiv)		222 (—)
	 (0.5 equiv)		222 (60) + (40)

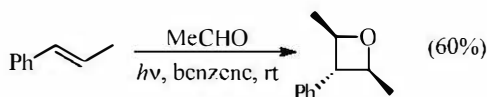
Table 2. *Continued*

Alkene	Carbonyl compound	Product (yield %)	Ref.
		 (13) dr 57:43 +	225
		 (19)	

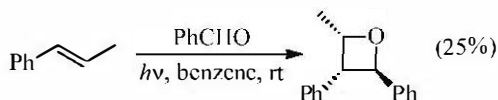
Different stereoselectivity is obtained when benzaldehyde is the carbonyl compound (Scheme 55) [212]. The variable stereoselectivities observed may be due to the different excited states involved in the reaction.



Scheme 53

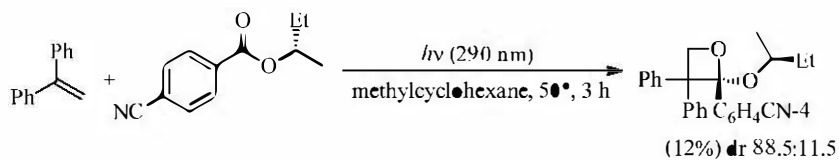


Scheme 54

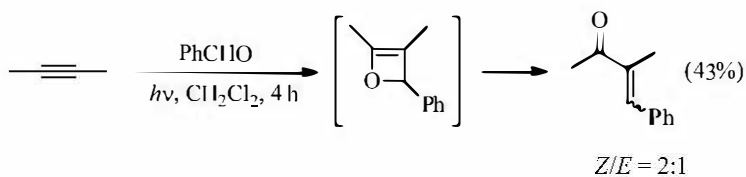


Scheme 55

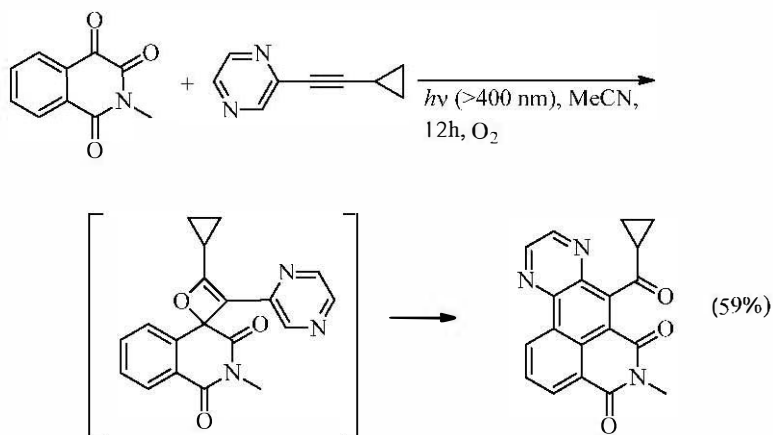
Allylic alcohols give the corresponding oxetanes with high stereoselectivity as described above (see Scheme 33). Chiral benzoates and phenylglyoxylates yield the corresponding diastereoisomeric oxetanes with good selectivity (Scheme 56) [79]. Further studies shows that an ester can also participate in a Paternò–Büchi reaction. The observed stereoselectivity in the reaction of allylic alcohols with phenylglyoxylates has been explained by considering a conformational memory effect during the ISC process of the triplet biradical [154].



Scheme 56



Scheme 57



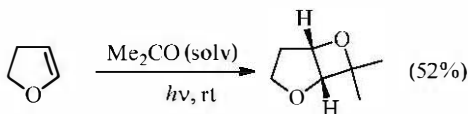
Scheme 58

Alkynes react with carbonyl compounds in Paternò–Büchi reactions (Table 3). However, the resulting oxetenes are not stable, and give the corresponding ring-opened products (Scheme 57) [226]. Good results are obtained when the ring opening products rearrange to provide aromatic products (Scheme 58) [227].

The reaction can be performed also on allenes and other cumulated double bonds. The reported data on this type of compounds are collected in Table 4. In this case, often ring opening products or transposition products deriving from the original oxetanes are recovered.

Reaction of Carbonyl Compounds with Enol Ethers and Enol Thioethers.

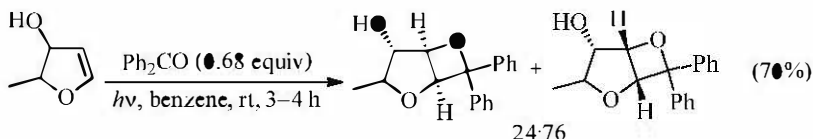
All the the available data are collected in Tables 5 and 6. 2,3-Dihydrofuran is the most studied enol ether used in the Paternò–Büchi reaction. Thus, 2,3-dihydrofuran reacts with acetone to give the corresponding adduct in 52% yield (Scheme 59) [69].



Scheme 59

The regiochemistry of the reaction can be explained considering the relative stability of the biradical intermediate. When 2,3-dihydrofuran reacts with aromatic aldehydes, *endo* selectivity is observed (cf. Scheme 18) [68,72].

If the enol ether bears an allylic alcohol group, good stereoselectivity is observed, governed by a hydroxyl directing effect (Scheme 60) [91].



Scheme 60

Table 3. Intermolecular reactions with electron-rich insaturated compounds. B. Alkynes


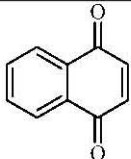
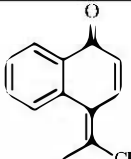
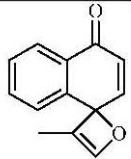

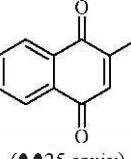
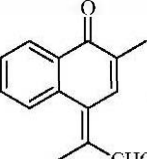
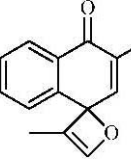

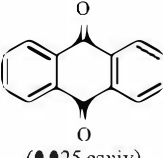
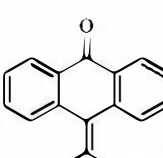
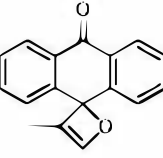

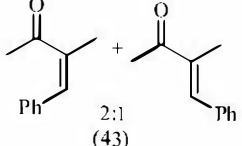
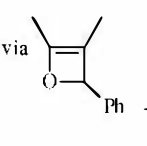
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 (0.025 equiv)	 (—)	via  228
	 (0.025 equiv)	 ()	via  228
	 (0.025 equiv)	 (40–90)	via  228
	PhCHO (0.4 equiv)	 2:1 (43)	via  226

Table 3. *Continued*

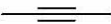
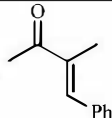

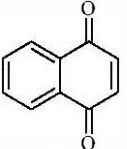
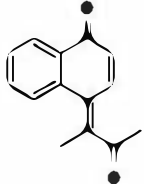
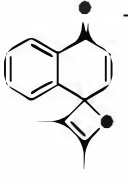

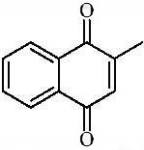
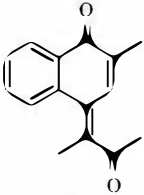
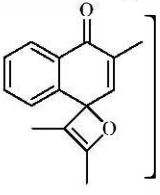

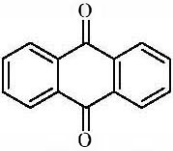
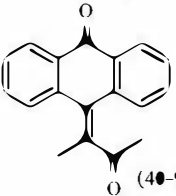
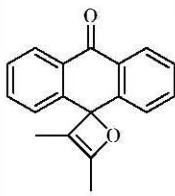
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	PhCHO (0.4 equiv)	 (—)	226
	 (0.025 equiv)	 (—) [via 	228
	 (0.025 equiv)	 (—) [via 	228
	 (0.025 equiv)	 (40–90) [via 	228

Table 3. *Continued*

Alkyne	Carbonyl compound	Product (Yields %)	Ref.																											
Bu-C≡C-	PhCHO (0.5 equiv)	 <table border="1"> <thead> <tr> <th>Irradiation time (h)</th> <th>I[%]</th> <th>II[%]</th> <th>III[%]</th> <th>IV[%]</th> <th>V[%]</th> <th>VI[%]</th> <th>VII[%]</th> <th>VIII[%]</th> </tr> </thead> <tbody> <tr> <td>1.5</td> <td>13</td> <td>12</td> <td>4</td> <td>0</td> <td>5</td> <td>4</td> <td>48</td> <td></td> </tr> <tr> <td>7.5</td> <td>8</td> <td>8</td> <td>4</td> <td>0.5</td> <td>3</td> <td>3</td> <td>57</td> <td></td> </tr> </tbody> </table>	Irradiation time (h)	I[%]	II[%]	III[%]	IV[%]	V[%]	VI[%]	VII[%]	VIII[%]	1.5	13	12	4	0	5	4	48		7.5	8	8	4	0.5	3	3	57		229
Irradiation time (h)	I[%]	II[%]	III[%]	IV[%]	V[%]	VI[%]	VII[%]	VIII[%]																						
1.5	13	12	4	0	5	4	48																							
7.5	8	8	4	0.5	3	3	57																							
Ph-C≡C-	 (0.25 equiv)	 (—) [via]	228																											
Ph-C≡C-	 (0.25 equiv)	 (—) [via]	228																											

Table 3. *Continued*

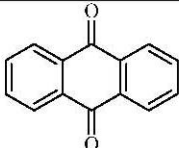
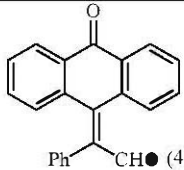
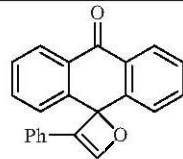
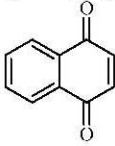
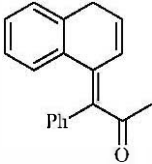
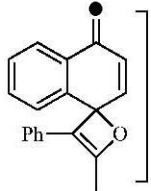
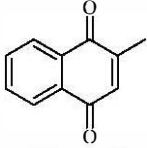
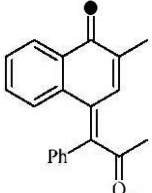
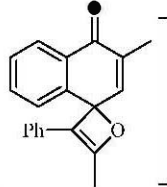
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
Ph-C≡C-	 (0.25 equiv)	 Ph-CH• (40-90)	[via ] 228
Ph-C≡C-	 (0.25 equiv)	 Ph-C(=O)CH ₃	(—) [via ] 228
Ph-C≡C-	 (0.25 equiv)	 Ph-C(=O)CH ₃	(—) [via ] 228

Table 3. *Continued*


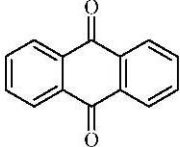
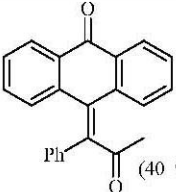
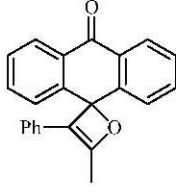
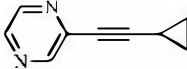
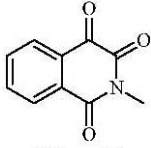
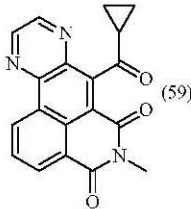
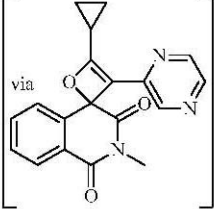
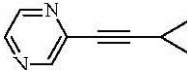
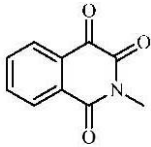
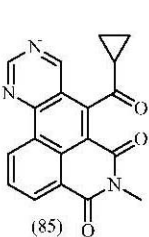
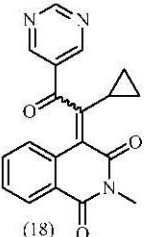
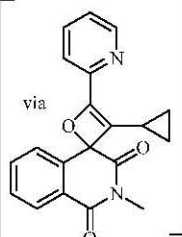
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 (0.24 equiv)	 (40-90) [via ]	228
	 (0.5 equiv)	 (59) [via ]	227
	 (0.5 equiv)	 (85)  (18) [via ]	227

Table 3. Continued


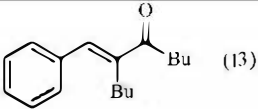
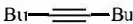
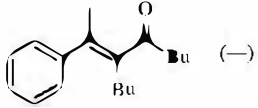
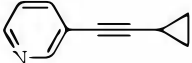
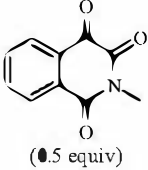
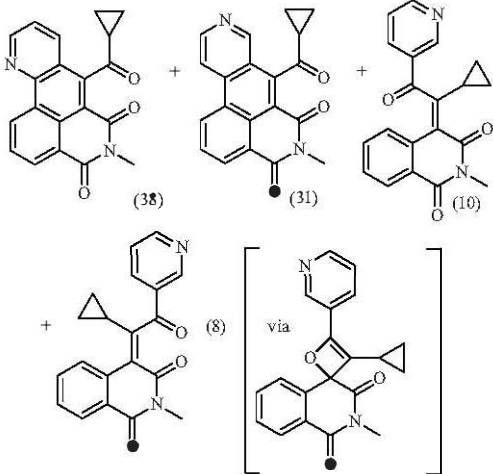
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	PhCHO (3 equiv)		230
	PhCOMe (1 equiv)		230
			227

Table 3. *Continued*

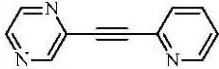
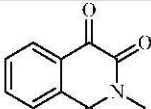
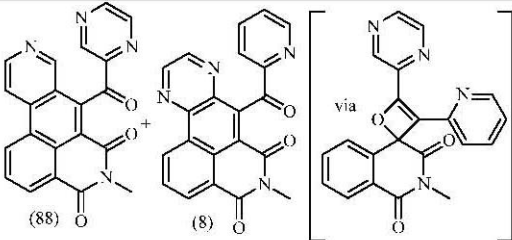
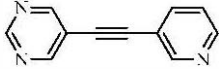
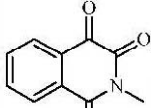
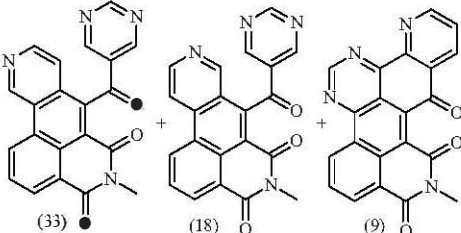
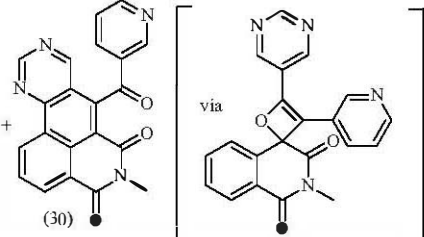
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(0.5 equiv)</p>	 <p>(88) (8)</p>	227
	 <p>(0.5 equiv)</p>	 <p>(33) (18) (9)</p>	227
		 <p>(30)</p>	

Table 3. *Continued*

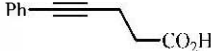
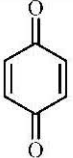
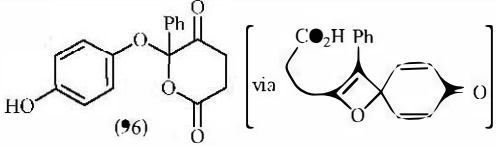
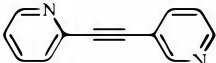
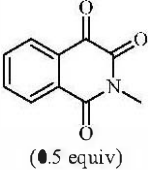
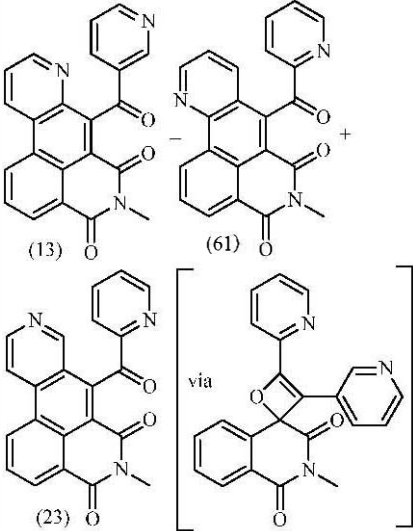
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
			152
	 <p>(0.5 equiv)</p>		227

Table 3. *Continued*

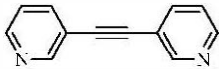
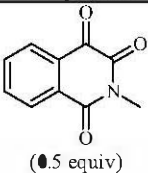
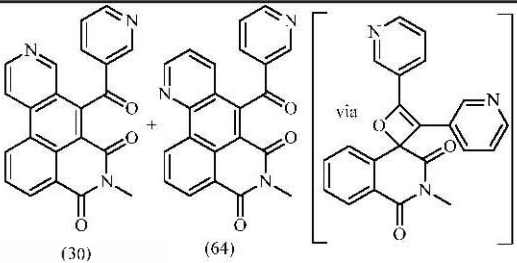
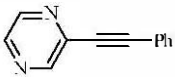
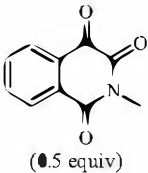
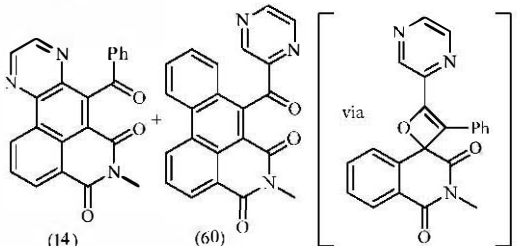
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(0.5 equiv)</p>	 <p>(30) (64)</p>	227
	 <p>(0.5 equiv)</p>	 <p>(14) (60)</p>	227

Table 3. *Continued*

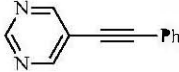
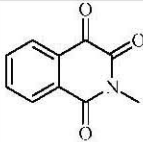
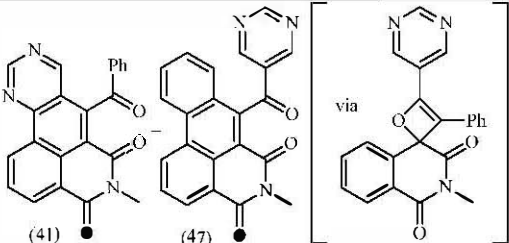
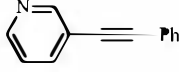
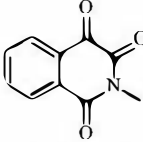
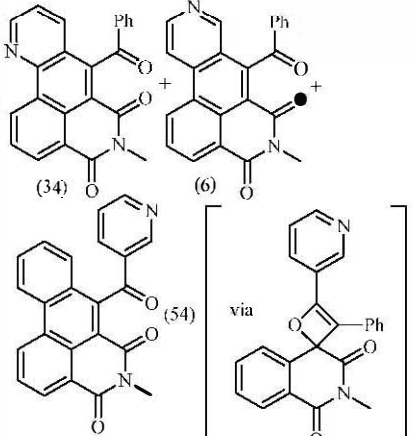
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(0.5 equiv)</p>	 <p>(41) (47)</p>	227
	 <p>(0.5 equiv)</p>	 <p>(34) (6) (54)</p>	227

Table 3. *Continued*


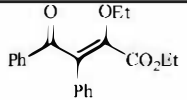
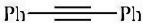

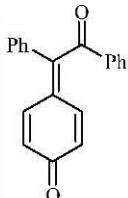
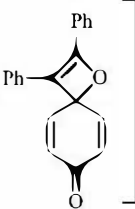


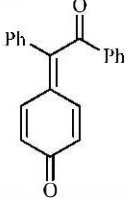
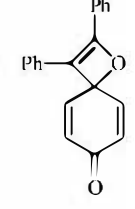

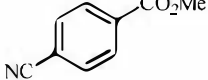
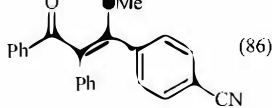
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	(CO ₂ Et) ₂ (3 equiv)	 (25)	231
	 (0.7 equiv)	 (60) [via ]	232
	 (1 equiv)	 (41) [via ]	232
	 (3 equiv)	 (86)	231

Table 3. *Continued*

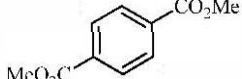
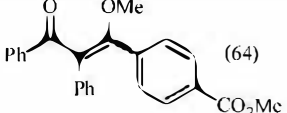
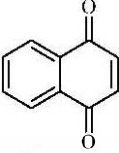
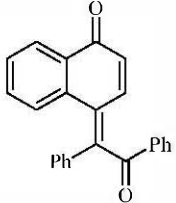
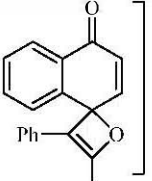
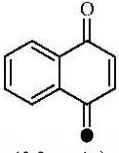
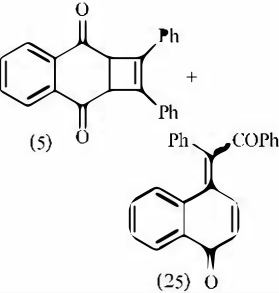
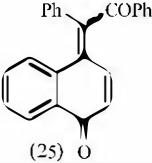
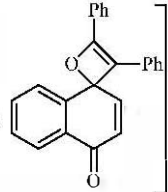
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
Ph—C≡C—Ph	 (3 equiv)	 (64)	231
Ph—C≡C—Ph	 (0.25 equiv)	 (—) via 	228
Ph—C≡C—Ph	 (0.2 equiv)	 (5) +  (25) O via 	233

Table 3. *Continued*


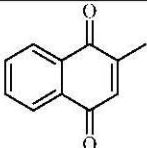
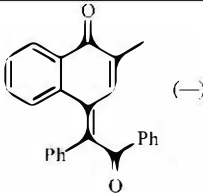
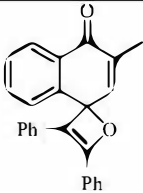
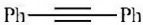
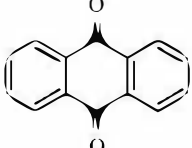
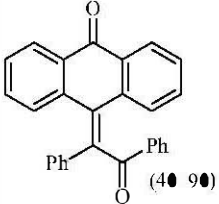
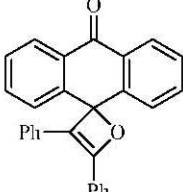
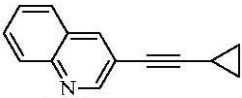
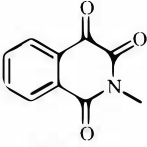
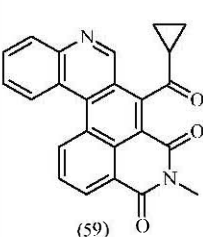
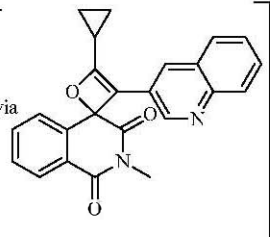
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 (0.25 equiv)	 (—) [via ]	228
	 (0.25 equiv)	 (40-90) [via ]	123 228
	 (0.5 equiv)	 (59) [via ]	227

Table 3. *Continued*

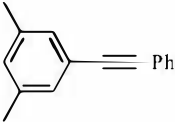
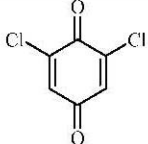
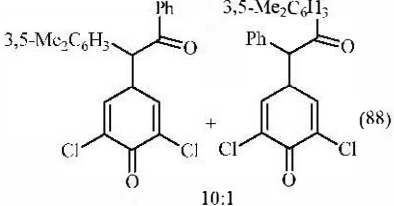
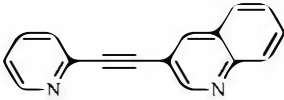
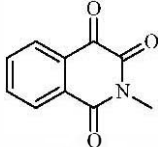
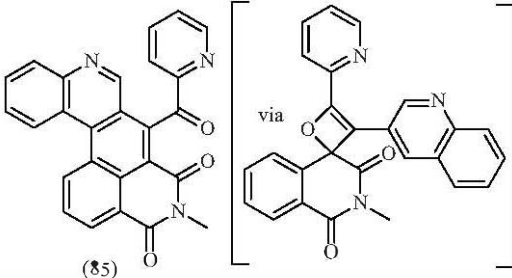
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 (1 equiv)		40
	 (0.5 equiv)		227

Table 3. *Continued*

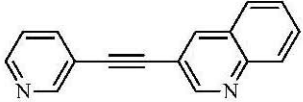
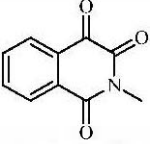
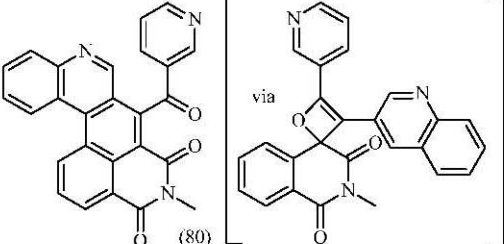
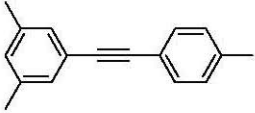
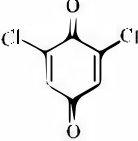
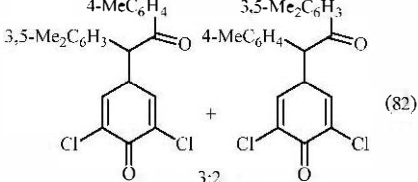
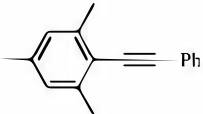
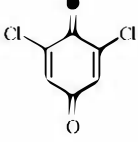
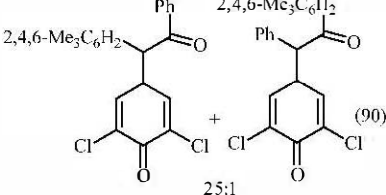
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(0.5 equiv)</p>	 <p>(80)</p>	227
		 <p>(82)</p> <p>3:2</p>	40
		 <p>(90)</p> <p>25:1</p>	40

Table 3. *Continued*

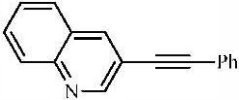
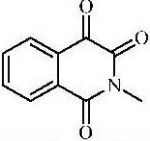
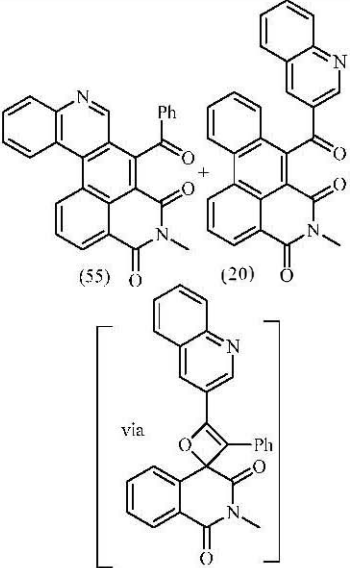
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 (0.5 equiv)	 (55) (20) via [Intermediate structure]	227

Table 3. *Continued*

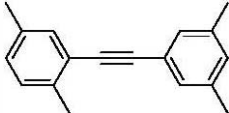
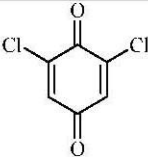
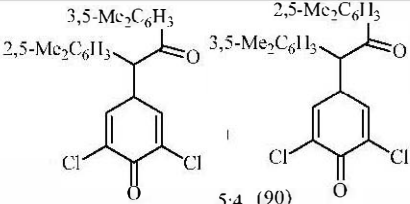
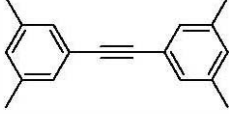
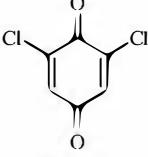
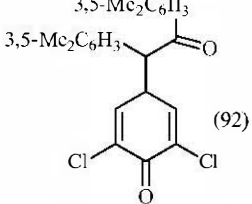
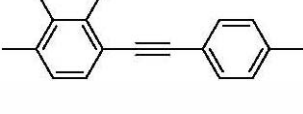
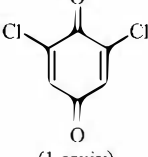
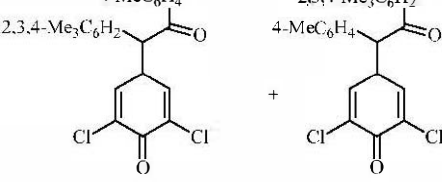
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(1 equiv)</p>	 <p>3,5-Me₂C₆H₃ 2,5-Me₂C₆H₃ 2,5-Me₂C₆H₃ 3,5-Me₂C₆H₃ 5:4 (90)</p>	40
	 <p>(1 equiv)</p>	 <p>3,5-Me₂C₆H₃ 3,5-Me₂C₆H₃ (92)</p>	40
	 <p>(1 equiv)</p>	 <p>4-MeC₆H₄ 2,3,4-Me₃C₆H₂ 2,3,4-Me₃C₆H₂ 4-MeC₆H₄ + (90)</p> <p>25:1</p>	40

Table 3. *Continued*

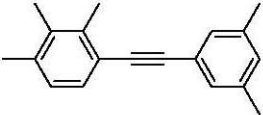
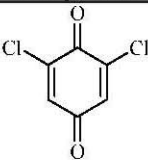
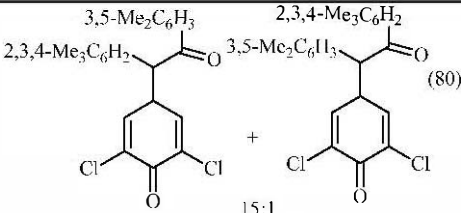
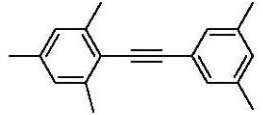
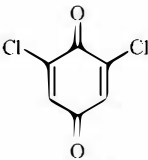
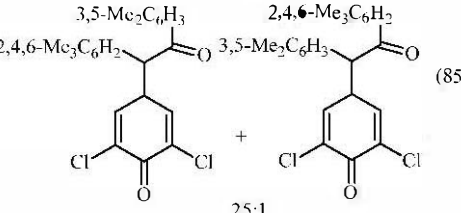
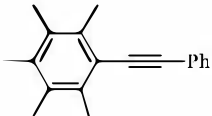
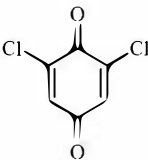
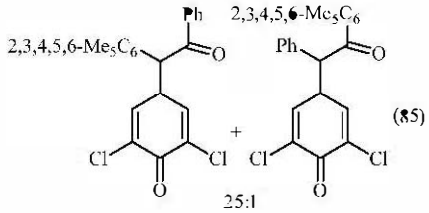
Alkyne	Carbonyl compound	Product (Yields %)	Ref.
	 (1 equiv)	 (80)	40
	 (1 equiv)	 (85)	40
	 (1 equiv)	 (85)	40

Table 4. Intermolecular reaction with electron-rich unsaturated compounds. C. Allenes and other cumulated double-bonds.



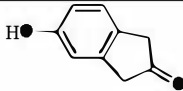

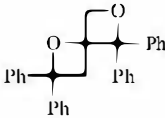

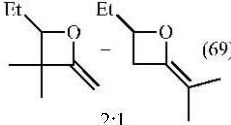

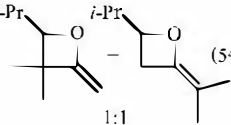

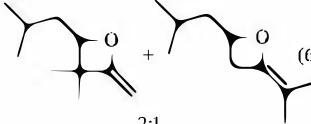
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.3 equiv)	 (—)	234
	Ph ₂ CO (0.05 equiv)	 (15–28)	235 236 237 238
	EtCHO (0.25 equiv)	 (69) 2:1	239
	<i>i</i> -PrCHO (0.25 equiv)	 (54) 1:1	239
	<i>i</i> -PrCH ₂ CHO (0.25 equiv)	 (66) 2:1	239

Table 4. Continued


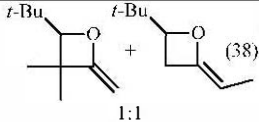


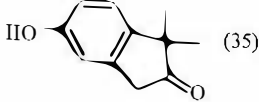

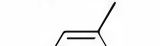
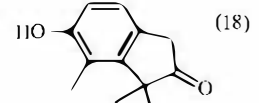

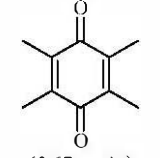
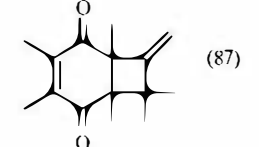

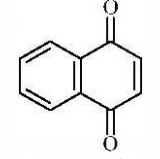
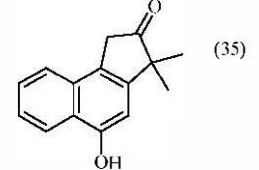
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	<i>t</i> -BuCHO (0.25 equiv)		239
	 (0.3 equiv)		234
	 (0.3 equiv)		234
	 (0.67 equiv)		240
	 (0.3 equiv)		234

Table 4. *Continued*


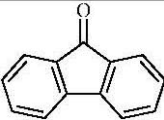
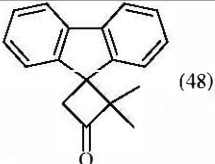

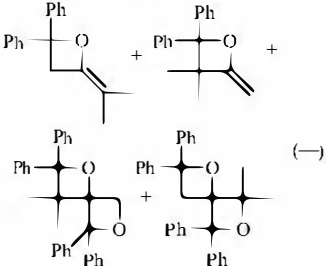

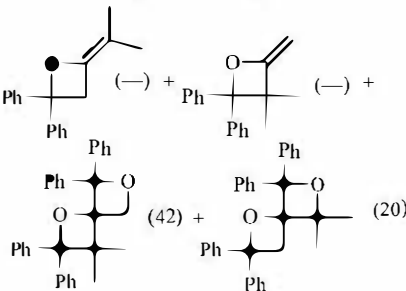
Substrate	Carbonyl compound	Product (Yields %)	Ref.
		 (48)	238
	Ph ₂ CO		237
	Ph ₂ CO		238

Table 4. *Continued*

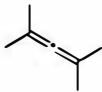

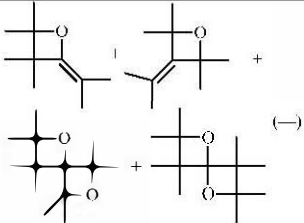
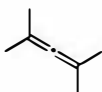

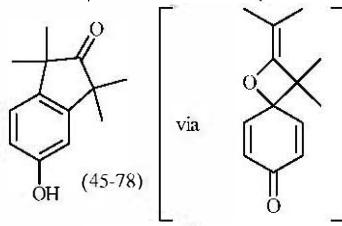
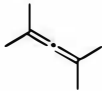
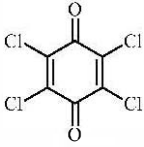
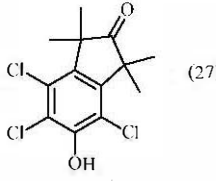
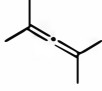

Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Me ₂ CO 		236 237 238
	 (●.28 equiv)		234 241
	 (●.3 equiv)		234
	PhCHO		237 238

Table 4. *Continued*

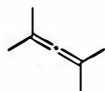
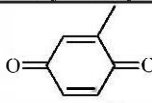
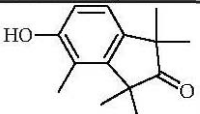
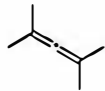
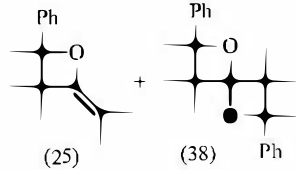
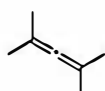
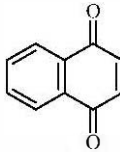
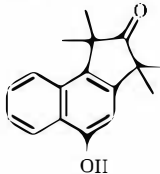
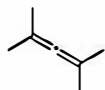
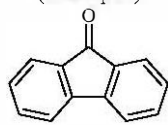
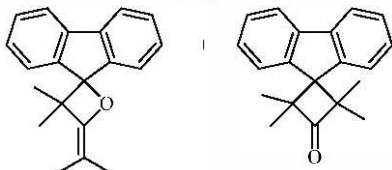
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.3 equiv)	 (8)	234
	PhCOMe	 (25) + (38)	237 238
	 (0.38 equiv)	 (40)	241
		 (—)	237 238

Table 4. *Continued*

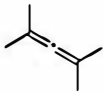
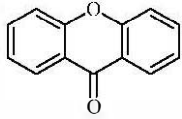
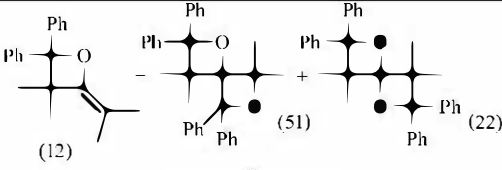
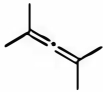
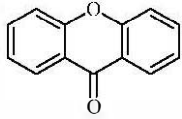
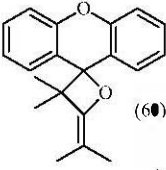
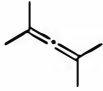
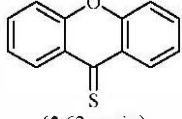
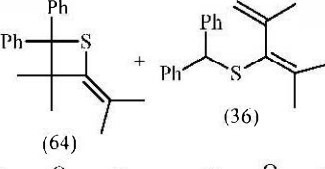
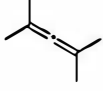
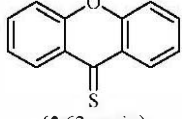
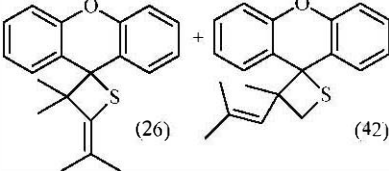
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Ph ₂ CO 		236 237 238
			237 238
	Ph ₂ CS (0.68 equiv) 		106c
	 (0.63 equiv)		106c

Table 4. *Continued*

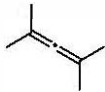
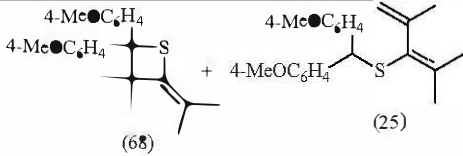
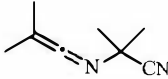
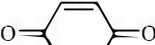

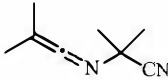

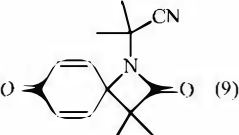
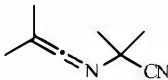

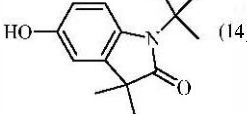
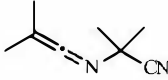
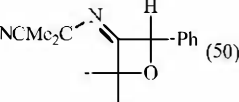
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	(4-MeOC ₆ H ₄) ₂ CS (0.52 equiv)	 (68) + (25)	106c
	 (1.5 h)	 (25)	242
	 (7 h)	 (9)	242
	 (20 h)	 (14)	242
	PhCHO (1 equiv)	 (50)	243 244

Table 4. *Continued*

Substrate	Carbonyl compound	Product (Yields %)	Ref.
	4-ClC ₆ H ₄ CHO (1 equiv)		243 (60)
	PhCOMe (1 equiv)		243 244 (43)
	4-MeOC ₆ H ₄ CHO (1 equiv)		243 (34)
		No reaction	243
			240 (31)
		No reaction	243 244 (1 equiv)

Table 4. *Continued*

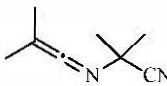
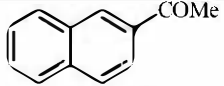
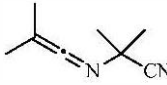
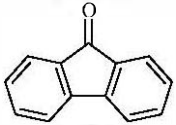
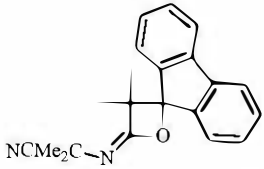
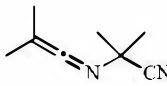
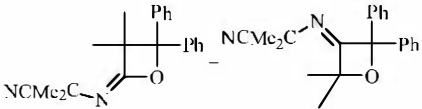
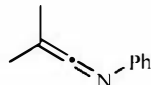
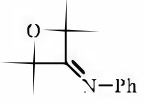
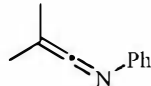

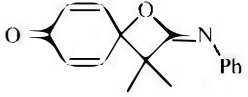
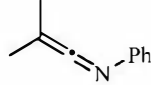

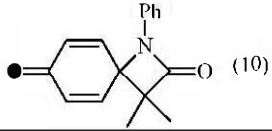
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (1 equiv)	No reaction	243
	 (1 equiv)	 (80)	243 244
	Ph ₂ CO (1 equiv)	 (95)	243 244
	Me ₂ CO	 (41)	245
		 (5)	242
		 (10)	242

Table 4. *Continued*

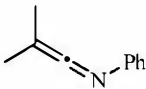
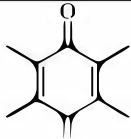
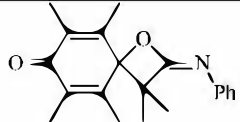
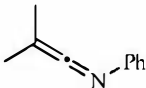
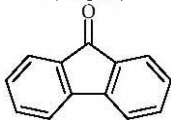
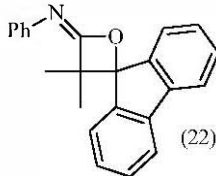
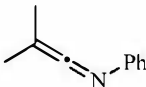
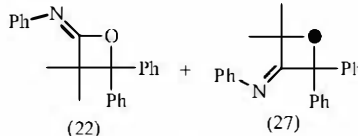
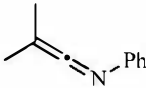
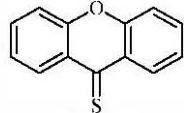
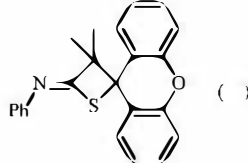
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (1 equiv)	 (41)	240
	 (1 equiv)	 (22)	246
	Ph_2CO (1 equiv)	 (22) + (27)	247
	 (0.8 equiv)	 ()	248

Table 4. *Continued*

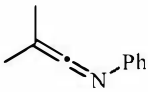
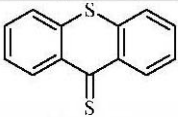
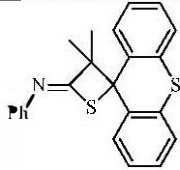
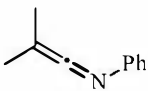
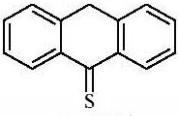
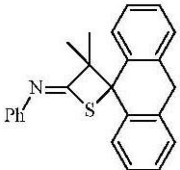
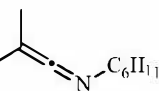
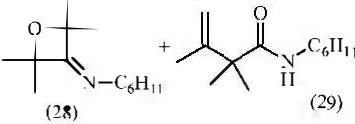
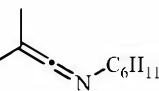
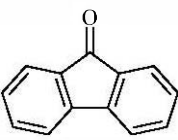
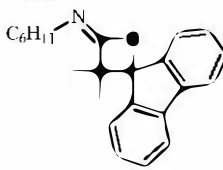
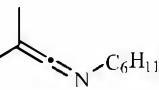
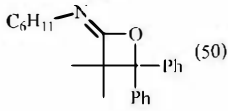
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(0.8 equiv)</p>	 (—)	248
	 <p>(0.8 equiv)</p>	 ()	248
	Me ₂ CO	 <p>(28) + (29)</p>	245
	 <p>(1 equiv)</p>	 (74)	246
	Ph ₂ CO (1 equiv)	 (50)	247

Table 4. Continued

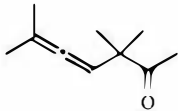

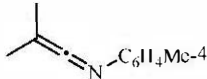

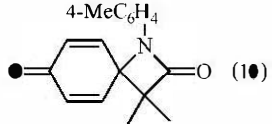
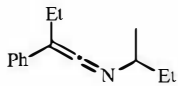
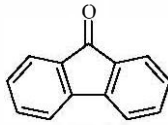
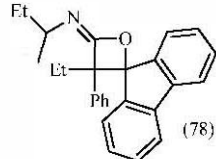
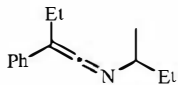
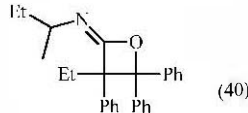
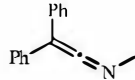
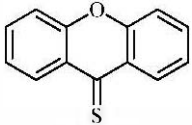
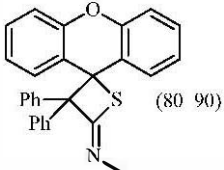
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Me ₂ CO	 (70)	249
	 (1 equiv)	 (10)	242
	 (1 equiv)	 (78)	246
	Ph ₂ CO (1 equiv)	 (40)	247
	 (0.8 equiv)	 (80 90)	248

Table 4. *Continued*

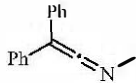
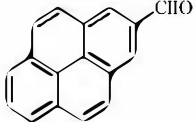
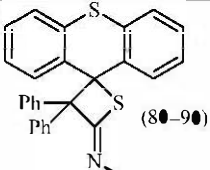
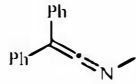
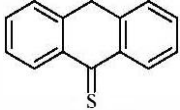
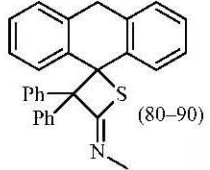
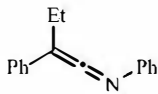
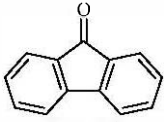
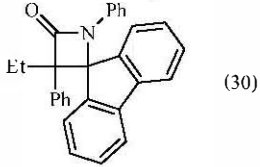
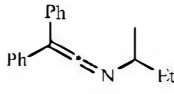
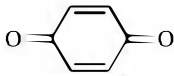
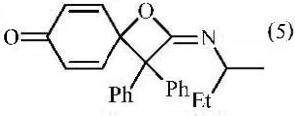
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 <p>(0.8 equiv)</p>	 <p>(80–90)</p>	248
	 <p>(0.8 equiv)</p>	 <p>(80–90)</p>	248
	 <p>(1 equiv)</p>	 <p>(30)</p>	246
	 <p>(1 equiv)</p>	 <p>(5)</p>	242

Table 4. Continued

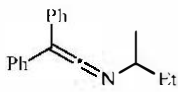
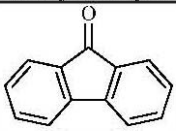
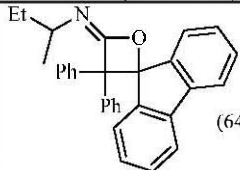
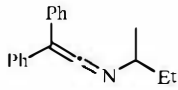
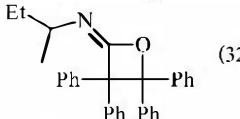
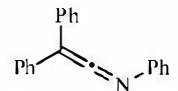

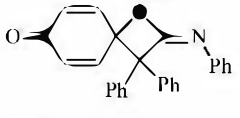
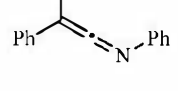
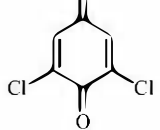
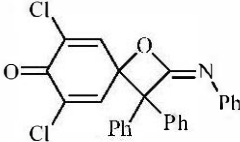
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (1 equiv)	 (64)	246
	Ph_2CO (1 equiv)	 (32)	247
	 (1 equiv)	 (47)	242
	 (1 equiv)	 (9)	242

Table 4. *Continued*

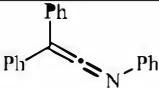
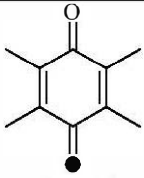
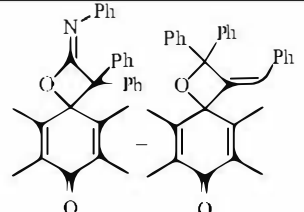
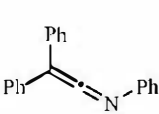
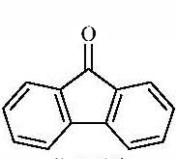
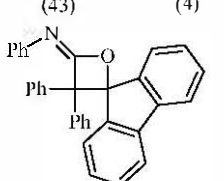
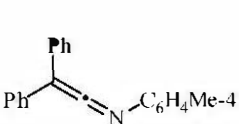
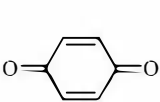
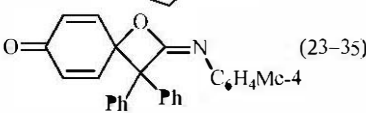
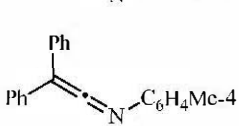
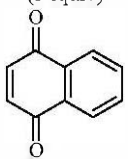
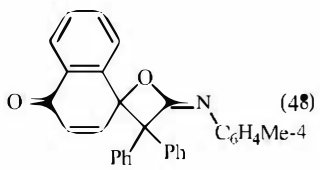
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.8 equiv)	 (43) (4)	240
	 (1 equiv)	 (50)	246
	 (1 equiv)	 (23-35)	242
	 (1 equiv)	 (48)	242

Table 4. Continued

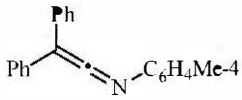
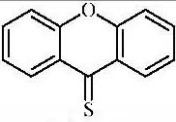
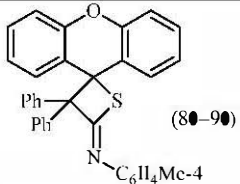
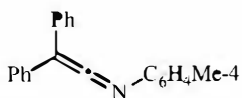
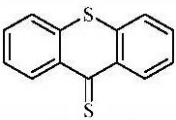
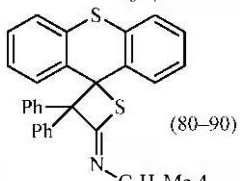
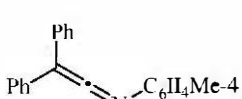
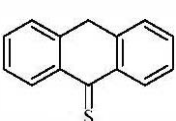
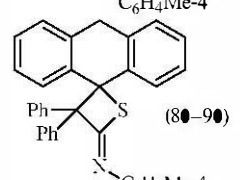
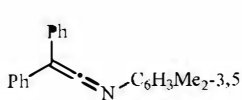
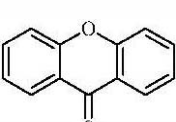
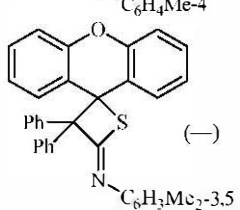
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.8 equiv)	 (80–90)	248
	 (0.8 equiv)	 (80–90)	248
	 (0.8 equiv)	 (80–90)	248
	 (0.8 equiv)	 (—)	248

Table 5. Intermolecular reaction with electron-rich unsaturated compounds. D. Enol ethers.


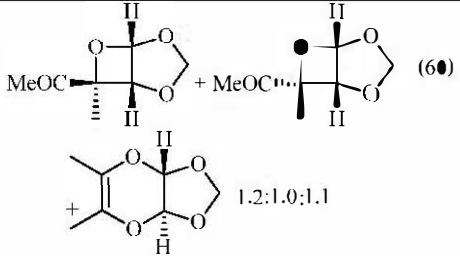

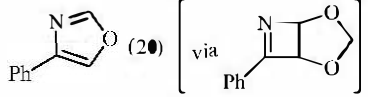

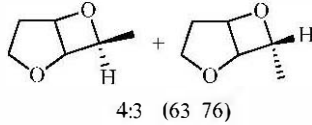

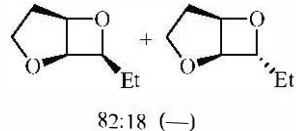


Substrate	Carbonyl compound	Product (Yields %)	Ref.
	MeCOCOMe (1 equiv)	 (6) 1.2:1.0:1.1	39
	PhCN (1 equiv)	 (20) via	250
	MeCHO	 4:3 (63 76)	68e 69 72
	EtCHO	 82:18 (—)	251
	Me ₂ CO	 (52)	69

Table 5. Continued


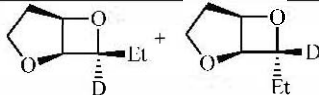

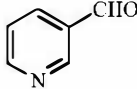
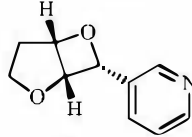

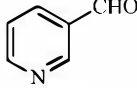
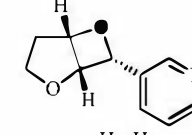

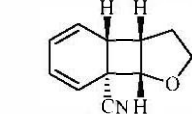

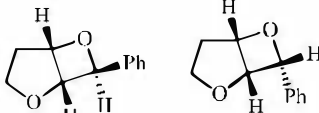
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	EtC(=O)D	 89:11 (—)	251
		 (80) dr 82:18	68g
	 (NaY)	 (76) dr 96:4	68g
	PhCN (1 equiv)	 (20)	250
	PhCHO	 12:88 (98)	68a 68c 68e

Table 5. *Continued*


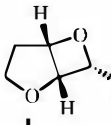
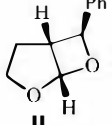

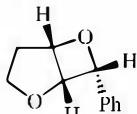

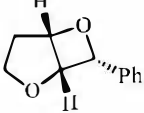

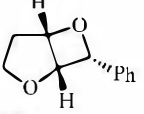

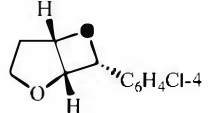
Substrate	Carbonyl compound	Product (Yields %)	Ref.												
	PhCHO (0.1 equiv)	<div style="display: flex; align-items: center;"> <div style="text-align: center; margin-right: 20px;">  <p>I</p> <p>dr 7.3:1</p> </div> <div style="text-align: center; margin-right: 20px;">  <p>II</p> <p>dr 5.7:1</p> </div> <table border="1" style="border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">Solvent</th> <th style="text-align: center;">I</th> <th style="text-align: center;">II</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td style="text-align: center;">29</td> <td style="text-align: center;">1</td> </tr> <tr> <td>MeCN</td> <td style="text-align: center;">4.8</td> <td style="text-align: center;">1</td> </tr> <tr> <td>ethanol</td> <td style="text-align: center;">100</td> <td style="text-align: center;">0</td> </tr> </tbody> </table> </div>	Solvent	I	II	benzene	29	1	MeCN	4.8	1	ethanol	100	0	68d 68f
Solvent	I	II													
benzene	29	1													
MeCN	4.8	1													
ethanol	100	0													
	PhCHO (0.3 equiv)	(-)  (50) dr 88:12	68b 68e												
	PhCHO (NaY)	 (74) dr 95:5	68g												
	PhCHO (NaY, (-)-ephedrine)	 () dr 98:2	68g												
	4-ClC ₆ H ₄ CHO	 (45) dr 98:2	68g												

Table 5. *Continued*


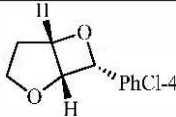

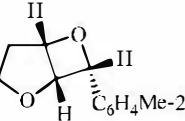

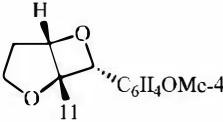

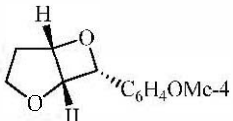

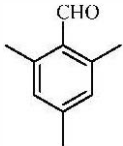
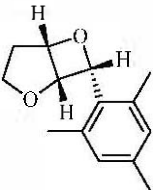
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	4-ClC ₆ H ₄ CHO (NaY)	 (36) dr 95:5	68g
	2-MeC ₆ H ₄ CHO (0.08 equiv)	 (94) dr 94:6	68b
	4-MeOC ₆ H ₄ CHO	 (76) dr 85:15	68g
	4-MeOC ₆ H ₄ CHO (NaY)	 (75) dr 88:12	68g
	 (0.03 equiv)	 (97) dr 98:2	68b 72

Table 5. *Continued*



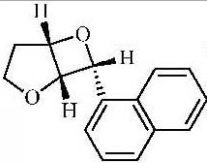

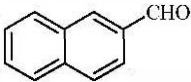
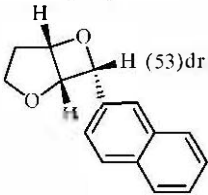

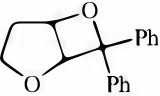

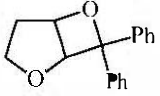

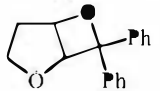
Substrate	Carbonyl compound	Product (Yields %)	Ref.
		 (55) dr 98:2	72
		 (53) dr 98:2	72
	Ph ₂ CO	 (—)	252
	Ph ₂ CO (NaY)	 (65)	68g
	Ph ₂ CO (NaY, (-)-ephedrine)	 (62) cr 55.5:44.5	68g

Table 5. Continued


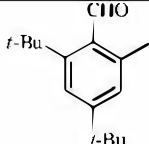
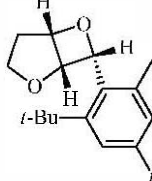

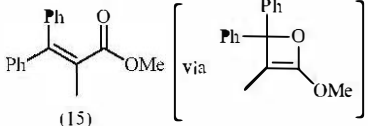
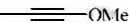
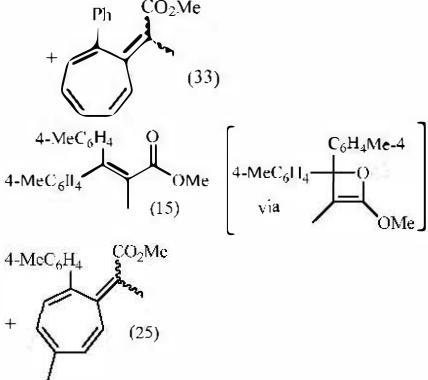
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 ClIO t-Bu t-Bu t-Bu (0.16 equiv)	 (28)	68b
	Ph_2CO (0.31 equiv)		253
	$(4\text{-MeC}_6\text{H}_4)_2\text{CO}$ (0.31 equiv)		253

Table 5. *Continued*

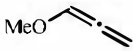
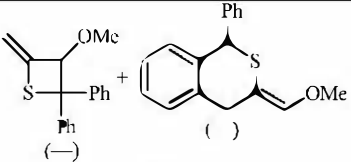
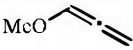
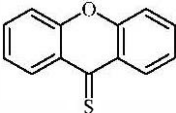
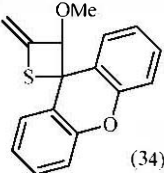
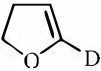
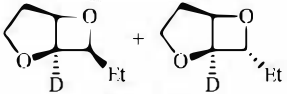
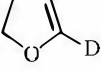
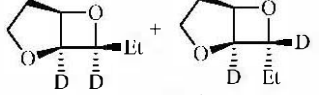

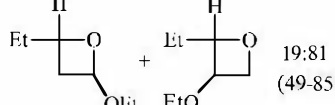
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Ph ₂ CS (0.25 equiv)	 (—)	254
	 (0.5 equiv)	 (34)	254
	EtCHO	 93:7 (—)	255
	EtC ¹⁸ O	 90:10 (—)	255
	EtCHO	 19:81 (49-85)	256 257

Table 5. Continued


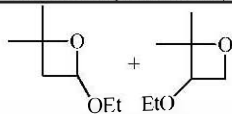

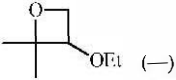

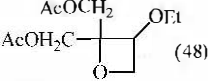

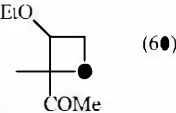

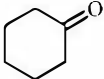
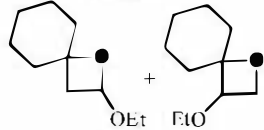

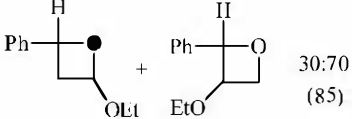
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Me ₂ CO	 30:70 (60-70)	256 258
	Me ₂ CO (ultrasound)	 (—)	259
	AcOCH ₂ COCH ₂ OAc	 (48)	260
	MeCOCOMe (1 equiv)	 (60)	105d 146
		 30:70 (50)	256
	PhCHO	 30:70 (85)	256

Table 5. *Continued*


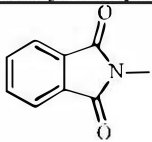
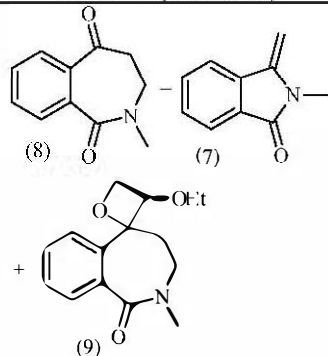

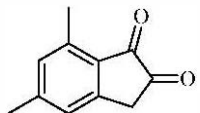
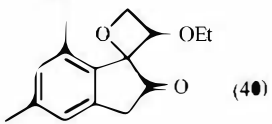

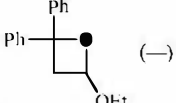

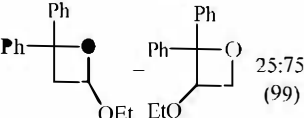
Substrate	Carbonyl compound	Product (Yields %)	Ref.
			261
	 (0.04 equiv)		151
	Ph ₂ CO		262
	Ph ₂ CO		256

Table 5. Continued


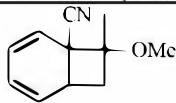
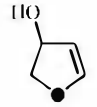
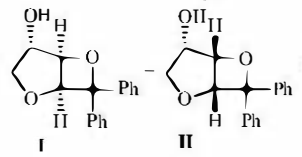
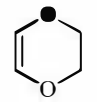
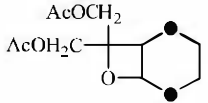

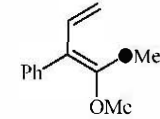

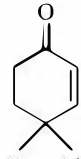
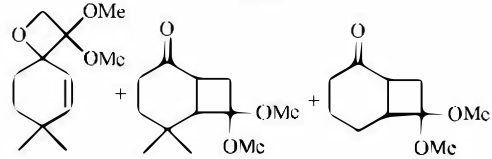
Substrate	Carbonyl compound	Product (Yields %)	Ref.												
	PhCN (0.1 equiv)	 (43)	147												
	Ph ₂ CO (0.68 equiv)	 <table border="1" data-bbox="1013 336 1292 464"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>I/II</th> </tr> </thead> <tbody> <tr> <td>Toluene</td> <td>-</td> <td>53:47 (78)</td> </tr> <tr> <td>Methanol</td> <td>-</td> <td>96:4 (40)</td> </tr> <tr> <td>Toluene</td> <td>-80</td> <td>86:14 (0)</td> </tr> </tbody> </table>	Solvent	Temp	I/II	Toluene	-	53:47 (78)	Methanol	-	96:4 (40)	Toluene	-80	86:14 (0)	91
Solvent	Temp	I/II													
Toluene	-	53:47 (78)													
Methanol	-	96:4 (40)													
Toluene	-80	86:14 (0)													
	AcOCH ₂ COCH ₂ OAc	 (25)	260												
	PhCN (0.16 equiv)	 (28)	147												
	 (2 equiv)	 (—)	263												

Table 5. *Continued*

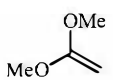
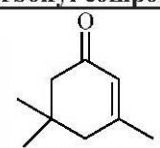
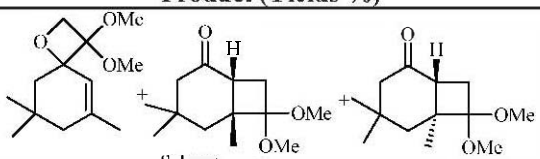
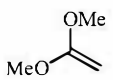
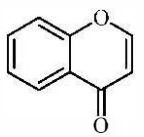
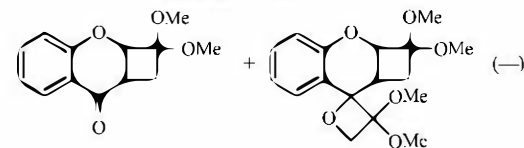
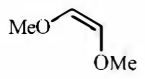
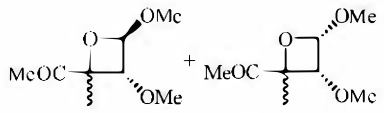
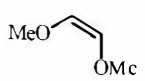
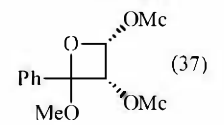
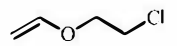
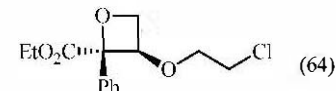
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (2 equiv)	 Solvent <i>n</i> -hexane (42) benzene (13)	263
	 (0.05 equiv)	 (—)	178
	MeCOCOMe (1 equiv)	 2:1 (—)	264
	PhCO ₂ Me	 (37)	170
	PhCOCO ₂ Et	 (64)	142

Table 5. Continued

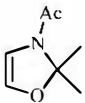
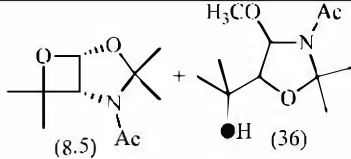
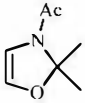
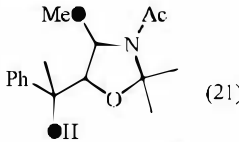
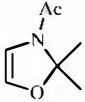
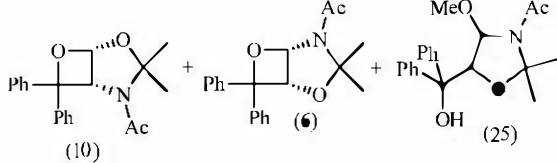
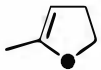
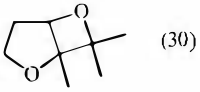
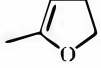
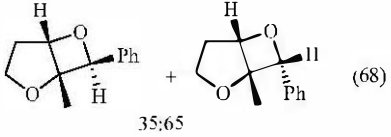
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Me ₂ CO		265
	PhCOMe		265
	Ph ₂ CO		265
	Me ₂ CO		69
	PhCHO		68c

Table 5. *Continued*


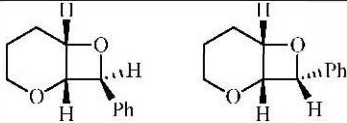

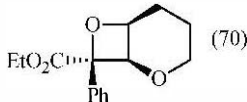

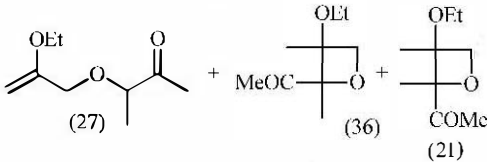

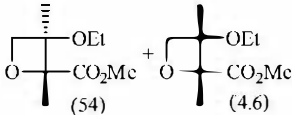
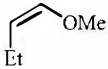
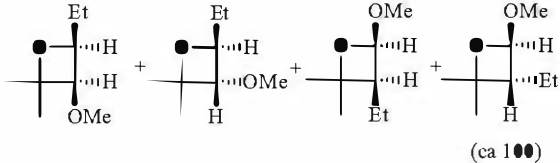
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	PhCHO (0.17 equiv)	 (45) 10:90	68a 68e
	PhCOCO ₂ Et	 (70)	142
	MeCOCOMe	 (27) + (36) + (21)	105d
	MeCOCO ₂ Me (1 equiv)	 (54) + (46)	114b
	Me ₂ CO	 (ca 100)	29 105k 266

Table 5. Continued

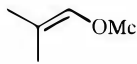
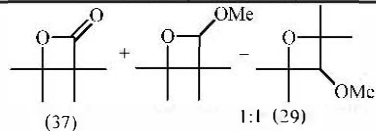
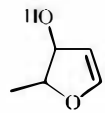
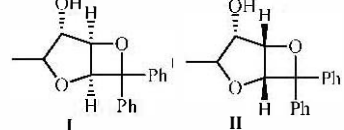

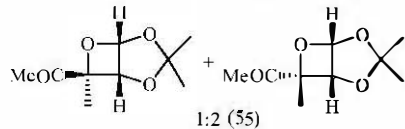

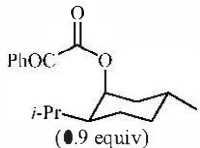
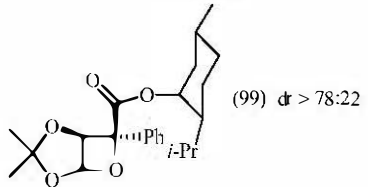
Substrate	Carbonyl compound	Product (Yields %)	Ref.															
	Me ₂ CO	 (37) + (29) 1:1 (29)	267															
	Ph ₂ CO (0.68 equiv)	 I II	91															
<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>I/II</th> </tr> </thead> <tbody> <tr> <td>Benzene</td> <td>-</td> <td>24:76 (70)</td> </tr> <tr> <td>Toluene</td> <td>-</td> <td>24:76 (57)</td> </tr> <tr> <td>Toluene</td> <td>56</td> <td>58:42 (0)</td> </tr> <tr> <td>Methanol</td> <td>-</td> <td>87:13 (55)</td> </tr> </tbody> </table>				Solvent	Temp	I/II	Benzene	-	24:76 (70)	Toluene	-	24:76 (57)	Toluene	56	58:42 (0)	Methanol	-	87:13 (55)
Solvent	Temp	I/II																
Benzene	-	24:76 (70)																
Toluene	-	24:76 (57)																
Toluene	56	58:42 (0)																
Methanol	-	87:13 (55)																
	MeCOCOMe	 1:2 (55)	39															
	 <i>i</i> -Pr (0.9 equiv)	 (99) <i>dr</i> > 78:22	80															

Table 5. *Continued*


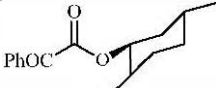
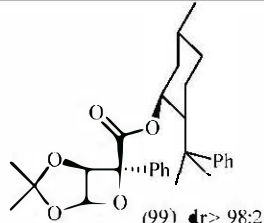
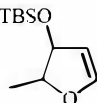
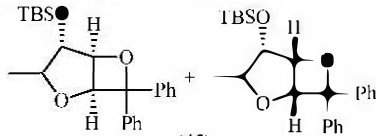
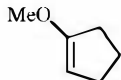
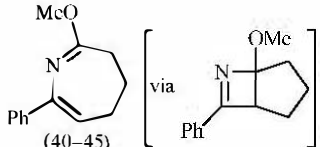

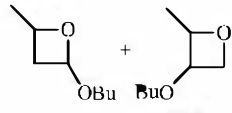
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.86 equiv)	 (99) <i>dr</i> > 98:2	80
	Ph_2CO (0.68 equiv)	 (45)	91
	PhCN (1 equiv)	 (40-45)	39b
	Me_2CO	 25:75 (60)	256

Table 5. Continued


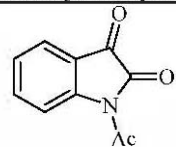
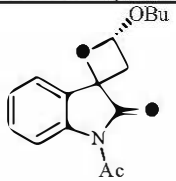
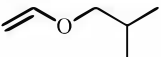
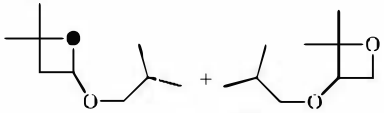
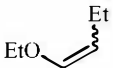
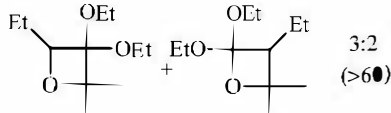
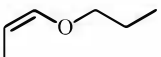
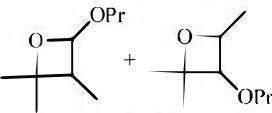
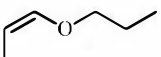
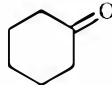
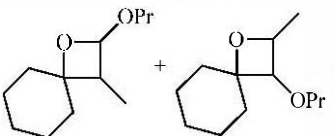
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.1 equiv)	 (95)	52
	Me ₂ CO	 25:75 (46)	256
	Me ₂ CO	 3:2 (>60)	258
	Me ₂ CO	 43:57 (—)	267
		 44:56 (—)	267

Table 5. Continued

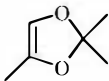
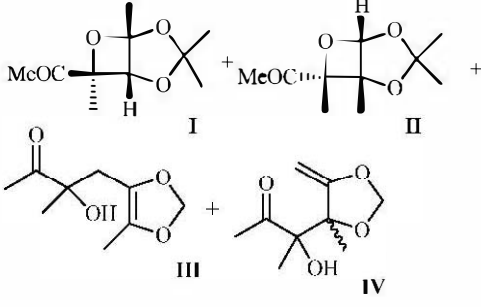

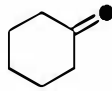
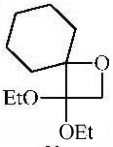

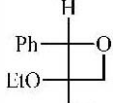

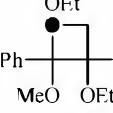
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	MeCOCOMe	 <p style="text-align: center;">I:II:III:IV = 21:19:25:36</p>	39
		 (24)	256
	PhCHO	 (39.5)	256
	PhCO ₂ Me (0.13 equiv)	 (29)	170

Table 5. Continued


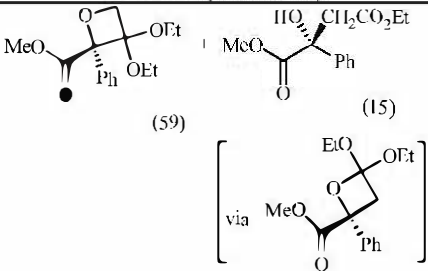

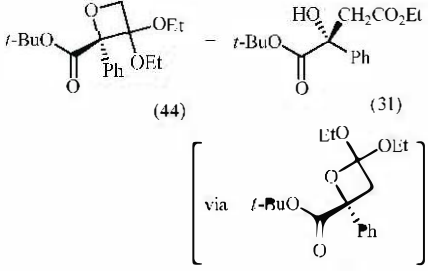

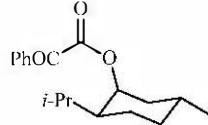
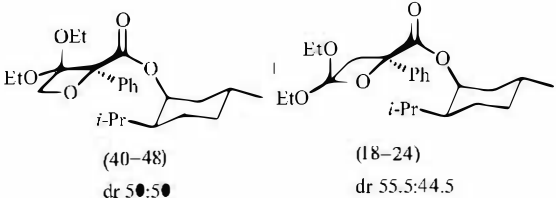
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	PhCOCO ₂ Me (0.13 equiv)	 (59) → (15)	78b
	PhCOCO ₂ <i>t</i> -Bu (0.13 equiv)	 (44) → (31)	78b
	 (0.13 equiv)	 (40-48) → (18-24) dr 50:50 (40-48) dr 55.5:44.5 (18-24)	78a 78b

Table 5. Continued


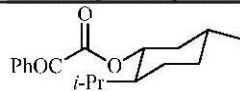
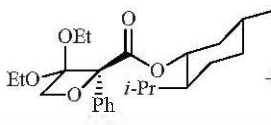
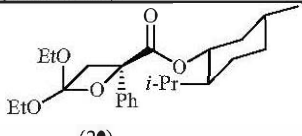

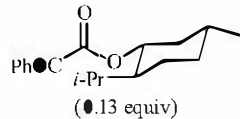
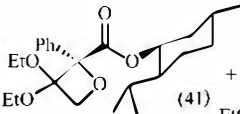
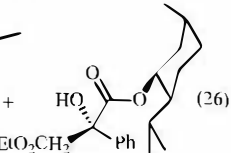
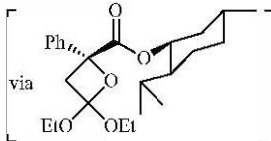
Substrate	Carbonyl compound	Product (Yields %)	Ref.																																												
		 (46) dr 69.5:30.5  (20) dr 64:36	78a																																												
		 (41)  (26)	78b																																												
		<p style="text-align: center;">I</p> <table border="1"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>-70</td> <td>(61)</td> <td>(21)</td> <td>68:32</td> </tr> <tr> <td>-45</td> <td>(51)</td> <td>(20)</td> <td>68.5:31.5</td> </tr> <tr> <td>30</td> <td>(40)</td> <td>(16)</td> <td>71.5:28.5</td> </tr> <tr> <td>-14</td> <td>(44)</td> <td>(2)</td> <td>70:30</td> </tr> <tr> <td>1</td> <td>(38)</td> <td>(21)</td> <td>69:31</td> </tr> <tr> <td>15</td> <td>(40)</td> <td>(25)</td> <td>69.5:30.5</td> </tr> <tr> <td>24</td> <td>(47)</td> <td>(30)</td> <td>71.5:28.5</td> </tr> <tr> <td>35</td> <td>(50)</td> <td>(29)</td> <td>69:31</td> </tr> <tr> <td>37</td> <td>(34)</td> <td>(25)</td> <td>67.5:32.5</td> </tr> <tr> <td>65</td> <td>(34)</td> <td>(25)</td> <td>67.5:32.5</td> </tr> </tbody> </table> <p style="text-align: center;">II</p> 	Temp	I	II	dr	-70	(61)	(21)	68:32	-45	(51)	(20)	68.5:31.5	30	(40)	(16)	71.5:28.5	-14	(44)	(2)	70:30	1	(38)	(21)	69:31	15	(40)	(25)	69.5:30.5	24	(47)	(30)	71.5:28.5	35	(50)	(29)	69:31	37	(34)	(25)	67.5:32.5	65	(34)	(25)	67.5:32.5	
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Table 5. Continued


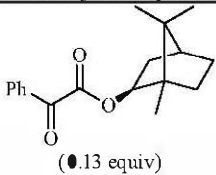
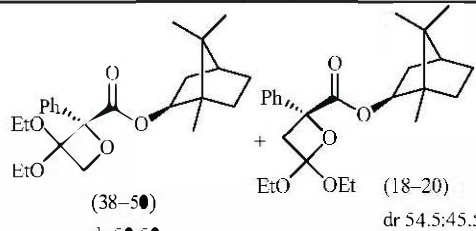

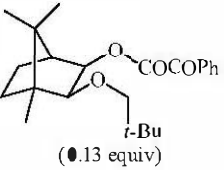
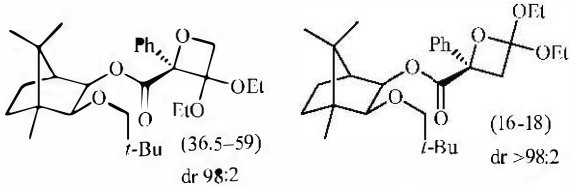

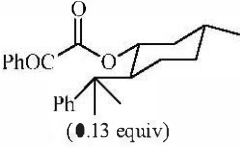
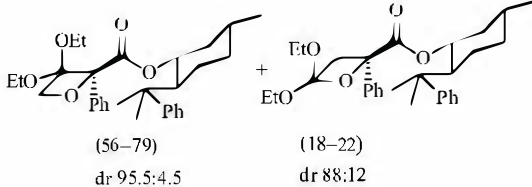

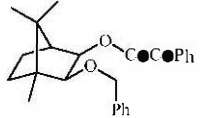
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.13 equiv)	 (38–50) + (18–20) dr 50:50 dr 54.5:45.5	78a 78b
	 (0.13 equiv)	 (36.5–59) + (16–18) dr 98:2 dr >98:2	78a 78b
	 (0.13 equiv)	 (56–79) + (18–22) dr 95.5:4.5 dr 88:12	78a 78b
		No reaction	78a

Table 5. *Continued*

Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Ph ₂ CO		256
	PhCN (●.18 equiv)		147 173
	PhCO ₂ Me (●.25 equiv)		17●
	PhCO ₂ Me		148
	Me ₂ CO		258

Table 5. *Continued*

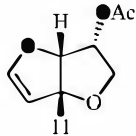
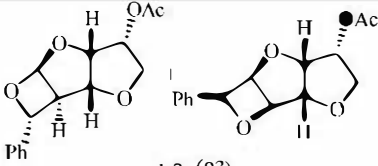
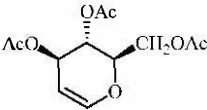
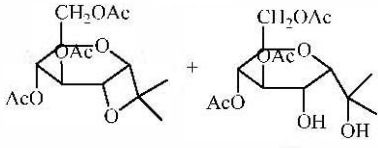
Substrate	Carbonyl compound	Product (Yields %)	Ref.
 <p>11</p>	<p>PhCHO (1.4 equiv, flux)</p>	 <p>1:2 (93)</p>	<p>268</p>
	<p>Me₂CO</p>	 <p>(27-33) (43)</p>	<p>269 270</p>

Table 5. *Continued*

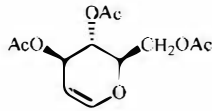
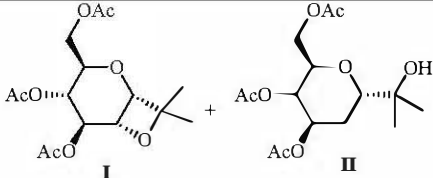
Substrate	Carbonyl compound	Product (Yields %)	Ref.																																																																
	Me ₂ CO		271 272																																																																
		<table border="1"> <thead> <tr> <th data-bbox="770 392 917 431">Acetone (ml)</th> <th data-bbox="917 392 1093 431">Isopropanol (ml)</th> <th data-bbox="1093 392 1173 431">I</th> <th data-bbox="1173 392 1236 431">II</th> </tr> </thead> <tbody> <tr><td>10.000</td><td>0.000</td><td>(14)</td><td>(0)</td></tr> <tr><td>10.000</td><td>0.008</td><td>(96)</td><td>(0)</td></tr> <tr><td>10.000</td><td>0.038</td><td>(97)</td><td>(0)</td></tr> <tr><td>9.500</td><td>0.500</td><td>(99)</td><td>trace</td></tr> <tr><td>9.000</td><td>1.000</td><td>(83)</td><td>trace</td></tr> <tr><td>8.000</td><td>2.000</td><td>(67)</td><td>(14)</td></tr> <tr><td>6.500</td><td>3.500</td><td>(64)</td><td>(32)</td></tr> <tr><td>5.000</td><td>5.000</td><td>(0)</td><td>(70)</td></tr> <tr><td>3.500</td><td>6.500</td><td>(0)</td><td>(77)</td></tr> <tr><td>2.000</td><td>8.000</td><td>(0)</td><td>(99)</td></tr> <tr><td>1.000</td><td>9.000</td><td>(0)</td><td>(100)</td></tr> <tr><td>0.500</td><td>9.500</td><td>(0)</td><td>(92)</td></tr> <tr><td>0.037</td><td>10.000</td><td>(0)</td><td>(99)</td></tr> <tr><td>0.007</td><td>10.000</td><td>(0)</td><td>(99)</td></tr> <tr><td>0.000</td><td>10.000</td><td>(0)</td><td>(43)</td></tr> </tbody> </table>	Acetone (ml)	Isopropanol (ml)	I	II	10.000	0.000	(14)	(0)	10.000	0.008	(96)	(0)	10.000	0.038	(97)	(0)	9.500	0.500	(99)	trace	9.000	1.000	(83)	trace	8.000	2.000	(67)	(14)	6.500	3.500	(64)	(32)	5.000	5.000	(0)	(70)	3.500	6.500	(0)	(77)	2.000	8.000	(0)	(99)	1.000	9.000	(0)	(100)	0.500	9.500	(0)	(92)	0.037	10.000	(0)	(99)	0.007	10.000	(0)	(99)	0.000	10.000	(0)	(43)	
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Table 5. Continued

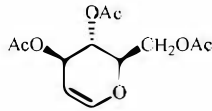
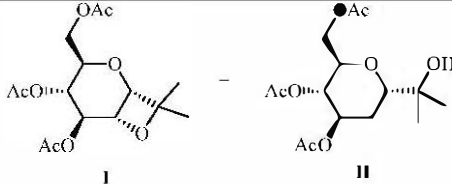
Substrate	Carbonyl compound	Product (Yields %)	Ref.																																																						
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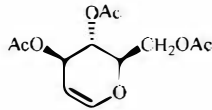
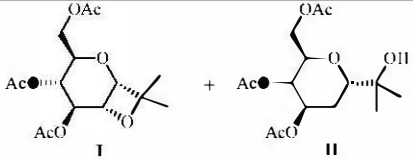
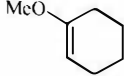
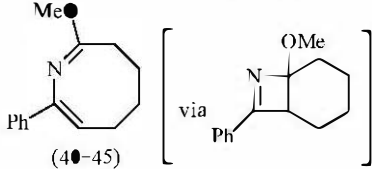
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1.000	9.000		(0)	(22)		(0)	(60)																																																																																												
0.150	9.900		(0)	(8)		(0)	(27)																																																																																												
0.037	10.00		(0)	(2)		(0)	(11)																																																																																												
0.007	10.00		(0)	(0)		(0)	(0)																																																																																												
	PhCN		250																																																																																																

Table 5. Continued

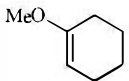
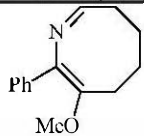
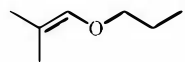
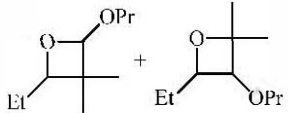
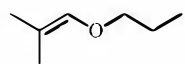
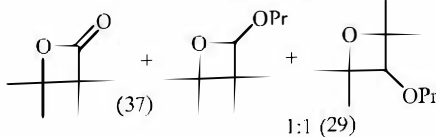
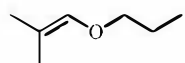
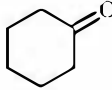
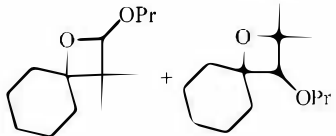
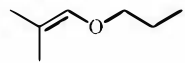
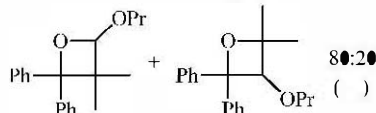
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	PhCN (0.19 equiv)	 (46)	147
	EtCHO	 + 60:40 (—)	273
	Me ₂ CO	 (37) + 1:1 (29)	267 273
		 + 64:46 (—)	273
	Ph ₂ CO	 + 80:20 ()	273

Table 5. *Continued*

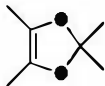
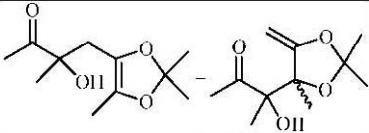

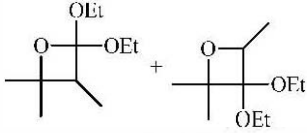

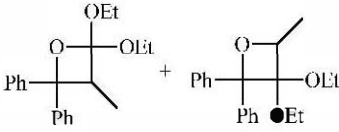
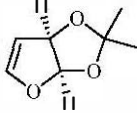
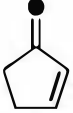
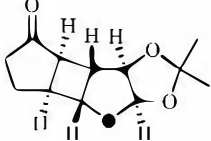
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	MeCOCOMe	 7:3 (65)	39
	Me ₂ CO	 45:53 (—)	273
	Ph ₂ CO	 45:55 (—)	273
	 (0.1 equiv)	 (50)	274

Table 5. Continued

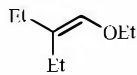
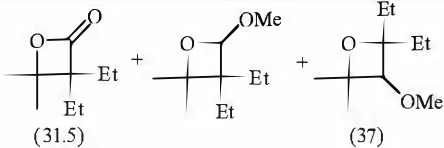
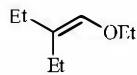
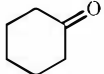
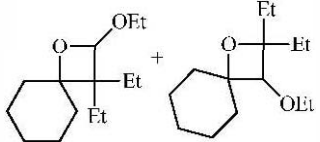
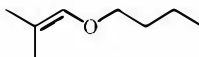
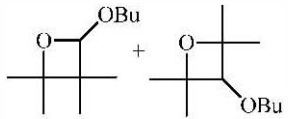
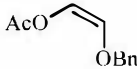
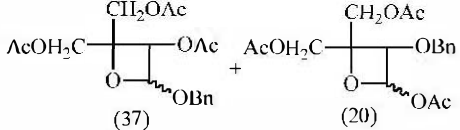
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Me ₂ CO	 <p>(31.5) + (37) + (37)</p>	267
		 <p>85:15 ()</p>	273
	Me ₂ CO	 <p>70:30 (—)</p>	273
	AcOCH ₂ COCH ₂ OAc (0.5 equiv)	 <p>(37) + (20)</p>	260

Table 5. Continued

Substrate	Carbonyl compound	Product (Yields %)	Ref.
	AcOCH ₂ COCH ₂ OAc (0.5 equiv)	 (37) + (20)	260
	PhCHO	 (60) + (25)	81
	MeCOCOMe	 (27) + (36) + (21)	114d
	MeCOCO ₂ Et	 30:20 (—)	275

Table 5. Continued

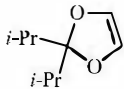
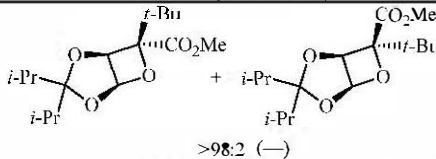
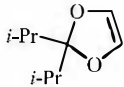
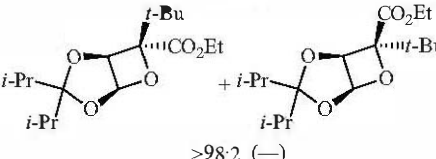
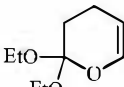
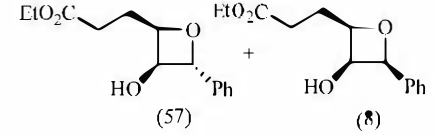
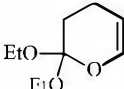
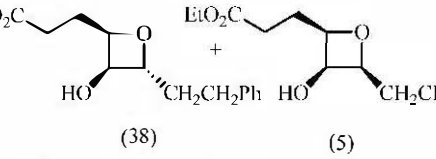
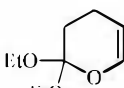
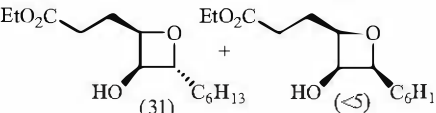
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	<i>t</i> -BuCOCO ₂ Me		275
	<i>t</i> -BuCOCO ₂ Et		275
	PhCHO		276
	PhCH ₂ CH ₂ CHO		276
	C ₆ H ₁₃ CHO		276

Table 5. Continued

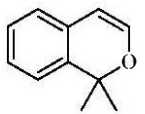
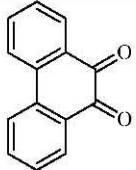
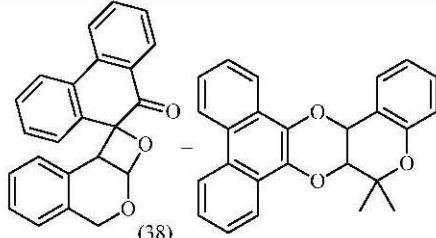
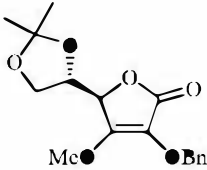
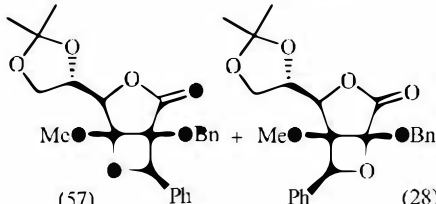
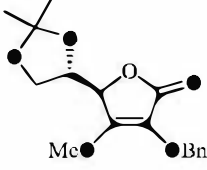
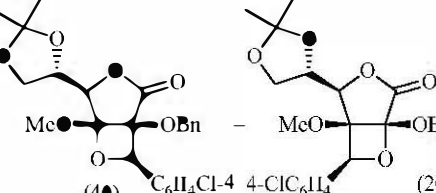
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	 (0.25 equiv)	 (38) (25)	211
	PhCHO (1.2 equiv)	 (57) (28)	81
	4-ClC ₆ H ₄ CHO (1.2 equiv)	 (40) (20)	81

Table 5. Continued

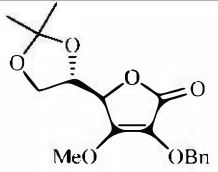
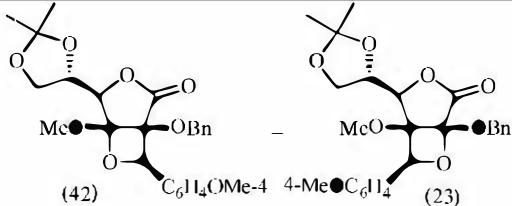
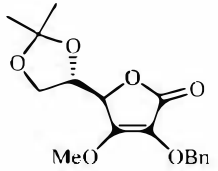
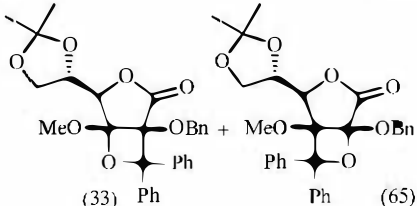
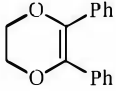
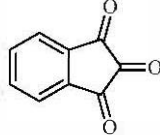
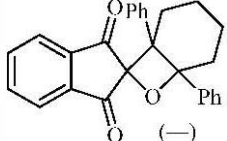
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	<p>4-MeOC₆H₄CHO (1.2 equiv)</p>	 <p>(42) C₆H₄OMe-4 4-MeOC₆H₄ (23)</p>	81
	<p>Ph₂CO (1.2 equiv)</p>	 <p>(33) Ph (65)</p>	81
		 <p>(—)</p>	150

Table 6. Intermolecular reactions with electron-rich unsaturated compounds. E. Enol thio- and selenylethers.

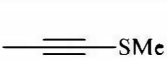
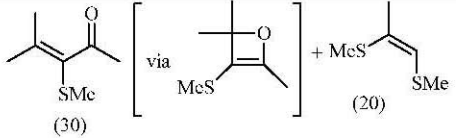
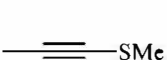
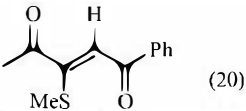
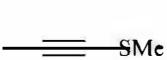
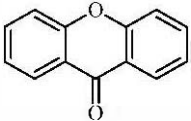
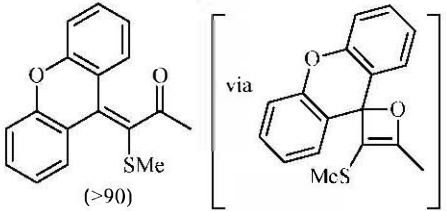
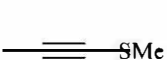
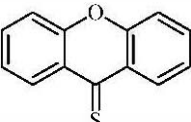
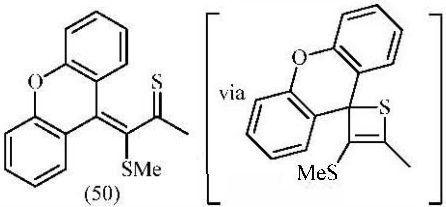
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Me ₂ CO (30)		277
	PhCOCHO (1 equiv)		278
	 (1.43 equiv)		277
	 (0.25 equiv)		277

Table 6. Continued

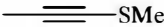
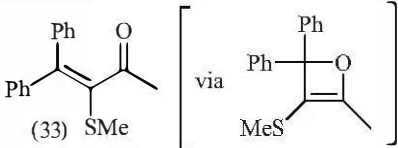
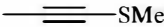
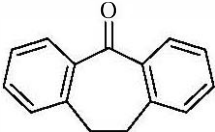
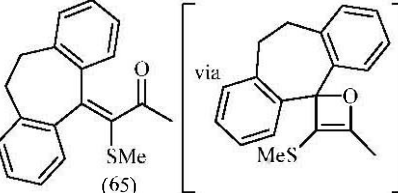

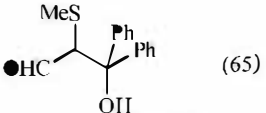

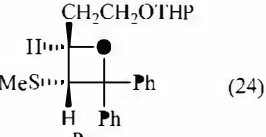

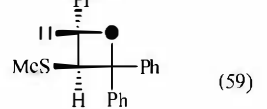
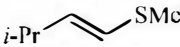
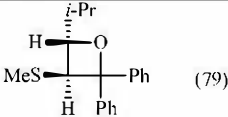
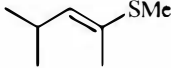
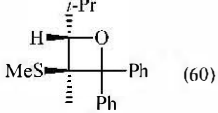
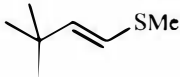
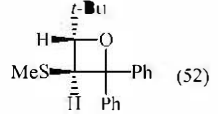
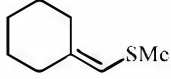
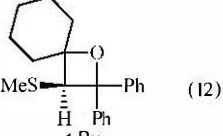
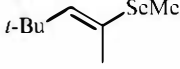
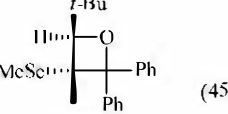
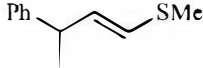
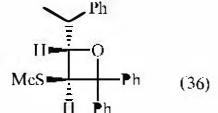
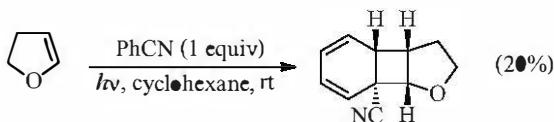
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (0.2 equiv)		277
	 (0.25 equiv)		277
	Ph ₂ CO (0.5 equiv)		279
	Ph ₂ CO (1 equiv)		280
	Ph ₂ CO (1 equiv)		280 281

Table 6. *Continued*

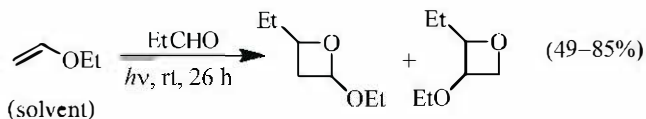
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (1 equiv)	 (79)	280 281
	Ph ₂ CO (1 equiv)	 (60)	280 281
	Ph ₂ CO (1 equiv)	 (52)	280 281
	Ph ₂ CO (1 equiv)	 (12)	280 281
	Ph ₂ CO (1 equiv)	 (45)	280
	Ph ₂ CO (1 equiv)	 (36)	280 281

In contrast, the reaction of 2,3-dihydrofuran with benzonitrile does not furnish the corresponding adduct derived from a reaction of the C≡N group on the alkene, but rather proceeds by a [2+2]-cycloaddition reaction involving the aromatic ring (Scheme 61) [250].

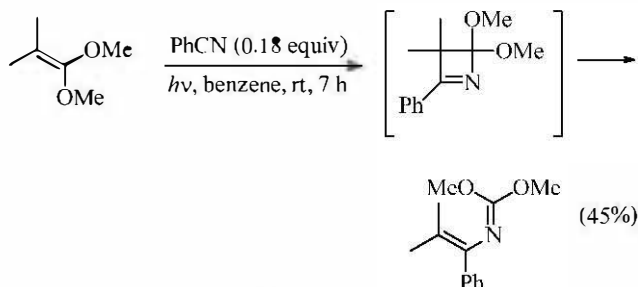


Scheme 61

Ethyl vinyl ether reacts with propanal, affording mainly the regioisomer derived from the most stable biradical intermediate (Scheme 62) [256, 257]. The same behavior has been observed with all of the carbonyl compounds tested, such as acetone, diacetyl, benzaldehyde, or benzophenone [105d, 146, 151, 164, 256, 258, 260, 261, 262].



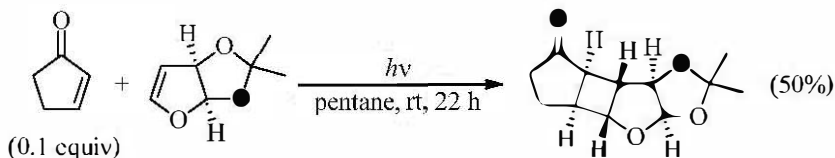
Scheme 62



Scheme 63

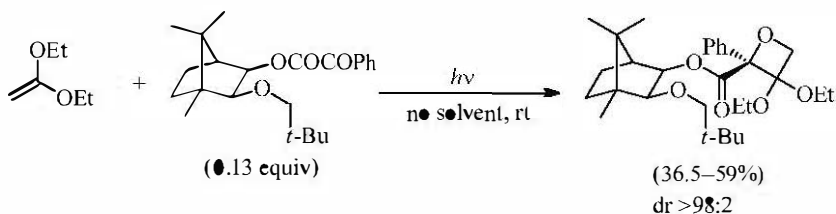
When 2-methoxypropene is irradiated in the presence of benzonitrile, a reaction occurs on the aromatic ring similar to that described in Scheme 61 [147]. On the other hand, methoxycyclopentene and 1,1-dimethoxy-2-methylpropene, when irradiated in the presence of benzonitrile, afford products derived from a ring opening of the Paternò-Büchi aza oxetane reaction product (Scheme 63) [147, 173, 250].

With α,β -unsaturated carbonyl compounds, competition between the Paternò-Büchi reaction and [2+2]-cycloaddition between carbon-carbon double bonds is observed [178, 263, 274]. The reaction of cyclopentenone with a 2,3-dihydrofuran derivative gives the corresponding cyclobutane derivative (Scheme 64) [274].



Scheme 64

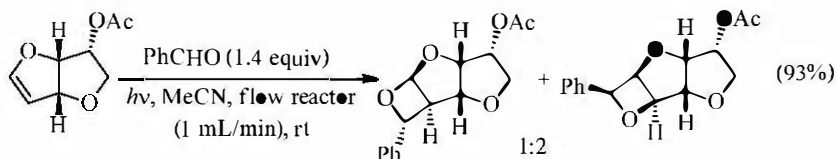
When enol ethers are treated with chiral phenylglyoxylate derivatives, good diastereoselectivity is observed (Scheme 65) [78a,b].



Scheme 65

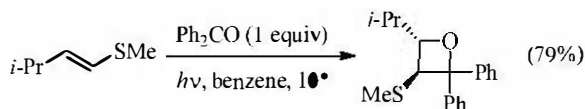
It is noteworthy that the reaction of enol ethers with carbonyl compounds has been effected in a flow reactor, yielding the reaction products in very good

overall yields and high diastereoselectivity (Scheme 66) [268]. However, poor regioselectivity is observed.



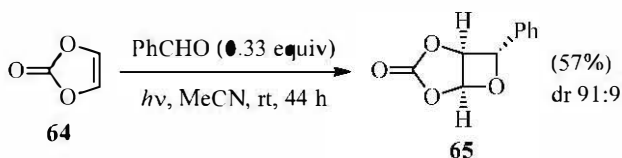
Scheme 66

There is little data available on the photochemical behavior of vinyl thioethers (Table 6). Good regio- and stereoselectivities have been observed in existing cases, in agreement with the formation of the most stable biradical intermediate (Scheme 67) [280, 281].



Scheme 67

Reactions of Carbonyl Compounds with Enol Esters, Enol Silyl Ethers, and Enamine Derivatives. The reaction of the enol ester **64** with benzaldehyde gives the adduct **65** with a clear preference for the *exo* isomer (Scheme 68) (Table 7) [282].



Scheme 68

Table 7. Intermolecular reactions with electron-rich unsaturated compounds. F. Enol esters.


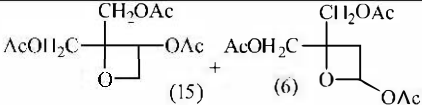

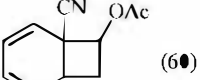

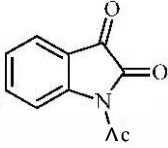
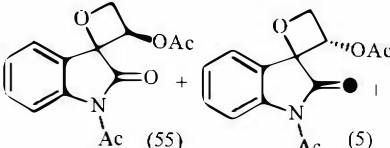

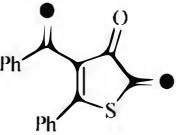
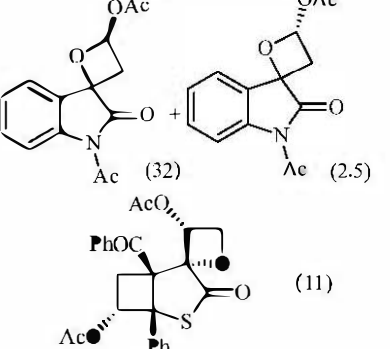
Substrate	Carbonyl compound	Product (yields %)	Ref.
	AcOCH ₂ COCH ₂ OAc (0.5 equiv)		260
	PhCN (0.1 equiv)		147
	 (0.1 equiv)		52
			283

Table 7. Continued

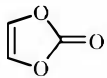
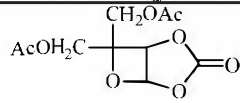
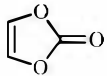
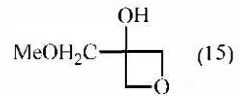
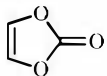
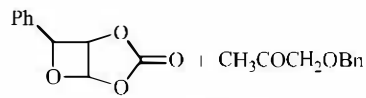
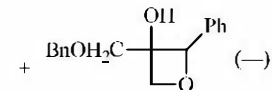
Substrate	Carbonyl compound	Product (yields %)	Ref.																											
	AcOCH ₂ COCH ₂ OAc (0.5 equiv)		260																											
		<table border="1"> <thead> <tr> <th>Solvent</th> <th colspan="2">Irradiation time (h)</th> </tr> </thead> <tbody> <tr> <td>No solvent</td> <td>26</td> <td>(55)</td> </tr> <tr> <td>acetonitrile</td> <td>15</td> <td>(47)</td> </tr> <tr> <td>pyridine</td> <td>15</td> <td>(55)</td> </tr> <tr> <td>Eethyl acetate</td> <td>15</td> <td>(43)</td> </tr> <tr> <td>diethyl carbonate</td> <td>15</td> <td>(40)</td> </tr> <tr> <td><i>t</i>-butyl alcohol</td> <td>15</td> <td>(59)</td> </tr> <tr> <td>acetic acid</td> <td>15</td> <td>(59)</td> </tr> <tr> <td>benzene</td> <td>15</td> <td>(72)</td> </tr> </tbody> </table>	Solvent	Irradiation time (h)		No solvent	26	(55)	acetonitrile	15	(47)	pyridine	15	(55)	Eethyl acetate	15	(43)	diethyl carbonate	15	(40)	<i>t</i> -butyl alcohol	15	(59)	acetic acid	15	(59)	benzene	15	(72)	
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No solvent	26	(55)																												
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acetic acid	15	(59)																												
benzene	15	(72)																												
	MeOCH ₂ COCH ₂ OMe (0.5 equiv)		260																											
	BnOCH ₂ COCH ₂ OBn (0.5 equiv)	 	260																											

Table 7. *Continued*

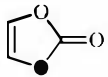
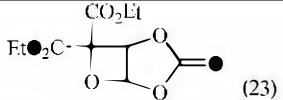
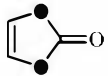
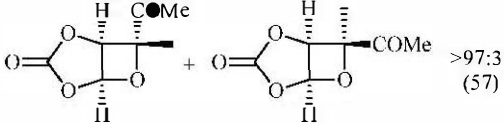
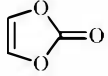
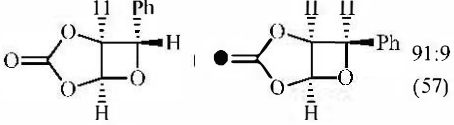
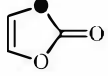
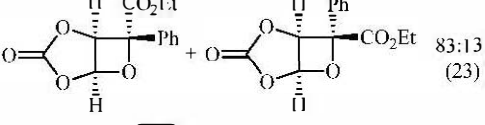
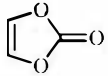
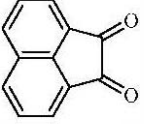
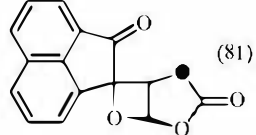
Substrate	Carbonyl compound	Product (yields %)	Ref.
	EtO ₂ CCOCO ₂ Et (0.5 equiv)	 (23)	260
	MeCOCOMe (0.33 equiv)	 >97:3 (57)	282
	PhCHO (0.33 equiv)	 91:9 (57)	282
	PhCOCO ₂ Et (0.33 equiv)	 83:13 (23)	282
	 (0.1 equiv)	 (81)	284

Table 7. Continued

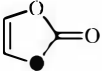
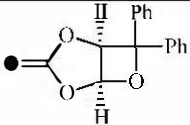
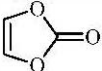
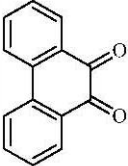
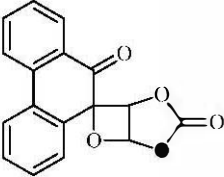
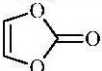
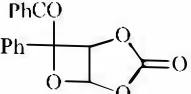

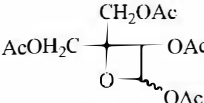
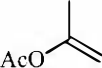
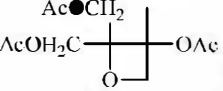
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (0.33 equiv)	 Solvent benzene (51–85) MeCN (89)	282 284
	 (0.25 equiv)	 (80)	284
	PhCOCOPh (0.2 equiv)	 (37)	284
	AcOCH ₂ COCH ₂ OAc (0.5 equiv)	 (71)	282
	AcOCH ₂ COCH ₂ OAc (0.2 equiv)	 (55)	282

Table 7. *Continued*

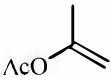
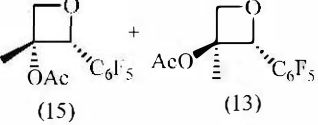
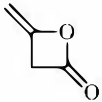
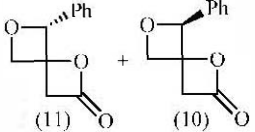
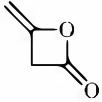
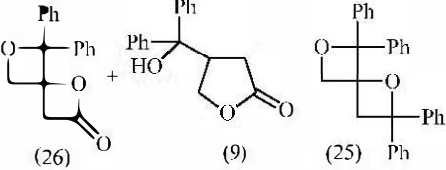
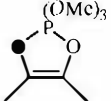
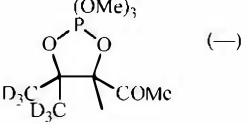
Substrate	Carbonyl compound	Product (yields %)	Ref.
	$\text{C}_6\text{F}_5\text{CHO}$ (0.44 equiv)	 (15) + (13)	285
	PhCHO (0.1 equiv)	 (11) + (10)	286
	$\text{Ph}_2\text{C=O}$ (0.08 equiv)	 (26) + (9) + (25)	286
	$(\text{CD}_3)_2\text{CO}$	 (—)	287

Table 7. Continued

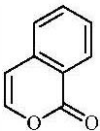
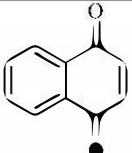
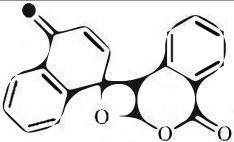
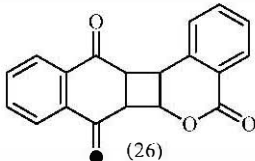
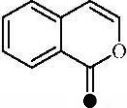
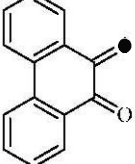
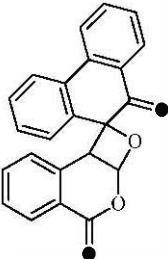
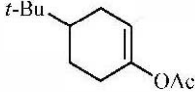
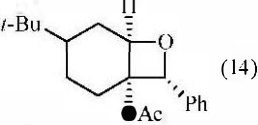
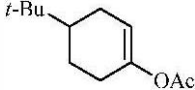
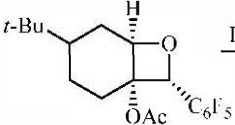
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 (35) ,  (26)	288
	 (0.25 equiv)	 (74)	211
	PhCHO (0.57 equiv)	 (14)	285
	C ₆ F ₅ CHO (0.57 equiv)	 Irradiation time (h) 20 (11) 72 (17)	285

Table 7. *Continued*

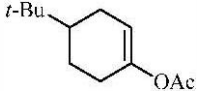
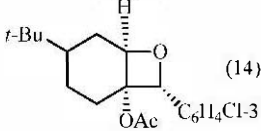
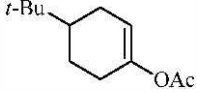
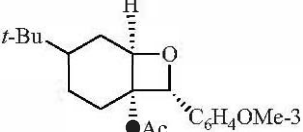
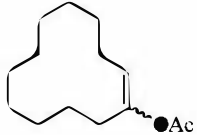
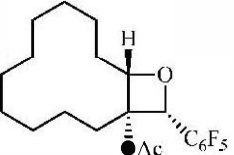
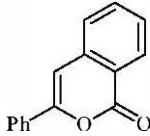
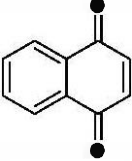
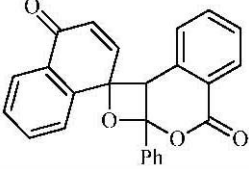
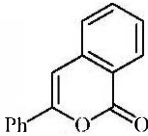
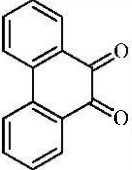
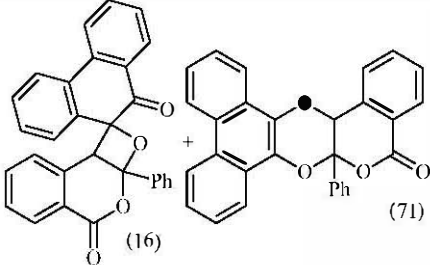
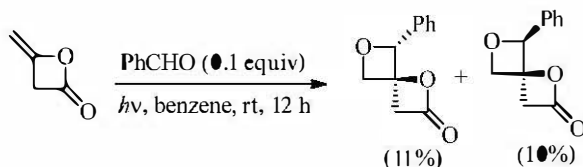
Substrate	Carbonyl compound	Product (yields %)	Ref.
	3-ClC ₆ H ₄ CHO (0.57 equiv)	 (14)	285
	3-MeOC ₆ H ₄ CHO (0.57 equiv)	 (6)	285
	C ₆ F ₅ CHO (0.5 equiv)	 (9)	285
	 (0.5 equiv)	 (65)	288

Table 7. Continued

Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 (16) + (71)	211

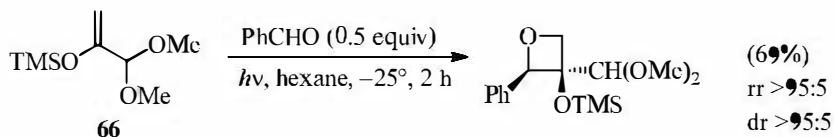
On the contrary, the same selectivity is not observed when diketene reacts with the same aromatic aldehyde (Scheme 69) [286].



Scheme 69

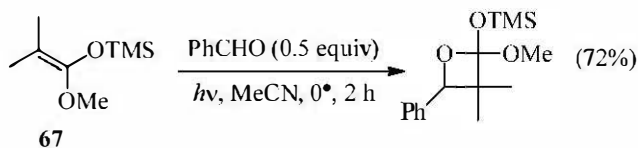
As described above, when α,β -unsaturated carbonyl compounds are used with enol esters, a competition between a Paternò-Büchi reaction and a [2+2]-cycloaddition reaction with the alkene bonds [288].

Enol silyl ethers react with benzaldehyde with interesting regio- and stereoselectivity [488]. The reaction of the enol silyl ether **66** with benzaldehyde in hexane at -25° shows significant regio- and stereoselectivity (Scheme 70) [289] (Table 8).



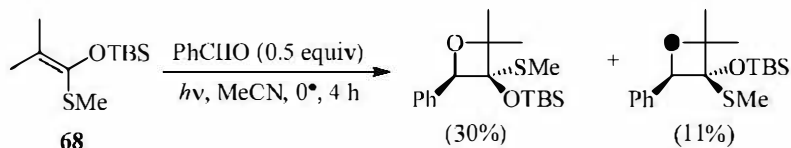
Scheme 70

When **67** is the substrate, unusual regiochemistry is observed, wherein the oxygen atom of the oxetane ring is adjacent to the TMS and the methoxy group (Scheme 71) [290]. This observed regioselectivity is rationalized by invoking an electron transfer mechanism [290a].

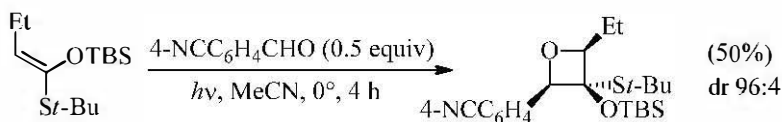


Scheme 71

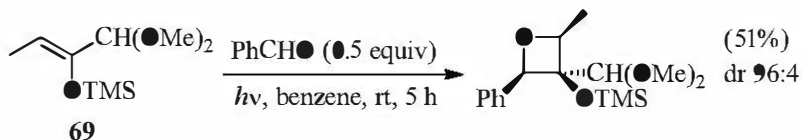
The silyl ether **68** reacts with benzaldehyde, but does not show the same regioselectivity observed above. Furthermore, this type of reaction usually does not show high stereoselectivity (Scheme 72), with some exceptions (Scheme 73) [62].



Scheme 72

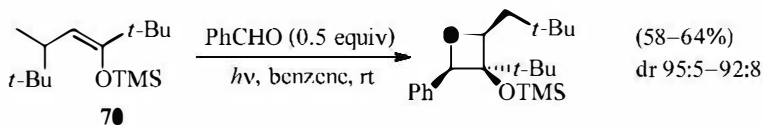


Scheme 73



Scheme 74

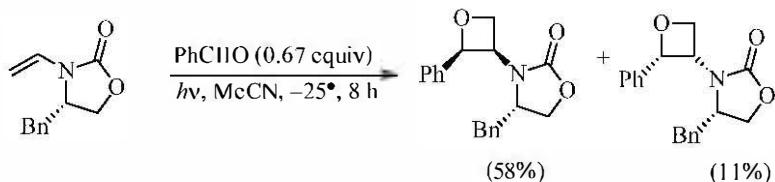
The (*Z*) alkenes **69** and **70** furnish the corresponding oxetanes with high stereoselectivity (Schemes 74 [57] and 75 [58, 59a]).



Scheme 75

Seleno-substituted silyl enol ethers also afford the corresponding oxetanes with good stereoselectivity [63].

Chiral enamine derivatives generally do not give the corresponding adduct with high diastereoselectivity (Table 9). The only exception is found using the enamine shown in Scheme 76, affording the corresponding adducts with a 81:19 dr using benzaldehyde [16r, 67].



Scheme 76

Table 10 collects the results obtained by using substrates bearing both electron-withdrawing and electron-donating groups.

Reactions with Heterocyclic Compounds

Reactions with Five-Membered Heterocycles. Thiophenes, pyrroles, furans, isoxazoles, oxazoles, imidazoles, pyrazoles, thiazoles, and isothiazoles are common five-membered, aromatic, heterocyclic compounds which upon the Paternò–Büchi reaction with carbonyl compounds result in the production of products that lack aromaticity (Table 11).

Table 8. Intermolecular reactions with electron-rich unsaturated compounds. G. Enol silyl ethers.

Substrate	Carbonyl compound	Product (yields %)	Ref.						
	AcOCH ₂ COCH ₂ OAc (0.5 equiv)	 (57)	291						
	PhCOMe (0.5 equiv)	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Irradiation time (h)</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>20 (46)</td> </tr> <tr> <td>benzene</td> <td>16 (53)</td> </tr> </tbody> </table>	Solvent	Irradiation time (h)	MeCN	20 (46)	benzene	16 (53)	290b
Solvent	Irradiation time (h)								
MeCN	20 (46)								
benzene	16 (53)								
	4-CNC ₆ H ₄ COMe (0.5 equiv)	 (46)	290b						
	4-MeOC ₆ H ₄ COMe (0.5 equiv)	No reaction	290b						
	PhCOPr (0.5 equiv)	 (10)	290b						
	Ph ₂ CO (0.5 equiv)	 (68)	290b						

Table 8. *Continued*

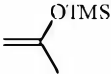
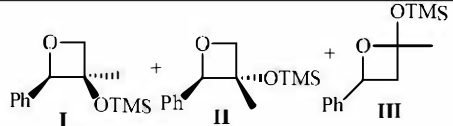
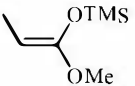
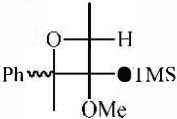
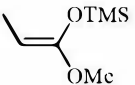
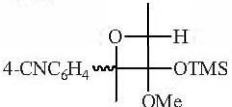
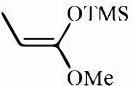
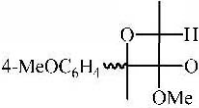
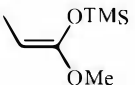
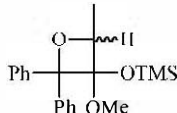
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	PhCHO (0.5 equiv)	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>time (h)</th> <th>I/II</th> <th>(I+II)/C</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td>rt</td> <td>4 (51)</td> <td>70:30</td> <td>90:10</td> </tr> <tr> <td>hexane</td> <td>-25</td> <td>5 (48)</td> <td>76:24</td> <td>90:10</td> </tr> </tbody> </table>	Solvent	Temp	time (h)	I/II	(I+II)/C	benzene	rt	4 (51)	70:30	90:10	hexane	-25	5 (48)	76:24	90:10	289
Solvent	Temp	time (h)	I/II	(I+II)/C														
benzene	rt	4 (51)	70:30	90:10														
hexane	-25	5 (48)	76:24	90:10														
	PhCOMe (0.5 equiv)	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Irr. time (h)</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>12 (22)</td> </tr> <tr> <td>benzene</td> <td>14 (55)</td> </tr> </tbody> </table>	Solvent	Irr. time (h)	MeCN	12 (22)	benzene	14 (55)	290b									
Solvent	Irr. time (h)																	
MeCN	12 (22)																	
benzene	14 (55)																	
	4-CNC ₆ H ₄ COMe (0.5 equiv)	 <table border="1"> <tbody> <tr> <td>(25)</td> </tr> </tbody> </table>	(25)	290b														
(25)																		
	4-MeOC ₆ H ₄ COMe (0.5 equiv)	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Irr. time (h)</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>50 (48)</td> </tr> <tr> <td>benzene</td> <td>19 (43)</td> </tr> </tbody> </table>	Solvent	Irr. time (h)	MeCN	50 (48)	benzene	19 (43)	290b									
Solvent	Irr. time (h)																	
MeCN	50 (48)																	
benzene	19 (43)																	
	Ph ₂ CO (0.5 equiv)	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Irr. time (h)</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>8 (37)</td> </tr> <tr> <td>benzene</td> <td>7 (36)</td> </tr> </tbody> </table>	Solvent	Irr. time (h)	MeCN	8 (37)	benzene	7 (36)	290b									
Solvent	Irr. time (h)																	
MeCN	8 (37)																	
benzene	7 (36)																	

Table 8. *Continued*

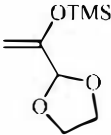
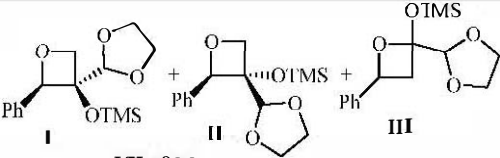
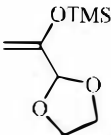
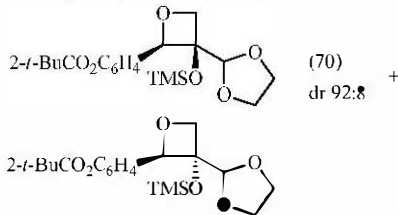
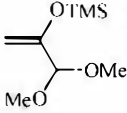
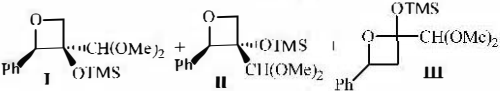
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	PhCHO (0.5 equiv)	 <p>I + II + III</p> <p>I/II >95:5 (I + II):III >95:5 (45)</p>	289															
	2- <i>t</i> -BuCO ₂ C ₆ H ₄ CHO (0.5 equiv)	 <p>(70) dr 92:8 +</p>	292															
	PhCHO (0.5 equiv)	 <p>I + II + III</p> <table border="1" data-bbox="821 778 1173 856"> <thead> <tr> <th>Solvent</th> <th>T(°)</th> <th>t(h)</th> <th>I/II</th> <th>(I+II)/III</th> </tr> </thead> <tbody> <tr> <td>Benzene</td> <td>rt</td> <td>4 (72)</td> <td>>95:5</td> <td>>95:5</td> </tr> <tr> <td>Hexane</td> <td>-25</td> <td>2 (69)</td> <td>>95:5</td> <td>>95:5</td> </tr> </tbody> </table>	Solvent	T(°)	t(h)	I/II	(I+II)/III	Benzene	rt	4 (72)	>95:5	>95:5	Hexane	-25	2 (69)	>95:5	>95:5	289
Solvent	T(°)	t(h)	I/II	(I+II)/III														
Benzene	rt	4 (72)	>95:5	>95:5														
Hexane	-25	2 (69)	>95:5	>95:5														

Table 8. *Continued*

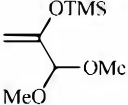
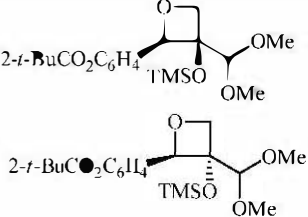
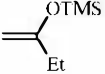
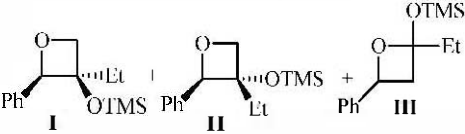
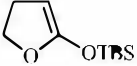
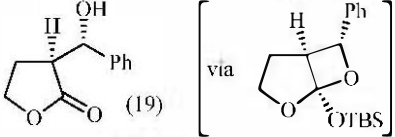
Substrate	Carbonyl compound	Product (yields %)	Ref.																		
	2- <i>t</i> -BuCO ₂ C ₆ H ₄ CHO (0.5 equiv)	 (63) dr 91:9 +	292																		
	PhCHO (0.5 equiv)		289																		
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>time (h)</th> <th>Yield (%)</th> <th>I/II</th> <th>(I+II)/III</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td>rt</td> <td>4</td> <td>(51)</td> <td>83:1</td> <td>>95:5</td> </tr> <tr> <td>hexane</td> <td>25</td> <td>4</td> <td>(60)</td> <td>92:8</td> <td>>95:5</td> </tr> </tbody> </table>	Solvent	Temp	time (h)	Yield (%)	I/II	(I+II)/III	benzene	rt	4	(51)	83:1	>95:5	hexane	25	4	(60)	92:8	>95:5	
Solvent	Temp	time (h)	Yield (%)	I/II	(I+II)/III																
benzene	rt	4	(51)	83:1	>95:5																
hexane	25	4	(60)	92:8	>95:5																
	PhCHO (0.5 equiv)	 (19) dr 81:19	293																		

Table 8. *Continued*

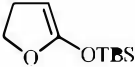
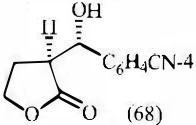
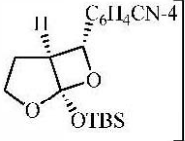
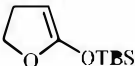
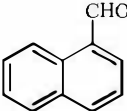
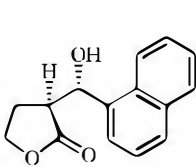
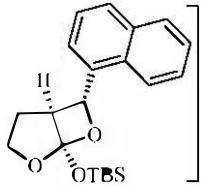
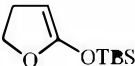
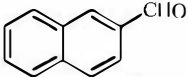
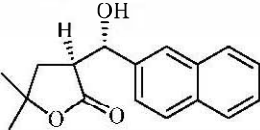
Substrate	Carbonyl compound	Product (yields %)	Ref.
	4-CN ₆ H ₄ CHO (0.5 equiv)	 (68) dr 78:22 [via ]	293
	 (0.5 equiv)	 (82) dr 93:7 [via ]	293
	 (0.5 equiv)	 (39) dr 84:16	290c 293

Table 8. *Continued*

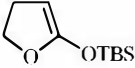
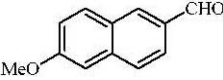
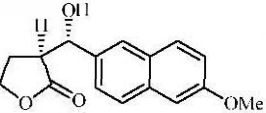
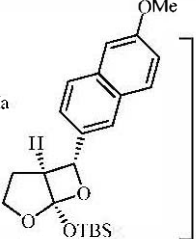
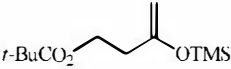
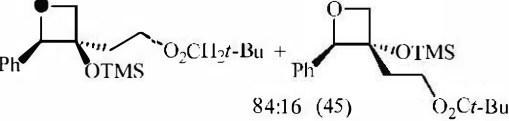
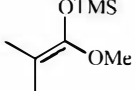
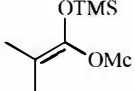
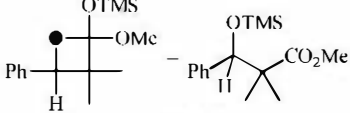
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 (47) dr 92:8 via 	293
	PhCHO (0.5 equiv)	 84:16 (45)	57
	PhCHO (0.5 equiv)	No reaction	290b
	PhCHO (0.5 equiv, \bullet)	 95:5 (72)	290a

Table 8. Continued

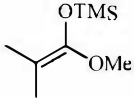
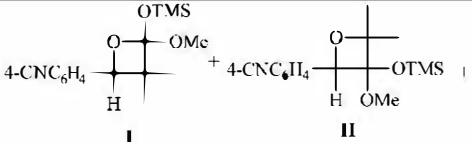
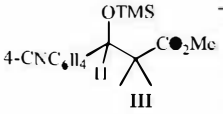
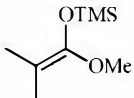
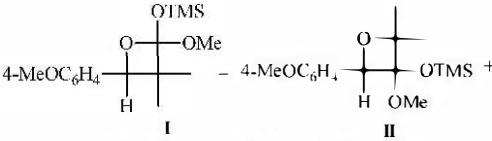
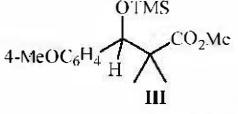
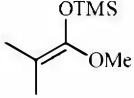
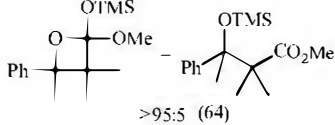
Substrate	Carbonyl compound	Product (yields %)	Ref.																				
	4-CNC ₆ H ₄ CHO (0.5 equiv)	  <table border="1" data-bbox="1013 386 1268 532"> <thead> <tr> <th>Solvent</th> <th>I:II</th> <th>I:III</th> <th></th> </tr> </thead> <tbody> <tr> <td>Hexane</td> <td>-</td> <td>-</td> <td>(0)</td> </tr> <tr> <td>Et₂O</td> <td>>95:5</td> <td>85:15</td> <td>(59)</td> </tr> <tr> <td>MeCN</td> <td>>95:5</td> <td>70:30</td> <td>(63)</td> </tr> <tr> <td>DCM</td> <td></td> <td>>95:5</td> <td>(88)</td> </tr> </tbody> </table>	Solvent	I:II	I:III		Hexane	-	-	(0)	Et ₂ O	>95:5	85:15	(59)	MeCN	>95:5	70:30	(63)	DCM		>95:5	(88)	290a
Solvent	I:II	I:III																					
Hexane	-	-	(0)																				
Et ₂ O	>95:5	85:15	(59)																				
MeCN	>95:5	70:30	(63)																				
DCM		>95:5	(88)																				
	4-MeOC ₆ H ₄ CHO (0.5 equiv)	  <table border="1" data-bbox="1013 677 1268 795"> <thead> <tr> <th>Solvent</th> <th>I:II</th> <th>I:III</th> <th></th> </tr> </thead> <tbody> <tr> <td>hexane</td> <td>79:21</td> <td>>95:5</td> <td>(75)</td> </tr> <tr> <td>Et₂O</td> <td>77:23</td> <td>>95:5</td> <td>(69)</td> </tr> <tr> <td>MeCN</td> <td>95:5</td> <td>94:6</td> <td>(59)</td> </tr> </tbody> </table>	Solvent	I:II	I:III		hexane	79:21	>95:5	(75)	Et ₂ O	77:23	>95:5	(69)	MeCN	95:5	94:6	(59)	290a				
Solvent	I:II	I:III																					
hexane	79:21	>95:5	(75)																				
Et ₂ O	77:23	>95:5	(69)																				
MeCN	95:5	94:6	(59)																				
	PhCOMe (0.5 equiv, \bullet^*)	 >95:5 (64)	290a																				

Table 8. *Continued*

Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOMe (0.5 equiv)	 Solvent Irr. time (h) <i>rr</i> MeCN 16 (94) 1:0.13 benzene 33 (82) 1:0.28	290b
	3-CNC ₆ H ₄ COMe (0.5 equiv)	 >95:5 (55)	290a
	4-CNC ₆ H ₄ COMe (0.5 equiv, ●)	 62:38 (43)	290a
	4-CNC ₆ H ₄ COMe (0.5 equiv)	No reaction	290b
	4-MeOC ₆ H ₄ COMe (0.5 equiv)	No reaction	290b

Table 8. *Continued*

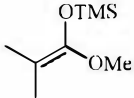
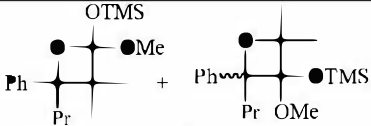
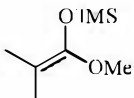
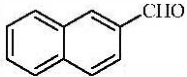
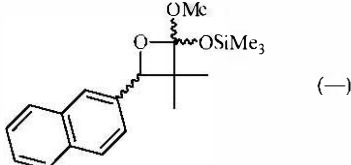
Substrate	Carbonyl compound	Product (yields %)	Ref.									
	PhCOPr (0.5 equiv)	<div style="text-align: center;">  </div> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Solvent</th> <th>hr. time (h)</th> <th>rr</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>9</td> <td>(12) 1:1.4</td> </tr> <tr> <td>Benzene</td> <td>8</td> <td>(21) 1:2.0</td> </tr> </tbody> </table>	Solvent	hr. time (h)	rr	MeCN	9	(12) 1:1.4	Benzene	8	(21) 1:2.0	290b
Solvent	hr. time (h)	rr										
MeCN	9	(12) 1:1.4										
Benzene	8	(21) 1:2.0										
			290c									

Table 8. *Continued*

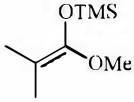
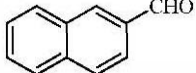
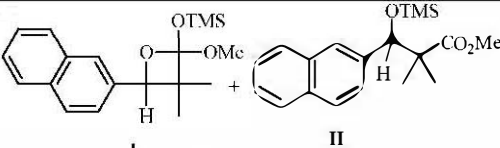
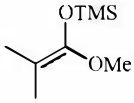
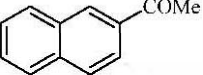
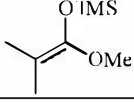
Substrate	Carbonyl compound	Product (yields %)	Ref.																											
	 (0.5 equiv, $\bullet\bullet$)		290a																											
		<table border="1"> <thead> <tr> <th data-bbox="917 397 1013 420">Solvent</th> <th data-bbox="1016 397 1125 420">I:II</th> <th data-bbox="1128 397 1252 420"></th> </tr> </thead> <tbody> <tr> <td data-bbox="917 425 1013 448">hexane</td> <td data-bbox="1016 425 1125 448">>95:5</td> <td data-bbox="1128 425 1252 448">(76)</td> </tr> <tr> <td data-bbox="917 453 1013 476">Et₂O</td> <td data-bbox="1016 453 1125 476">>95:5</td> <td data-bbox="1128 453 1252 476">(79)</td> </tr> <tr> <td data-bbox="917 481 1013 504">benzene</td> <td data-bbox="1016 481 1125 504">>95:5</td> <td data-bbox="1128 481 1252 504">(59)</td> </tr> <tr> <td data-bbox="917 509 1013 532">THF</td> <td data-bbox="1016 509 1125 532">>95:5</td> <td data-bbox="1128 509 1252 532">(84)</td> </tr> <tr> <td data-bbox="917 537 1013 560">DCM</td> <td data-bbox="1016 537 1125 560">88:12</td> <td data-bbox="1128 537 1252 560">(87)</td> </tr> <tr> <td data-bbox="917 565 1013 588">MeCN</td> <td data-bbox="1016 565 1125 588">79:21</td> <td data-bbox="1128 565 1252 588">(88)</td> </tr> <tr> <td data-bbox="917 593 1013 616">DMF</td> <td data-bbox="1016 593 1125 616">75:25</td> <td data-bbox="1128 593 1252 616">(68)</td> </tr> <tr> <td data-bbox="917 621 1013 644">HMPA</td> <td data-bbox="1016 621 1125 644">59:41</td> <td data-bbox="1128 621 1252 644">(67)</td> </tr> </tbody> </table>	Solvent	I:II		hexane	>95:5	(76)	Et ₂ O	>95:5	(79)	benzene	>95:5	(59)	THF	>95:5	(84)	DCM	88:12	(87)	MeCN	79:21	(88)	DMF	75:25	(68)	HMPA	59:41	(67)	
Solvent	I:II																													
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HMPA	59:41	(67)																												
	 (0.5 equiv)	No reaction	290b																											
	PhCOBu (0.5 equiv)	<table border="1"> <thead> <tr> <th data-bbox="917 812 1013 834">Solvent</th> <th data-bbox="1016 812 1252 834">Irr. time (h)</th> <th data-bbox="1256 812 1289 834"></th> </tr> </thead> <tbody> <tr> <td data-bbox="917 840 1013 862">MeCN</td> <td data-bbox="1016 840 1252 862">5.5</td> <td data-bbox="1256 840 1289 862">(3)</td> </tr> <tr> <td data-bbox="917 868 1013 890">benzene</td> <td data-bbox="1016 868 1252 890">8</td> <td data-bbox="1256 868 1289 890">(21)</td> </tr> </tbody> </table>	Solvent	Irr. time (h)		MeCN	5.5	(3)	benzene	8	(21)	290b																		
Solvent	Irr. time (h)																													
MeCN	5.5	(3)																												
benzene	8	(21)																												

Table 8. *Continued*

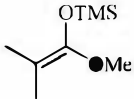
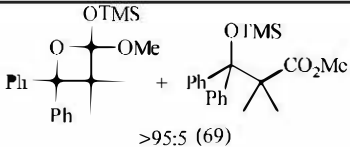
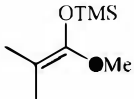
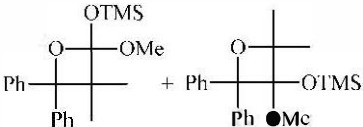
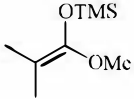
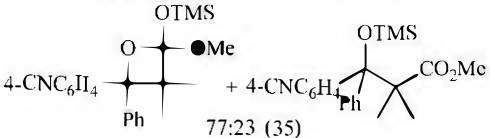
Substrate	Carbonyl compound	Product (yields %)	Ref.									
	Ph_2CO (0.5 equiv, 0°)	 <p style="text-align: center;">>95:5 (69)</p>	290a									
	Ph_2CO (0.5 equiv)		290b									
		<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">Solvent</th> <th style="text-align: left;">Irr. time (h)</th> <th style="text-align: left;">rr</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>6</td> <td>(65) 1:0.00</td> </tr> <tr> <td>benzene</td> <td>4</td> <td>(30) 1:0.11</td> </tr> </tbody> </table>	Solvent	Irr. time (h)	rr	MeCN	6	(65) 1:0.00	benzene	4	(30) 1:0.11	
Solvent	Irr. time (h)	rr										
MeCN	6	(65) 1:0.00										
benzene	4	(30) 1:0.11										
	$4\text{-CNC}_6\text{H}_4\text{COPh}$ (0.5 equiv, 0°)	 <p style="text-align: center;">77:23 (35)</p>	290b									

Table 8. *Continued*

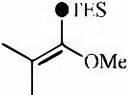
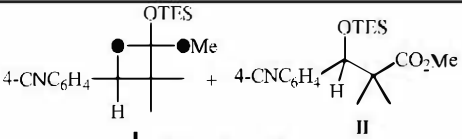
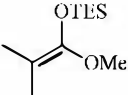
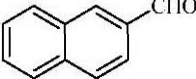
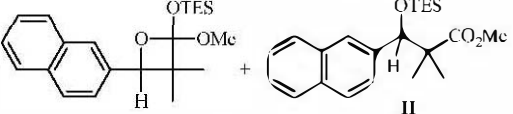
Substrate	Carbonyl compound	Product (yields %)	Ref.										
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 <table border="1" data-bbox="954 375 1150 498"> <thead> <tr> <th>Solvent</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Et₂O</td> <td>- (●)</td> </tr> <tr> <td>CH₂Cl₂</td> <td>>95:5 (92)</td> </tr> <tr> <td>MeCN</td> <td>89:11 (92)</td> </tr> </tbody> </table>	Solvent	I:II	Et ₂ O	- (●)	CH ₂ Cl ₂	>95:5 (92)	MeCN	89:11 (92)	290a		
Solvent	I:II												
Et ₂ O	- (●)												
CH ₂ Cl ₂	>95:5 (92)												
MeCN	89:11 (92)												
	 (0.5 equiv)	 <table border="1" data-bbox="975 630 1161 777"> <thead> <tr> <th>Solvent</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>hexane</td> <td>>95:5 (73)</td> </tr> <tr> <td>Et₂O</td> <td>>95:5 (60)</td> </tr> <tr> <td>CH₂Cl₂</td> <td>>95:5 (63)</td> </tr> <tr> <td>MeCN</td> <td>88:12 (64)</td> </tr> </tbody> </table>	Solvent	I:II	hexane	>95:5 (73)	Et ₂ O	>95:5 (60)	CH ₂ Cl ₂	>95:5 (63)	MeCN	88:12 (64)	290a
Solvent	I:II												
hexane	>95:5 (73)												
Et ₂ O	>95:5 (60)												
CH ₂ Cl ₂	>95:5 (63)												
MeCN	88:12 (64)												

Table 8. *Continued*

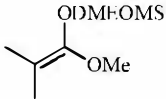
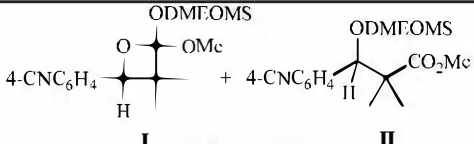
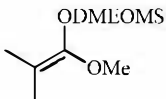
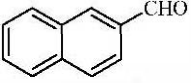
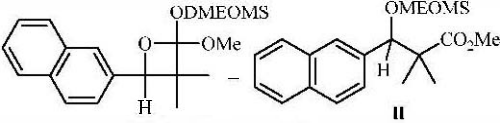
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 <table border="1" data-bbox="957 375 1165 498"> <thead> <tr> <th>Solvent</th> <th>I:II</th> <th></th> </tr> </thead> <tbody> <tr> <td>Et₂O</td> <td>58:42</td> <td>(94)</td> </tr> <tr> <td>CH₂Cl₂</td> <td>54:46</td> <td>(94)</td> </tr> <tr> <td>MeCN</td> <td>32:6</td> <td>(75)</td> </tr> </tbody> </table>	Solvent	I:II		Et ₂ O	58:42	(94)	CH ₂ Cl ₂	54:46	(94)	MeCN	32:6	(75)	290a			
Solvent	I:II																	
Et ₂ O	58:42	(94)																
CH ₂ Cl ₂	54:46	(94)																
MeCN	32:6	(75)																
	 (0.5 equiv)	 <table border="1" data-bbox="957 632 1165 778"> <thead> <tr> <th>Solvent</th> <th>I:II</th> <th></th> </tr> </thead> <tbody> <tr> <td>hexane</td> <td>71:29</td> <td>(83)</td> </tr> <tr> <td>Et₂O</td> <td>86:14</td> <td>(34)</td> </tr> <tr> <td>CH₂Cl₂</td> <td>56:44</td> <td>(89)</td> </tr> <tr> <td>MeCN</td> <td>48:52</td> <td>(96)</td> </tr> </tbody> </table>	Solvent	I:II		hexane	71:29	(83)	Et ₂ O	86:14	(34)	CH ₂ Cl ₂	56:44	(89)	MeCN	48:52	(96)	290a
Solvent	I:II																	
hexane	71:29	(83)																
Et ₂ O	86:14	(34)																
CH ₂ Cl ₂	56:44	(89)																
MeCN	48:52	(96)																

Table 8. *Continued*

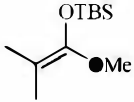
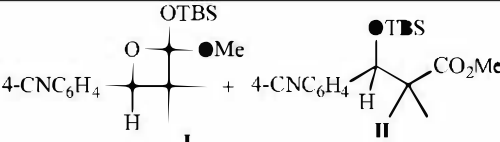
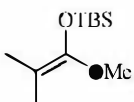
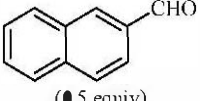
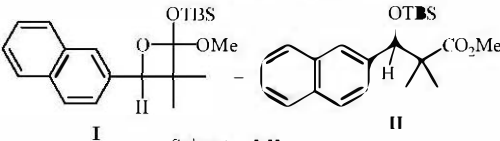
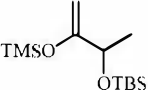
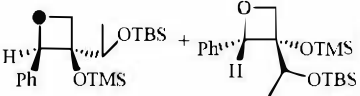
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 <table border="1" data-bbox="925 386 1181 520"> <thead> <tr> <th>Solvent</th> <th>I:II</th> <th></th> </tr> </thead> <tbody> <tr> <td>Et₂</td> <td>-</td> <td>(●)</td> </tr> <tr> <td>CH₂Cl₂</td> <td>>95:5</td> <td>(94)</td> </tr> <tr> <td>MeCN</td> <td>>95:5</td> <td>(75)</td> </tr> </tbody> </table>	Solvent	I:II		Et ₂	-	(●)	CH ₂ Cl ₂	>95:5	(94)	MeCN	>95:5	(75)	290a			
Solvent	I:II																	
Et ₂	-	(●)																
CH ₂ Cl ₂	>95:5	(94)																
MeCN	>95:5	(75)																
	 (0.5 equiv)	 <table border="1" data-bbox="925 666 1133 803"> <thead> <tr> <th>Solvent</th> <th>I:II</th> <th></th> </tr> </thead> <tbody> <tr> <td>hexane</td> <td>>95:5</td> <td>(72)</td> </tr> <tr> <td>Et₂</td> <td>>95:5</td> <td>(76)</td> </tr> <tr> <td>CH₂Cl₂</td> <td>>95:5</td> <td>(89)</td> </tr> <tr> <td>MeCN</td> <td>>95:5</td> <td>(79)</td> </tr> </tbody> </table>	Solvent	I:II		hexane	>95:5	(72)	Et ₂	>95:5	(76)	CH ₂ Cl ₂	>95:5	(89)	MeCN	>95:5	(79)	290a
Solvent	I:II																	
hexane	>95:5	(72)																
Et ₂	>95:5	(76)																
CH ₂ Cl ₂	>95:5	(89)																
MeCN	>95:5	(79)																
	PhCHO (0.5 equiv, -25°)	 (56) dr 57:43	59b															

Table 8. *Continued*

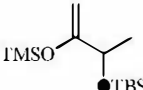
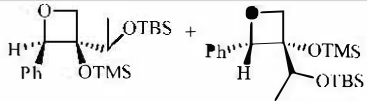
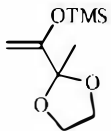
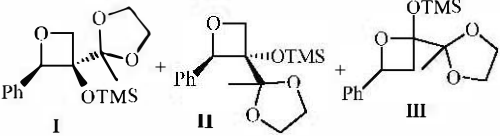
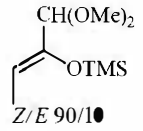
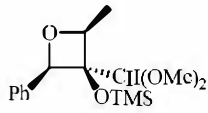
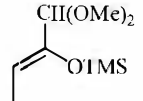
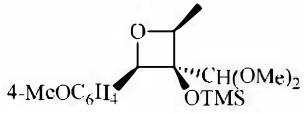
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	PhCHO (0.5 equiv)	 (67) dr 55:45	59b															
	PhCHO (0.5 equiv)		289															
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>time (h)</th> <th>I/II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td>rt</td> <td>4</td> <td>(54)</td> <td>>95:5</td> </tr> <tr> <td>hexane</td> <td>-25</td> <td>4</td> <td>(54)</td> <td>>95:5</td> </tr> </tbody> </table>	Solvent	Temp	time (h)	I/II	(I+II):III	benzene	rt	4	(54)	>95:5	hexane	-25	4	(54)	>95:5	
Solvent	Temp	time (h)	I/II	(I+II):III														
benzene	rt	4	(54)	>95:5														
hexane	-25	4	(54)	>95:5														
	PhCHO (0.5 equiv)	 (51) dr 98:6	57															
	4-MeOC ₆ H ₄ CHO (0.5 equiv)	 (45) dr 97:7	57															

Table 8. *Continued*

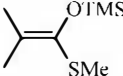
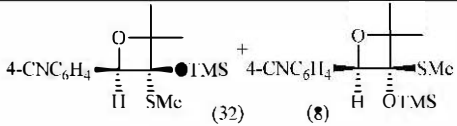
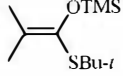
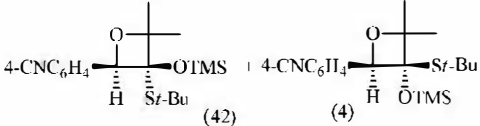
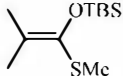
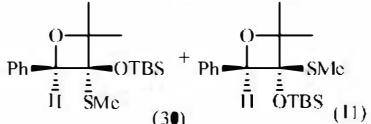
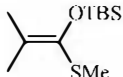
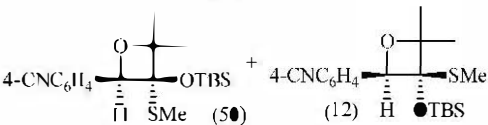
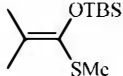
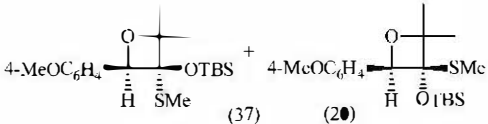
Substrate	Carbonyl compound	Product (yields %)	Ref.
	4-CNC ₆ H ₄ CHO (0.5 equiv)		62
	4-CNC ₆ H ₄ CHO (0.5 equiv)		62
	PhCHO (0.5 equiv)		62
	4-CNC ₆ H ₄ CHO (0.5 equiv)		62
	4-MeOC ₆ H ₄ CHO (0.5 equiv)		62

Table 8. *Continued*

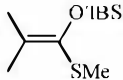
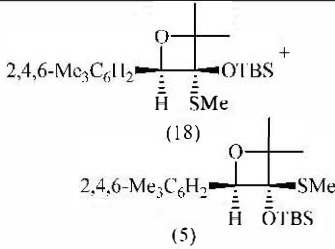
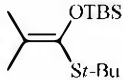
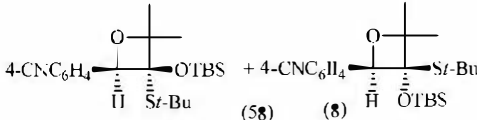
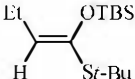
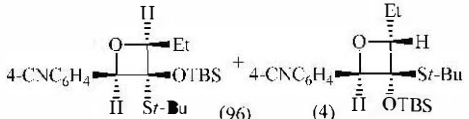
Substrate	Carbonyl compound	Product (yields %)	Ref.
	2,4,6-Me ₃ C ₆ H ₂ CHO (0.5 equiv)	 (18) + (5)	62
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 (58) + (8)	62
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 (96) + (4)	62

Table 8. *Continued*

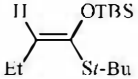
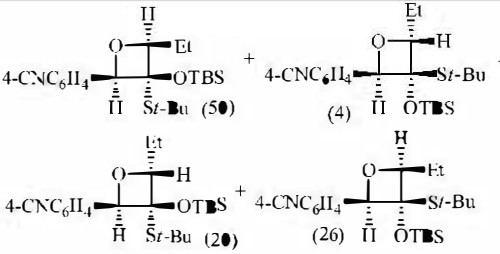
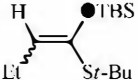
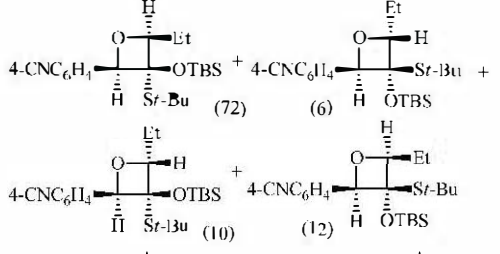
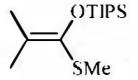
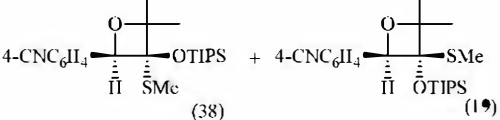
Substrate	Carbonyl compound	Product (yields %)	Ref.
	4-CNC ₆ H ₅ CHO (0.5 equiv)		62
	4-CNC ₆ H ₅ CHO (0.5 equiv)		62
	4-CNC ₆ H ₅ CHO (0.5 equiv)		62

Table 8. *Continued*

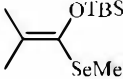
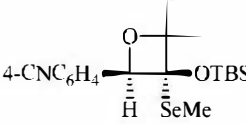
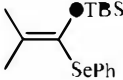
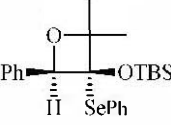
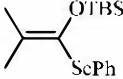
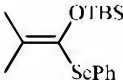
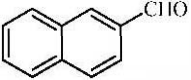
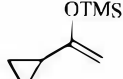
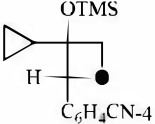
Substrate	Carbonyl compound	Product (yields %)	Ref.												
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 (70) <i>cis/trans</i> 86:14	63												
	PhCHO (0.5 equiv)	 (81) <i>cis/trans</i> 68:32	63												
	4-CNC ₆ H ₄ CHO (0.5 equiv)	<table border="1" data-bbox="775 512 1283 636"> <thead> <tr> <th rowspan="3">4-CNC₆H₄</th> <th colspan="2">Solvent</th> <th rowspan="3"><i>cis/trans</i></th> </tr> <tr> <th>Yield (%)</th> <th><i>cis/trans</i></th> </tr> </thead> <tbody> <tr> <td>McCN (94)</td> <td>68:32</td> </tr> <tr> <td>benzene (85)</td> <td>62:38</td> </tr> <tr> <td>CH₂Cl₂ (81)</td> <td>62:38</td> </tr> </tbody> </table>	4-CNC ₆ H ₄	Solvent		<i>cis/trans</i>	Yield (%)	<i>cis/trans</i>	McCN (94)	68:32	benzene (85)	62:38	CH ₂ Cl ₂ (81)	62:38	63
4-CNC ₆ H ₄	Solvent			<i>cis/trans</i>											
	Yield (%)	<i>cis/trans</i>													
	McCN (94)	68:32													
benzene (85)	62:38														
CH ₂ Cl ₂ (81)	62:38														
	 (0.5 equiv)	No reaction	63												
	4-CNC ₆ H ₄ CHO (0.67 equiv)	 (46)	294												

Table 8. *Continued*

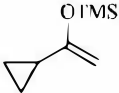
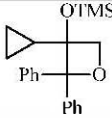
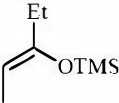
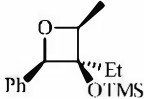
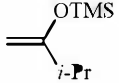
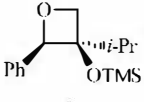
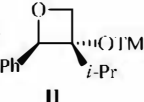
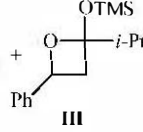
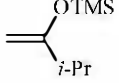
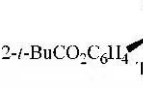
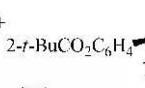
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	Ph ₂ CO (1.17 equiv)	 (73)	294															
	PhCHO (0.5 equiv)	 $\frac{E/Z}{25:75}$ (47) $\frac{dr}{86:14}$ $\frac{81:19}{(35)}$ $\frac{87:13}{(35)}$	57															
	PhCHO (0.5 equiv)	 I +  II +  III	289															
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>time (h)</th> <th>I/II</th> <th>(I+II)/C</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td>rt</td> <td>6</td> <td>(52) 88:12</td> <td>>95:5</td> </tr> <tr> <td>hexane</td> <td>25</td> <td>4</td> <td>(59) 94:6</td> <td>>95:5</td> </tr> </tbody> </table>	Solvent	Temp	time (h)	I/II	(I+II)/C	benzene	rt	6	(52) 88:12	>95:5	hexane	25	4	(59) 94:6	>95:5	
Solvent	Temp	time (h)	I/II	(I+II)/C														
benzene	rt	6	(52) 88:12	>95:5														
hexane	25	4	(59) 94:6	>95:5														
	2- <i>t</i> -BuCO ₂ C ₆ H ₄ CHO (0.5 equiv)	 +  (68) dr 70:30	292															

Table 8. Continued

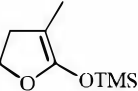
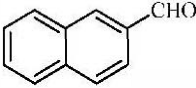
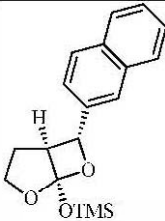
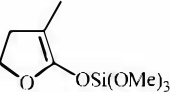
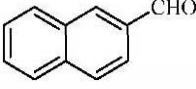
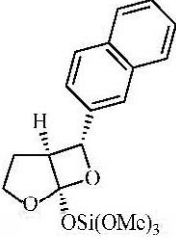
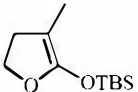
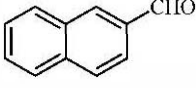
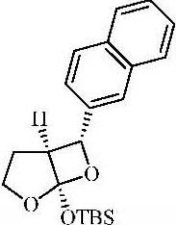
Substrate	Carbonyl compound	Product (yields %)	Ref.												
		 <table border="1" data-bbox="1042 277 1225 395"> <thead> <tr> <th>Solvent</th> <th colspan="2">dr</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>(28)</td> <td>85:15</td> </tr> <tr> <td>CH₂Cl₂</td> <td>(73)</td> <td>91:9</td> </tr> <tr> <td>HMPA</td> <td>(0)</td> <td></td> </tr> </tbody> </table>	Solvent	dr		MeCN	(28)	85:15	CH ₂ Cl ₂	(73)	91:9	HMPA	(0)		290c
Solvent	dr														
MeCN	(28)	85:15													
CH ₂ Cl ₂	(73)	91:9													
HMPA	(0)														
		 <table border="1" data-bbox="1042 517 1249 608"> <thead> <tr> <th>Solvent</th> <th colspan="2">dr</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>(20)</td> <td>81:19</td> </tr> <tr> <td>CH₂Cl₂</td> <td>(55)</td> <td>92:8</td> </tr> </tbody> </table>	Solvent	dr		MeCN	(20)	81:19	CH ₂ Cl ₂	(55)	92:8	290c			
Solvent	dr														
MeCN	(20)	81:19													
CH ₂ Cl ₂	(55)	92:8													
		 <table border="1" data-bbox="1042 781 1249 904"> <thead> <tr> <th>Solvent</th> <th colspan="2">dr</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>(75)</td> <td>93:7</td> </tr> <tr> <td>CH₂Cl₂</td> <td>(75)</td> <td>90:10</td> </tr> <tr> <td>HMPA</td> <td>(73)</td> <td>87:13</td> </tr> </tbody> </table>	Solvent	dr		MeCN	(75)	93:7	CH ₂ Cl ₂	(75)	90:10	HMPA	(73)	87:13	290c
Solvent	dr														
MeCN	(75)	93:7													
CH ₂ Cl ₂	(75)	90:10													
HMPA	(73)	87:13													

Table 8. *Continued*

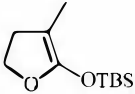
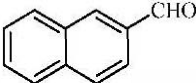
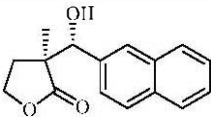
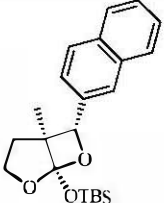
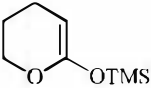
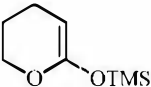
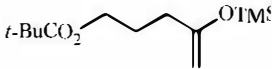
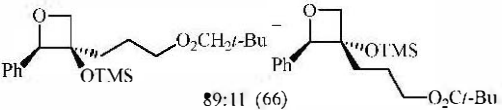
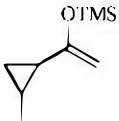
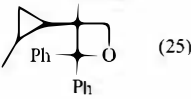
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 (86) dr 90:10 [via ]	293
	PhCOMe (0.5 equiv)	No reaction	290b
	4-CNC ₆ H ₄ COMe (0.5 equiv)	No reaction	290b
	PhCHO (0.5 equiv)	 89:11 (66)	57
	Ph ₂ CO (1.08 equiv)	 (25)	294

Table 8. *Continued*

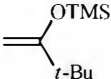
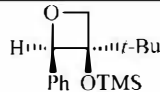
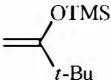
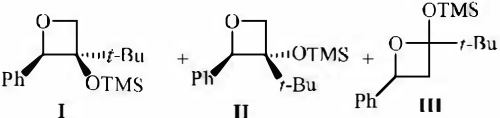
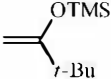
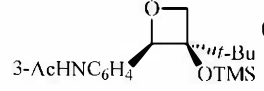
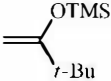
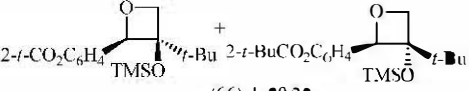
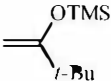
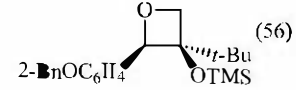
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.57 equiv, 0°)	 (59) dr >93/7	56b
	PhCHO (0.5 equiv)	 I + II + III Solvent T(°) t(h) I/II (I+II)/III Benzene rt 6 (65) 91:9 >95:5 Hexane -25 6 (66) >95:5 >95:5	289
	3-AcHNC ₆ H ₄ CHO (0.5 equiv)	 (42)	57
	2- <i>t</i> -BuCO ₂ C ₆ H ₄ CHO (0.5 equiv)	 (66) dr 80:20	292
	2BnOC ₆ H ₄ CHO (0.5 equiv)	 (56)	57

Table 8. *Continued*

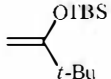
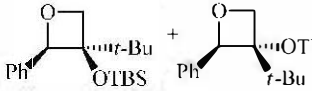
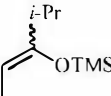
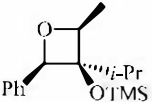
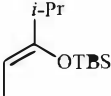
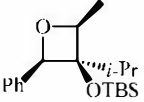
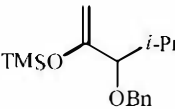
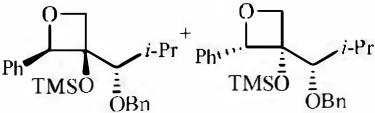
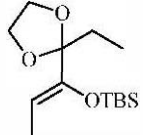
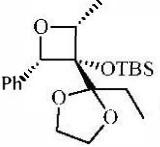
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (61) 85:15	289
	PhCHO (0.5 equiv)	 (69) dr 95.5:4.5	57
	PhCHO (0.5 equiv)	 (69) dr 95:5	57
	PhCHO (0.5 equiv)	 (35) dr 67:33	59b
	PhCHO (0.5 equiv)	 (65) dr 96.5:3.5	57

Table 8. *Continued*

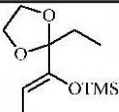
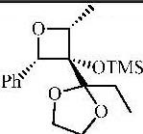
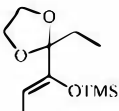
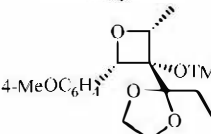
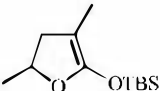
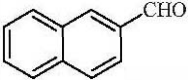
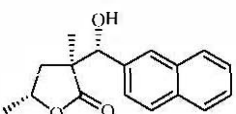
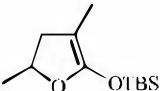
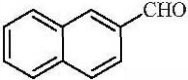
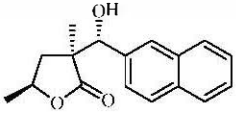
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (67) dr 97:3	57
	4-MeOC ₆ H ₄ CHO (0.5 equiv)	 (68) dr >97.5:2.5	57
	 (0.5 equiv)	 (44) dr 87:13 +	293
	 (0.5 equiv)	 (19) dr >95:5 +	

Table 8. *Continued*

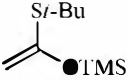

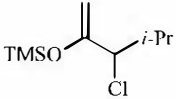
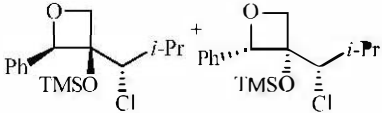
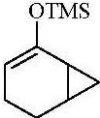
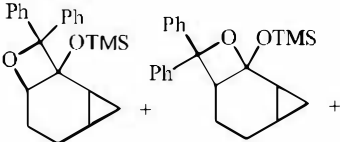
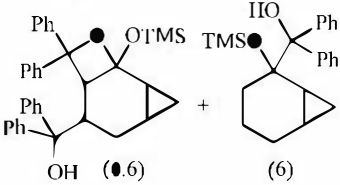
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (27) dr >95/5	56b
	PhCHO (0.5 equiv)	 (28) dr 15:85	59b
	Ph ₂ CO (1.2 equiv)	 (1.5) + (2)	294
		 (0.6) + (6)	

Table 8. Continued

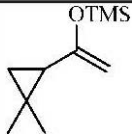
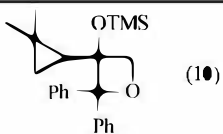
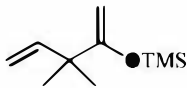
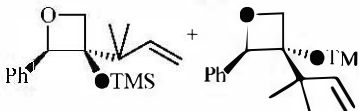
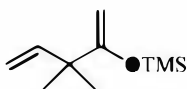
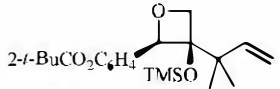

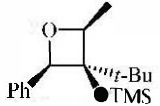
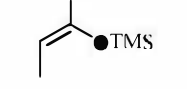
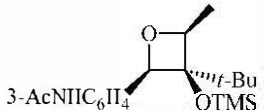
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph_2CO (1 equiv)	 (10)	294
	PhCHO (0.5 equiv)	 (70)	>95:5 57
	$2\text{-}t\text{-BuCO}_2\text{C}_6\text{H}_4\text{CHO}$ (0.5 equiv)	 (60)	292 dr 82:18
	PhCHO (0.5 equiv)	 (82)	dr >97.5:2.5 57
	$3\text{-AcHNiC}_6\text{H}_4\text{CHO}$ (0.5 equiv)	 (60)	dr >97.5:2.5 57

Table 8. *Continued*

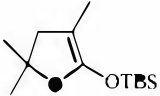
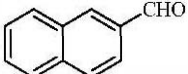
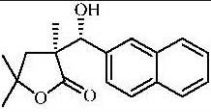
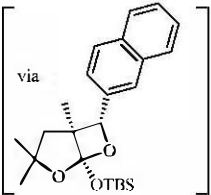
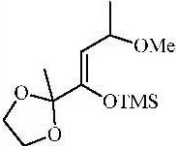
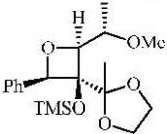
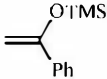
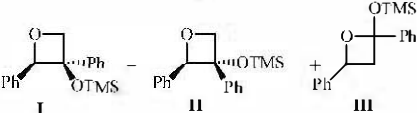
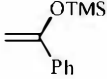
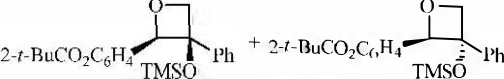
Substrate	Carbonyl compound	Product (yields %)	Ref.																				
	 (0.5 equiv)	 (69-75) [via ]	290c 293																				
	PhCHO (0.29 equiv)	 (52) dr 79:21	59a																				
	PhCHO (0.5 equiv)	 I II III	56b 289																				
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>time (h)</th> <th>I/II</th> <th>(I-II):III</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td>rt</td> <td>24</td> <td>(46)</td> <td>92:8</td> </tr> <tr> <td>hexane</td> <td>-25</td> <td>8</td> <td>(32)</td> <td>95:5</td> </tr> <tr> <td>hexane</td> <td>0</td> <td></td> <td>(39)</td> <td>>95:5</td> </tr> </tbody> </table>	Solvent	Temp	time (h)	I/II	(I-II):III	benzene	rt	24	(46)	92:8	hexane	-25	8	(32)	95:5	hexane	0		(39)	>95:5	
Solvent	Temp	time (h)	I/II	(I-II):III																			
benzene	rt	24	(46)	92:8																			
hexane	-25	8	(32)	95:5																			
hexane	0		(39)	>95:5																			
	2- <i>t</i> -BuCO ₂ C ₆ H ₄ CHO (0.5 equiv)	 (61) dr 95:5	292																				

Table 8. *Continued*


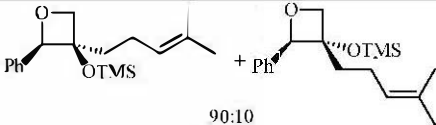
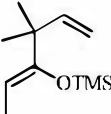
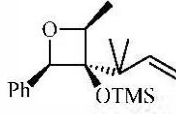
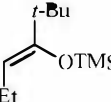
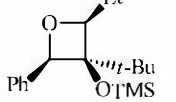
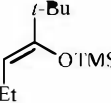
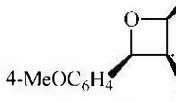
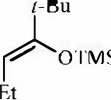

Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (23) 90:10	57
	PhCHO (0.5 equiv)	 (76) dr > 97.5:2.5	57
	PhCHO (0.5 equiv)	 (87) dr > 97.5:2.5	57
	4-MeOC ₆ H ₄ CHO (0.5 equiv)	 (73) dr > 97.5:2.5	57
	4-CNC ₆ H ₄ CHO (0.5 equiv)	 (62) dr 80:20	62

Table 8. *Continued*

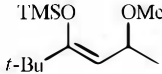
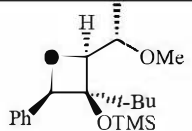
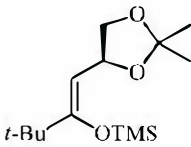
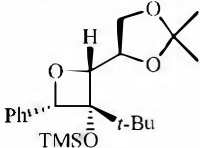
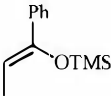
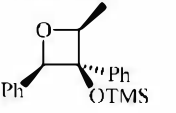
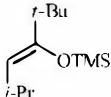
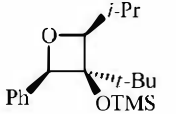
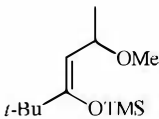
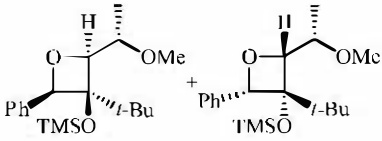
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (54) dr 85:15	58
	PhCHO (0.5 equiv)	 (70) dr 90:10	59a
	PhCHO (0.5 equiv)	 (53) dr 82.5:17.5	57
	PhCHO (0.5 equiv)	 (84) dr >97.5:2.5	57
	PhCHO (0.5 equiv)	 (64) dr 85:15	59a

Table 8. *Continued*

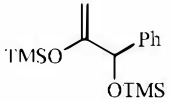
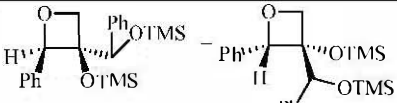
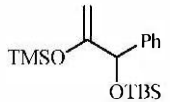
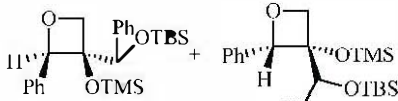
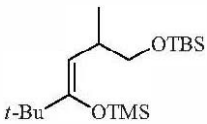
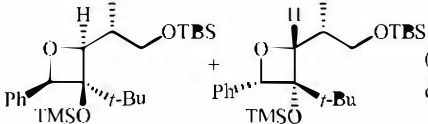
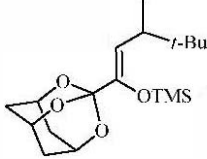
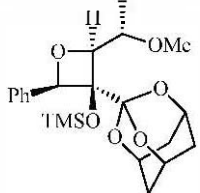
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (58) dr 51:49	59b
	PhCHO (0.5 equiv)		59b
		Solvent Temp dr	
		Hexane -25 (66) 51:49	
		Benzene 30 (60) 53:47	
	PhCHO (0.5 equiv)	 (59) dr 51:49	59a
	PhCHO (0.5 equiv)	 (52) dr 95:5	59a

Table 8. *Continued*

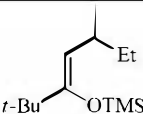
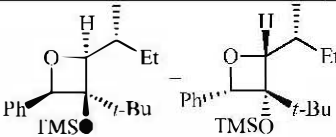
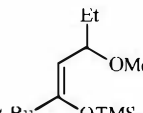
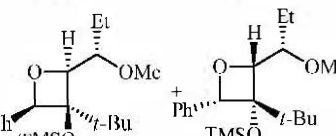
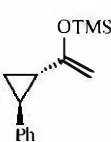
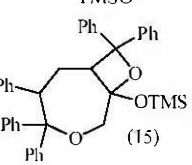
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (61) dr 61:39	58 59a
	PhCHO (0.5 equiv)	 (35) dr 80:20	59a
	Ph ₂ CO (1.2 equiv)	 (15)	294

Table 8. *Continued*

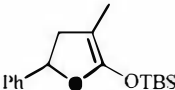
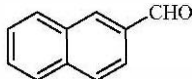
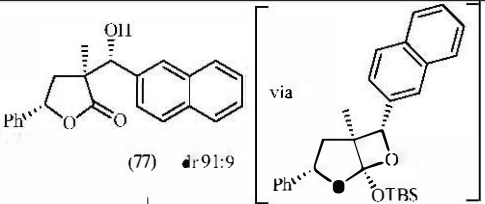
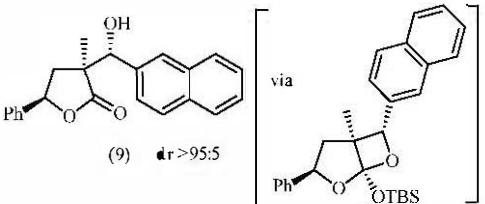
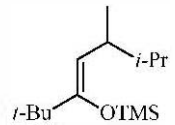
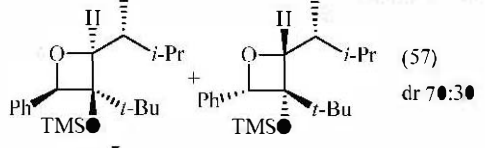
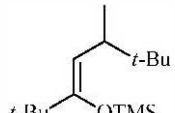
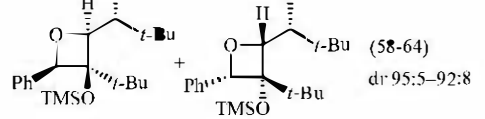
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 (77) dr 91:9	293
		 (9) dr >95:5	
	PhCHO (0.5 equiv)	 (57) dr 70:30	59a
	PhCHO (0.5 equiv)	 (58-64) dr 95:5–92:8	58 59a

Table 8. *Continued*

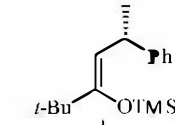
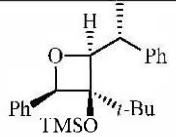
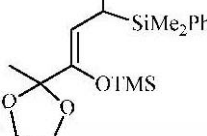
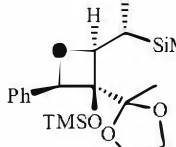
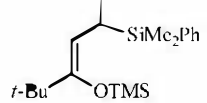
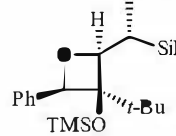
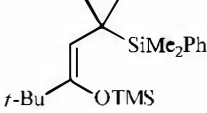
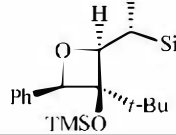
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (72-76) <i>dr</i> 69:31-71:29	59a
	PhCHO (0.5 equiv)	 (51) <i>dr</i> 83:17	59a
	PhCHO (0.5 equiv)	 (44) <i>dr</i> 95:5	58 59a
	PhCHO (0.5 equiv)	 (63) <i>dr</i> 62:38 (30*) <i>dr</i> 68-32 (65*)	56a

Table 9. Intermolecular reactions with electron-rich unsaturated compounds. H. Enamine derivatives.

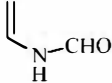
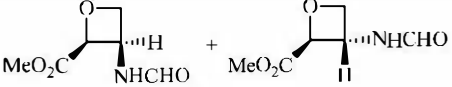
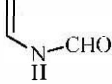
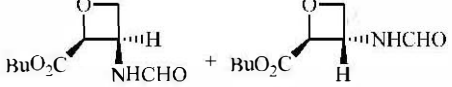
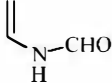
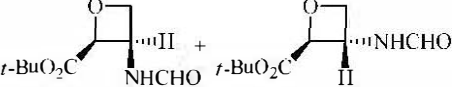
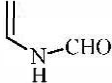
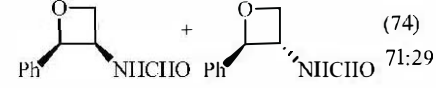
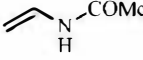
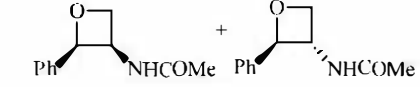
Substrate	Carbonyl compound	Product (yields %)	Ref.
	HCOCO ₂ Me (0.5 equiv)	 50:50 (37-45)	295
	HCOCO ₂ Bu (0.5 equiv)	 51:49 (37-46)	295
	HCOCO ₂ <i>t</i> -Bu (0.5 equiv)	 54:46 (37)	295
	PhCHO (0.5 equiv)	 (74) 71:29	64
	PhCHO (0.5 equiv)	 79:21 (58)	64

Table 9. *Continued*

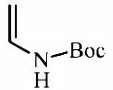
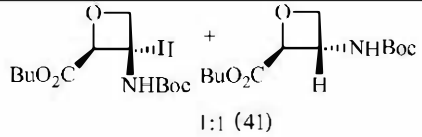
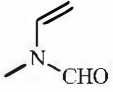
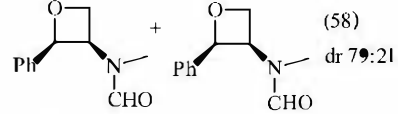
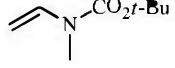
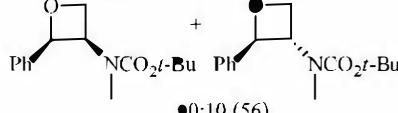
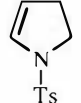
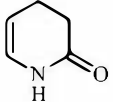
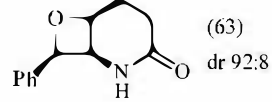
Substrate	Carbonyl compound	Product (yields %)	Ref.
	HCOCOC ₂ Bu (0.5 equiv)	 1:1 (41)	295
	PhCHO (0.5 equiv)	 (58) dr 79:21	65a
	PhCHO (0.5 equiv)	 90:10 (56)	64
	PhCHO (0.67 equiv)	No reaction	296
	PhCHO (0.67 equiv)	 (63) dr 92:8	65b

Table 9. *Continued*

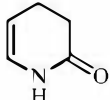
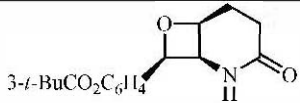
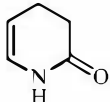
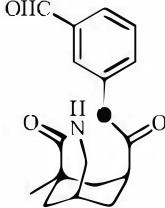
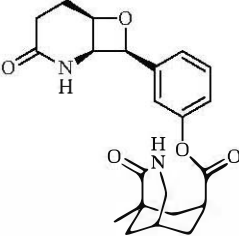
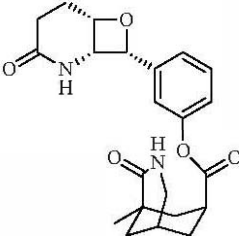
Substrate	Carbonyl compound	Product (yields %)	Ref.															
	3- <i>t</i> -BuCO ₂ C ₆ H ₄ CHO (0.5 equiv)	 (54) dr 88:12	65b															
		 + 	82															
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>65 (56)</td> <td>50:50</td> </tr> <tr> <td>MeCN</td> <td>30 (—)</td> <td>50:50</td> </tr> <tr> <td>Benzene</td> <td>30 (50)</td> <td>89:11</td> </tr> <tr> <td>Toluene</td> <td>-10 (56)</td> <td>95:5</td> </tr> </tbody> </table>	Solvent	Temp	dr	MeCN	65 (56)	50:50	MeCN	30 (—)	50:50	Benzene	30 (50)	89:11	Toluene	-10 (56)	95:5	
Solvent	Temp	dr																
MeCN	65 (56)	50:50																
MeCN	30 (—)	50:50																
Benzene	30 (50)	89:11																
Toluene	-10 (56)	95:5																

Table 9. *Continued*

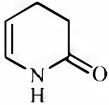
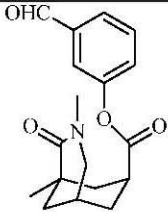
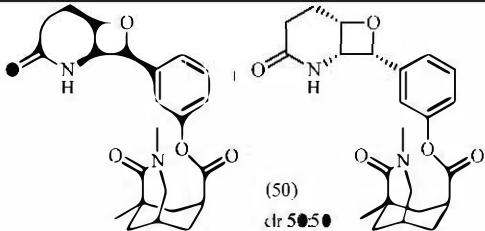
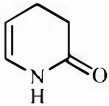
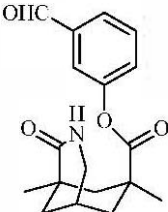
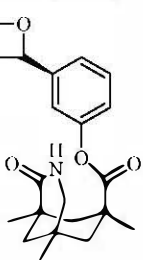
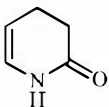
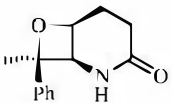
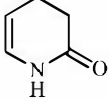
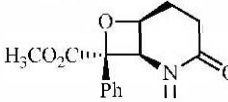
Substrate	Carbonyl compound	Product (yields %)	Ref.									
		 <p>(50) dr 5:5</p>	82									
	 <p>(0.5 equiv)</p>	<table border="1" data-bbox="807 586 1091 676"> <thead> <tr> <th data-bbox="807 586 895 609">Substrate</th> <th data-bbox="895 586 1091 609">dr</th> <th data-bbox="1091 586 1315 609">er</th> </tr> </thead> <tbody> <tr> <td data-bbox="807 620 895 642">rac</td> <td data-bbox="895 620 1091 642">(56)</td> <td data-bbox="1091 620 1315 642">>95:5</td> </tr> <tr> <td data-bbox="807 654 895 676">(+) (—)</td> <td data-bbox="895 654 1091 676">(—)</td> <td data-bbox="1091 654 1315 676">>97.5:2.5</td> </tr> </tbody> </table> 	Substrate	dr	er	rac	(56)	>95:5	(+) (—)	(—)	>97.5:2.5	65b
Substrate	dr	er										
rac	(56)	>95:5										
(+) (—)	(—)	>97.5:2.5										
	PhCOMe (0.5 equiv)	 <p>(51) dr 90:10</p>	65b									
	PhCOCO ₂ Me (0.5 equiv)	 <p>(52) dr 90:10</p>	65b									

Table 9. *Continued*

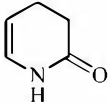
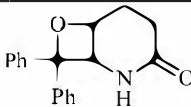
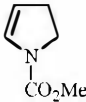
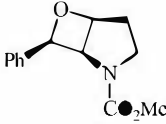
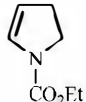
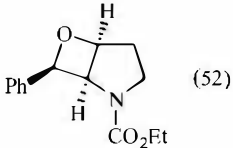
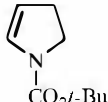
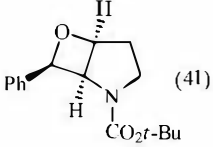
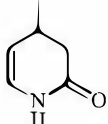
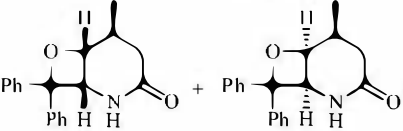
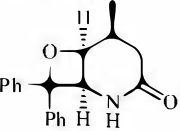
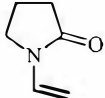
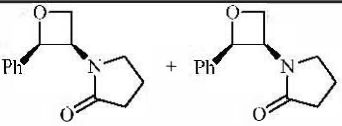
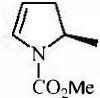
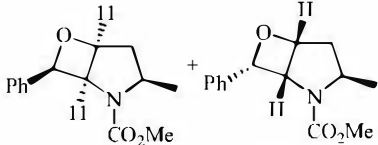
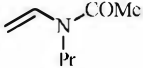
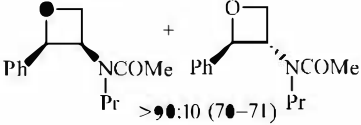
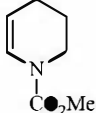
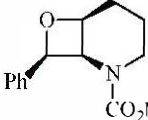
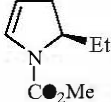
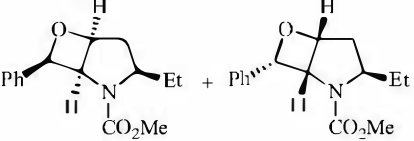
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph_2CO (0.5 equiv)	 (56)	65b
	PhCHO (0.67 equiv)	 (57)	65a 296
	PhCHO (0.67 equiv)	 (52)	296
	PhCHO (0.67 equiv)	 (41)	296
	Ph_2CO (0.5 equiv)	 +  (39) dr 55:45	65b

Table 9. *Continued*

Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.67 equiv)	 (82) dr 88:12	65a
	PhCHO (0.67 equiv)	 (57) 76:24	296
	PhCHO (0.67 equiv)	 >90:10 (70–71)	64 65a
	PhCHO (0.67 equiv)	 (17)	296
	PhCHO (0.67 equiv)	 (—)	296

71:29

Table 9. Continued

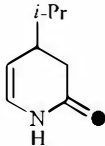
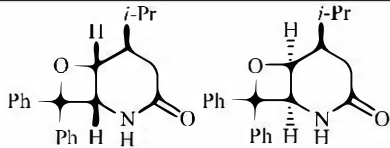
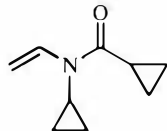
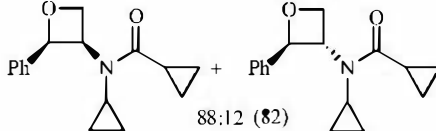
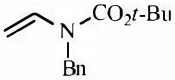
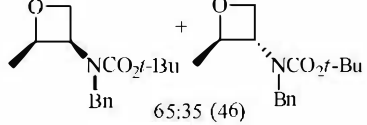
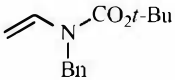
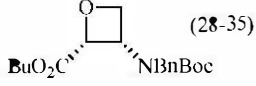
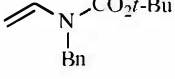
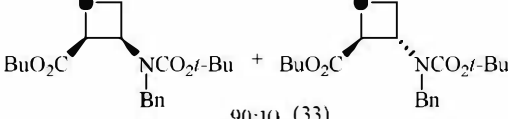
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (0.5 equiv)	 (31) dr 60:40	65b
	PhCHO (0.5 equiv)	 88:12 (82)	64
	MeCHO (0.67 equiv)	 65:35 (46)	64
	HCOCOC ₂ H ₅ (0.5 equiv)	 (28-35)	297
	BuO ₂ CCHO (0.67 equiv)	 90:10 (33)	64

Table 9. *Continued*

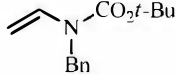
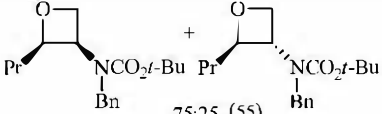
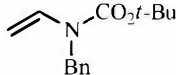
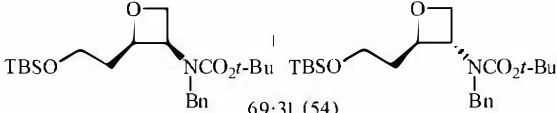
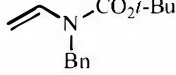
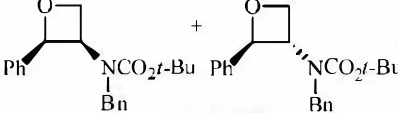
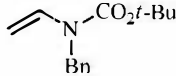
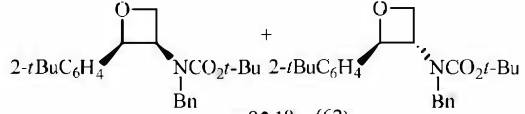
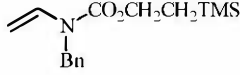
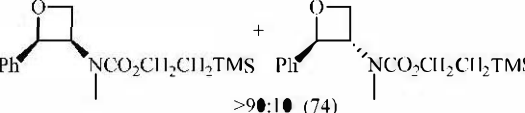
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PrCHO (0.67 equiv)	 75:25 (55)	64
	TBSOCH ₂ CH ₂ CHO (0.67 equiv)	 69:31 (54)	64
	PhCHO (0.5 equiv)	 87:13 (77)	64 65a 66
	2- <i>t</i> -BuC ₆ H ₄ CHO (0.5 equiv)	 >90:10 (62)	64
	PhCHO (0.5 equiv)	 >90:10 (74)	64

Table 9. *Continued*

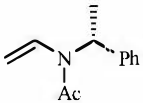
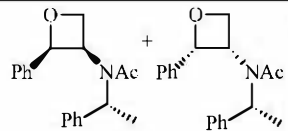
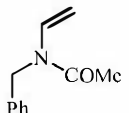
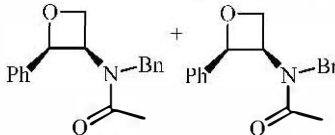
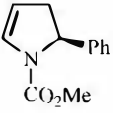
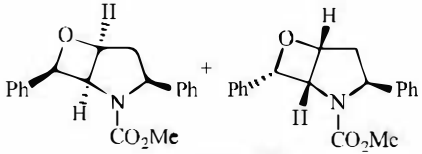
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (74) 2:1	67
	PhCHO (0.5 equiv)	 (73) dr 89:11	64 65a
	PhCHO (0.67 equiv)	 68:32 (63)	296

Table 9. *Continued*

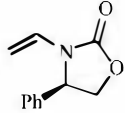
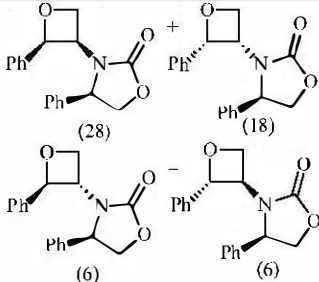
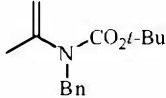
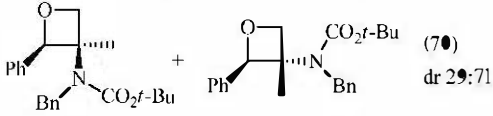
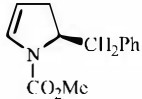
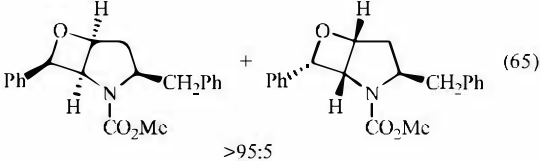
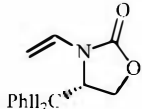
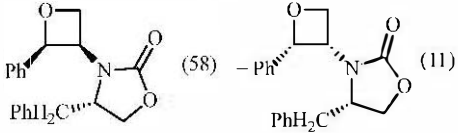
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)		67
	PhCHO (0.5 equiv)		66
	PhCHO (0.67 equiv)		296
	PhCHO (0.67 equiv)		67

Table 9. Continued

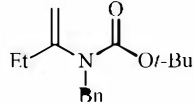
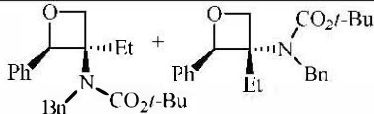
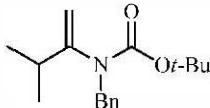
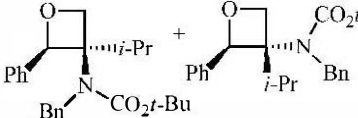
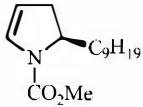
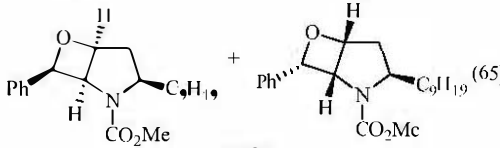
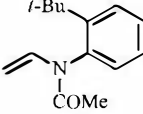
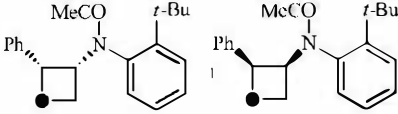
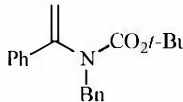
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (69) dr 34:66	66
	PhCHO (0.5 equiv)	 (71) dr 54:46	66
	PhCHO (0.67 equiv)	 (65) 75:25	296 298
	PhCHO	 (63) dr 81:19	90
	PhCHO (0.5 equiv)	No reaction	66

Table 9. *Continued*


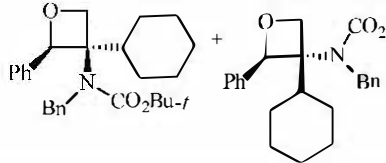
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)	 (46) dr 57:43	66

Table 10. Reactions with substrates bearing both electron-withdrawing and electron-donating groups.

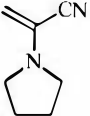
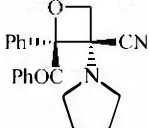
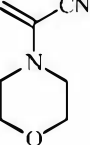
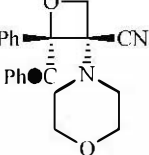
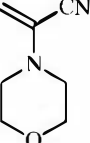
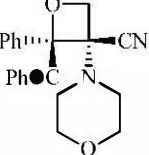
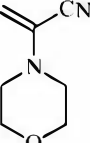
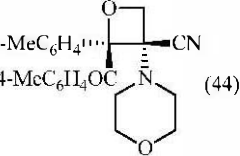
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCOPh (1 equiv)	 (29)	299
	PhCOCOPh (1 equiv)	 (30)	300
	PhCOCOPh (1 equiv)	 (53)	299
	(4-MeC ₆ H ₄ CO) ₂ (1 equiv)	 (44)	299

Table 10. *Continued*

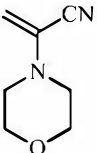
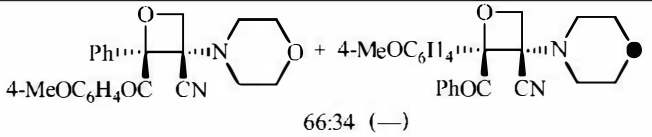
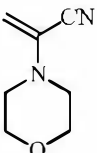
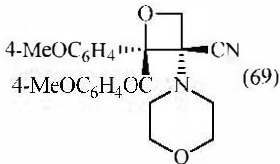
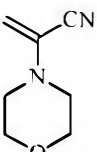
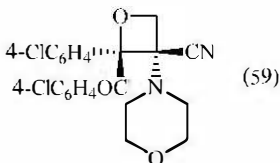
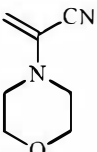
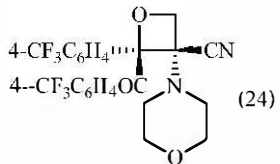
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCOC ₆ H ₄ OMe- 4 (1 equiv)	 66:34 (—)	299
	(4-MeOC ₆ H ₄ CO) ₂ (1 equiv)	 (69)	299
	(4-ClC ₆ H ₄ CO) ₂ (1 equiv)	 (59)	299
	(4-CF ₃ C ₆ H ₄ CO) ₂ (1 equiv)	 (24)	299

Table 10. *Continued*

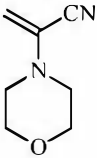
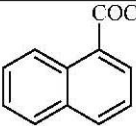
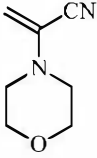
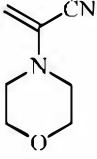
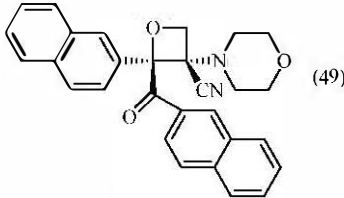
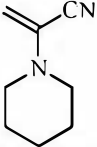
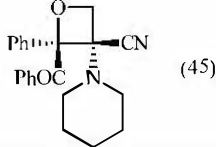
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 COCOPh (1 equiv)	No reaction	299
	(1-NaphthylCO) ₂ (1 equiv)	No reaction	299
	(2-NaphthylCO) ₂ (1 equiv)	 (49)	299
	PhCOCOPh (1 equiv)	 (45)	299

Table 10. *Continued*

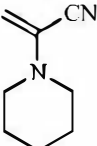
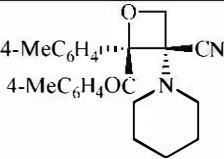
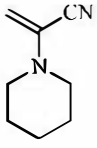
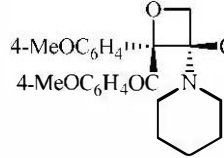
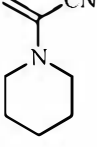
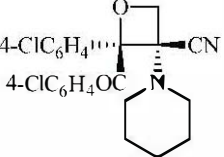
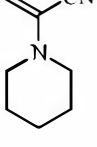
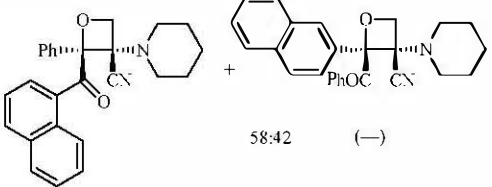
Substrate	Carbonyl compound	Product (yields %)	Ref.
	(4-MeC ₆ H ₄ CO) ₂ (1 equiv)	 (61)	299
	(4-MeOC ₆ H ₄ CO) ₂ (1 equiv)	 (69)	299
	(4-ClC ₆ H ₄ CO) ₂ (1 equiv)	 (63)	299
	PhCOCONaphthyl-2 (1 equiv)	 58:42 (—)	299

Table 10. *Continued*

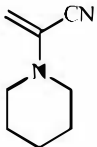
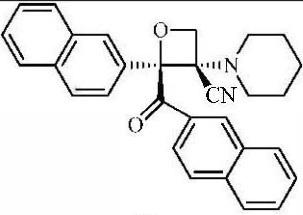
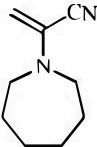
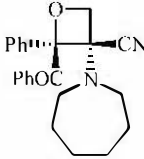
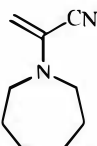
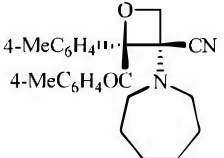
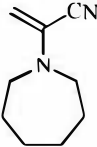
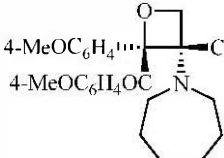
Substrate	Carbonyl compound	Product (yields %)	Ref.
	(2-NaphthylCO) ₂ (1 equiv)	 (75)	299
	PhCOCOPh (1 equiv)	 (63)	299
	(4-MeC ₆ H ₄ CO) ₂ (1 equiv)	 (68)	299
	(4-MeOC ₆ H ₄ CO) ₂ (1 equiv)	 (90)	299

Table 10. *Continued*

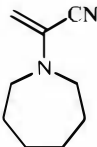
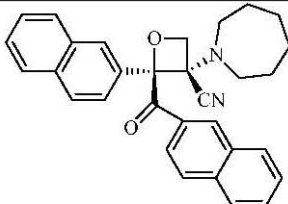
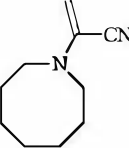
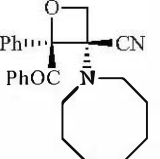
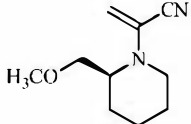
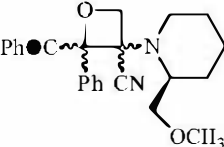
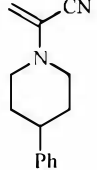
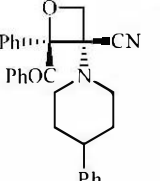
Substrate	Carbonyl compound	Product (yields %)	Ref.
	(2-NaphthylCO) ₂ (1 equiv)	 (55)	299
	PhCOCOPh (1 equiv)	 (9)	299
	PhCOCOPh	 (not isolated)	301
	PhCOCOPh (1 equiv)	 (46)	299

Table 11. Intermolecular reactions with five-membered heterocyclic compounds.


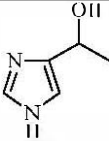

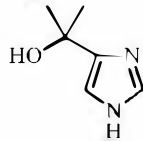
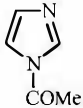
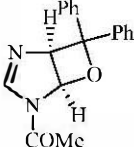
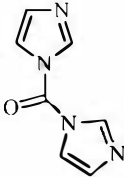
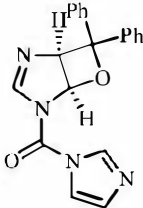
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCHO	 (64–88)	302
	Me ₂ CO	 (9.1)	303
	Ph ₂ CO	 (50)	304
	Ph ₂ CO (3 equiv)	 (51)	304 305

Table 11. *Continued*

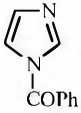
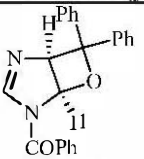

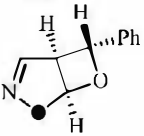


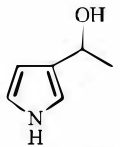

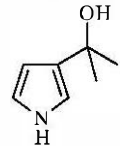
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (2 equiv)	 (34-50)	304 305
	PhCHO (1 equiv)	 (0-5)	306
	Ph ₂ CO	No reaction	305
	MeCHO	 (28)	302
	Me ₂ CO	 (6)	302

Table 11. *Continued*


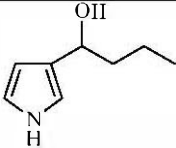

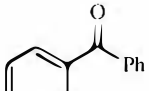
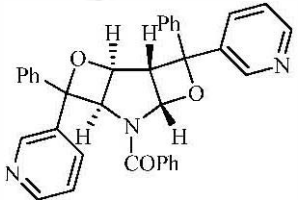

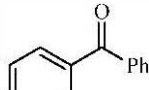
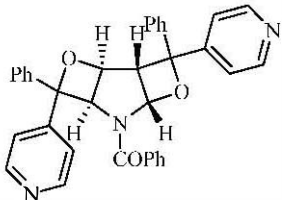

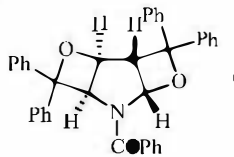
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PrCHO	 (24)	302
	 (2.82 equiv)	 (20)	307
	 (2.82 equiv)	 (30)	307
	Ph ₂ CO (2.82 equiv)	 (12)	307 308

Table 11. *Continued*


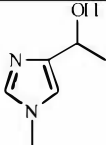
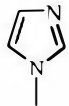
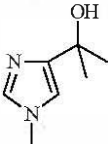

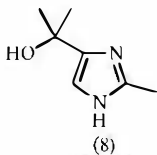
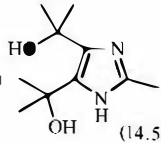
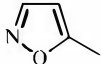
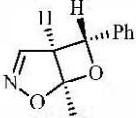

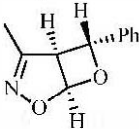
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCHO	 (64–88)	302
	Me ₂ CO	 (64–88)	302
	Me ₂ CO	 (8)  (14.5)	303
	PhCHO (1 equiv)	 (0–15)	306
	PhCHO (1 equiv)	 (0–10)	306

Table 11. *Continued*


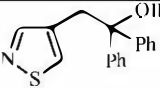

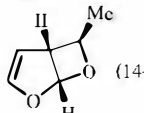

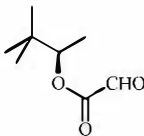
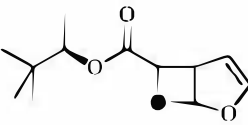

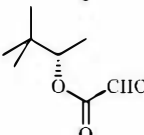
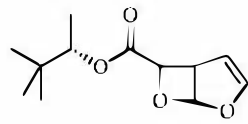

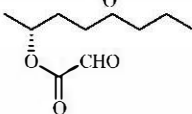
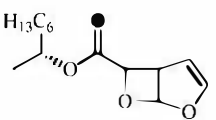

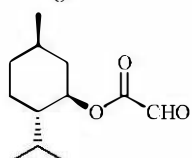
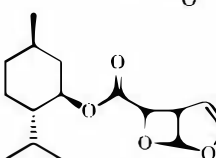
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (0.5 equiv)	 (33)	305
	MeCHO	 (14–72) dr 97:3	72 73b
		 (67)	83a
		 (66)	83a
		 (71)	83a
		 (80)	83a

Table 11. *Continued*


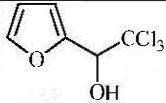

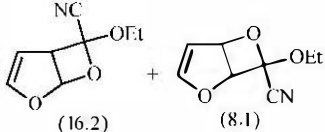

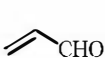
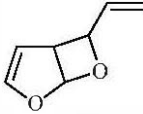

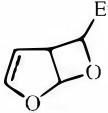



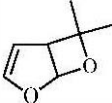
Substrate	Carbonyl compound	Product (yields %)	Ref.
	CCl ₃ CHO (0.1 equiv)	 (30)	309
	NCCO ₂ Et (0.3 equiv)	 (16.2) (8.1)	199
	 CHO	 (11)	73b
	EtCHO (0.06 equiv)	 (69–80)	73a 73b 310
	EtCHO (0.06 equiv, MeSO ₃ H)	 (39)	310
	Me ₂ CO	 (1.7)	73b

Table 11. *Continued*


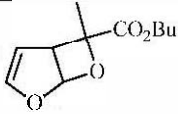

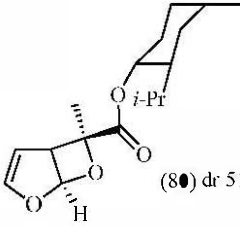

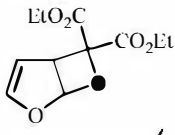

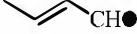
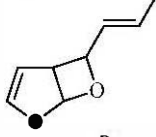

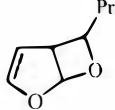
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCOCO ₂ Bu	 (77.3)	73f
	MeOCCO ₂ <i>i</i> -Pr	 (80) dr 51.5:48.5	83b
	EtO ₂ CCOCO ₂ Et	 (30)	73f
		 (11)	73b
	PrCHO	 (27)	73b

Table 11. *Continued*


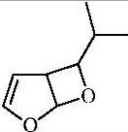

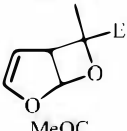

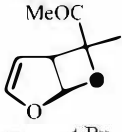

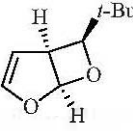


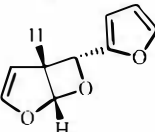


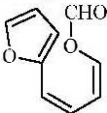
Substrate	Carbonyl compound	Product (yields %)	Ref.
	<i>i</i> -PrCHO	 (18)	73b
	EtCOMe	 (1.1)	73b
	MeCOCOMe (1 equiv)	 (—)	105d 146
	<i>t</i> -BuCHO (0.1 equiv)	 (—) dr > 250:1	68d
	 -CHO (0.07 equiv)	 (16)	73b 311
	 -Cl	 (76)	311 312

Table 11. *Continued*



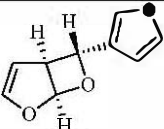

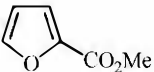
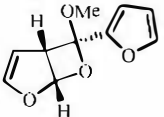

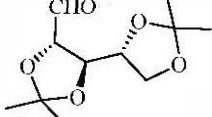
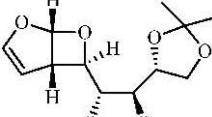

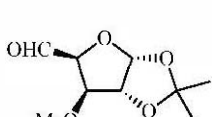
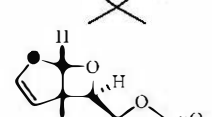

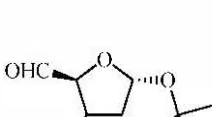
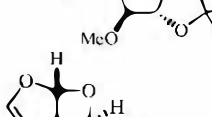
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 (67)	312
		 (→)	311
		 (18.6)	313
		 (18.7)	313
		 (23.8)	313

Table 11. *Continued*


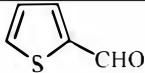
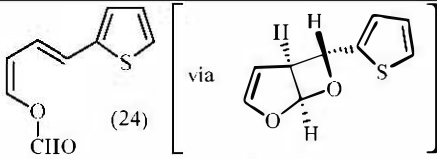

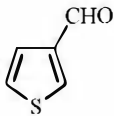
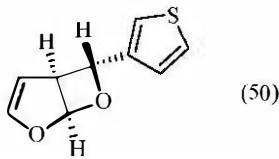

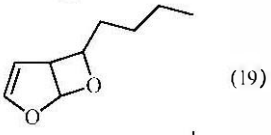

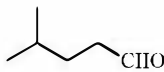
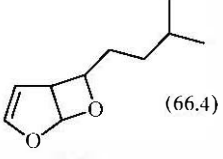

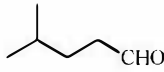
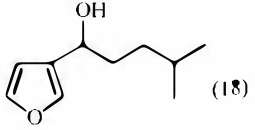
Substrate	Carbonyl compound	Product (yields %)	Ref.
			312
			312
	C_3H_7CHO		73b
			73f
			310

Table 11. Continued


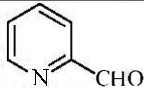
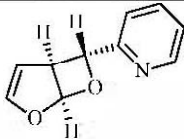

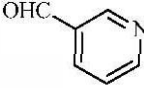
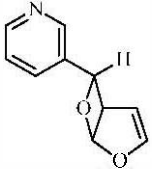

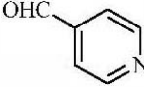
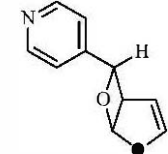

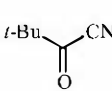
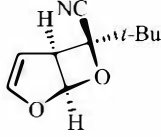

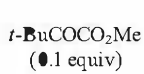
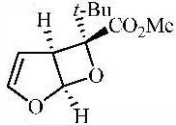
Substrate	Carbonyl compound	Product (yields %)	Ref.						
		 (36)	312						
		 (13–78)	74 312						
		 (27)	74						
		 <table border="1" data-bbox="1029 711 1204 812"> <thead> <tr> <th>Temp</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>(86) 8.9:1</td> </tr> <tr> <td>-55</td> <td>(89) 9.3:1</td> </tr> </tbody> </table>	Temp	dr	rt	(86) 8.9:1	-55	(89) 9.3:1	314
Temp	dr								
rt	(86) 8.9:1								
-55	(89) 9.3:1								
	 (0.1 equiv)	 (—) dr >49:1	68d						

Table 11. *Continued*


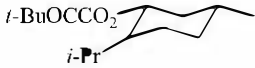
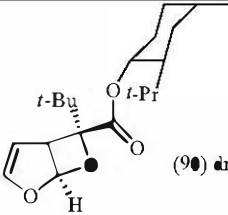

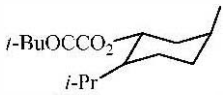
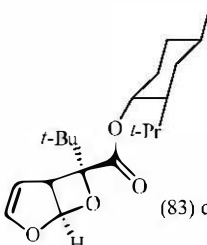

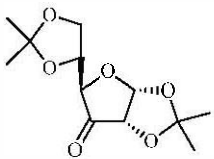
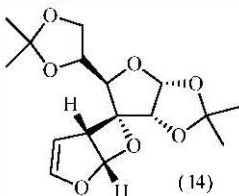
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 <p>(90) dr 65.5:34.5</p>	83b
		 <p>(83) dr 79:21</p>	83b
		 <p>(14)</p>	313

Table 11. Continued


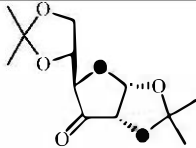
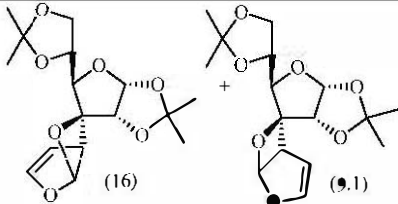

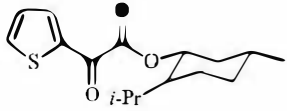
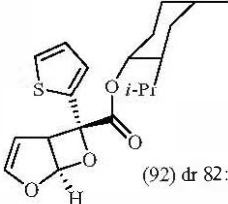

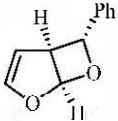

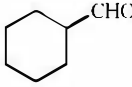
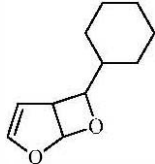
Substrate	Carbonyl compound	Product (yields %)	Ref.
			315
			83b
	<p>PhCHO (0.1 equiv)</p>	 <p>(56–88) dr 212:1</p>	68b 68d 73a 311 316
		 <p>(27)</p>	73b

Table 11. *Continued*


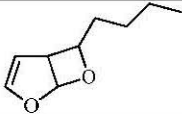

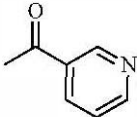
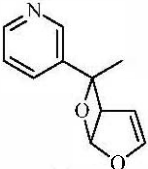

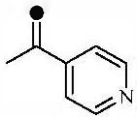
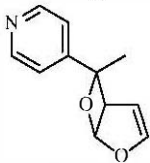

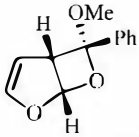

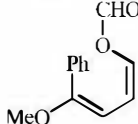
Substrate	Carbonyl compound	Product (yields %)	Ref.
	$C_6H_{13}CHO$	 (19)	73b
		 (25)	74
		 (72)	74
	$PhCO_2Me$ (0.1 equiv, 44h)	 (37–62)	68d 311
	$PhCO_2Me$ (0.1 equiv, 72–100h)	 (90)	311

Table 11. *Continued*



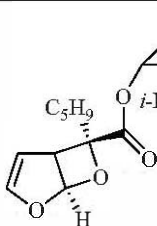

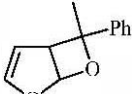

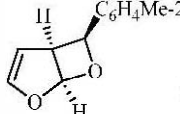

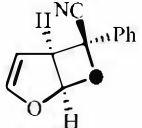
Substrate	Carbonyl compound	Product (yields %)	Ref.
	$C_5H_9OCCO_2$ <i>i</i> -Pr 	 (65) <i>dr</i> 73.5:26.5	83b
	PhCOMe	 (0.4)	73b
	2-MeC ₆ H ₄ CHO	 (97)	68b
	Ph C=O CN	 Temp <i>dr</i> rt (77) 3.7:1 55 (95) 5.3:1	314

Table 11. *Continued*


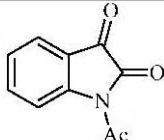
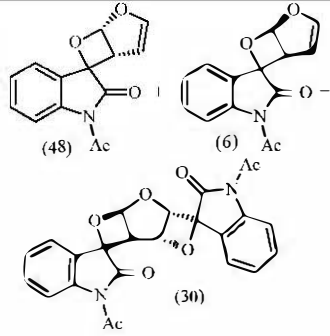

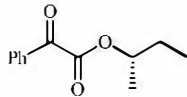
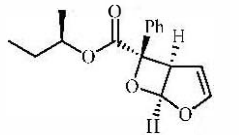

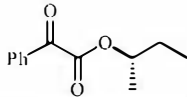
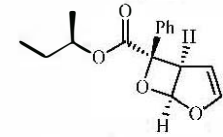

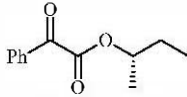
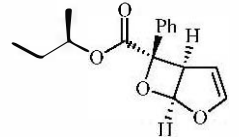
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.1 equiv)	 (48) Ac (6) Ac (30)	52
		 (66) dr 57.5:42.5	84
	 (NaY zeolite, ephedrine)	 (37) dr 50:50	84
	 (NaY zeolite)	 (30) dr 68.5:31.5	84

Table 11. *Continued*


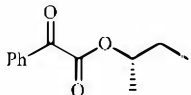
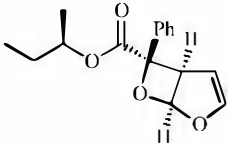

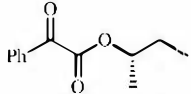
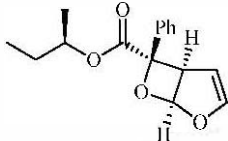

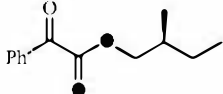
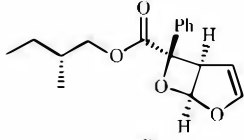

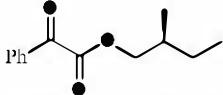
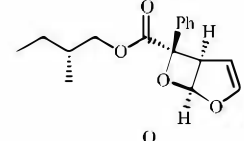

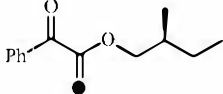
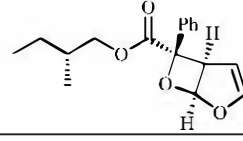
Substrate	Carbonyl compound	Product (yields %)		Ref.															
		zeolite	dr																
			<table border="1"> <tr> <td>NaY</td> <td>(30)</td> <td>68.5:31.5</td> </tr> <tr> <td>LiY</td> <td>(35)</td> <td>65:35</td> </tr> <tr> <td>KY</td> <td>(39)</td> <td>53:47</td> </tr> <tr> <td>CsY</td> <td>(30)</td> <td>53:47</td> </tr> <tr> <td>RbY</td> <td>(31)</td> <td>52:48</td> </tr> </table>	NaY	(30)	68.5:31.5	LiY	(35)	65:35	KY	(39)	53:47	CsY	(30)	53:47	RbY	(31)	52:48	33
NaY	(30)	68.5:31.5																	
LiY	(35)	65:35																	
KY	(39)	53:47																	
CsY	(30)	53:47																	
RbY	(31)	52:48																	
	 (β -cyclodextrin)		(33) dr 54:46	33															
			(66) dr 50:50	34															
	 (NaY zeolite, ephedrine)		(16) dr 50:50	34															
	 (NaY zeolite)		(58) dr 59:41	34															

Table 11. *Continued*


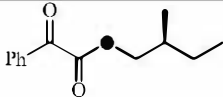
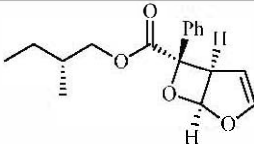

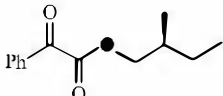
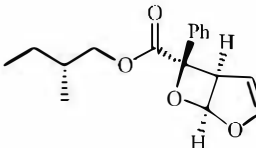

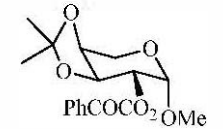
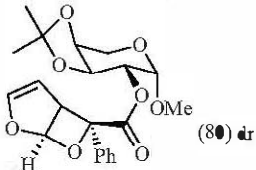

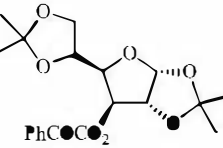
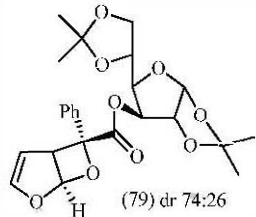
Substrate	Carbonyl compound	Product (yields %)	Ref.												
		 <table border="1" data-bbox="1053 218 1276 408"> <thead> <tr> <th>zeolite</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>NaY (58)</td> <td>59:41</td> </tr> <tr> <td>LiY (63)</td> <td>58.5:41.5</td> </tr> <tr> <td>KY (49)</td> <td>61:39</td> </tr> <tr> <td>CsY (41)</td> <td>60:40</td> </tr> <tr> <td>RbY (40)</td> <td>59.5:40.5</td> </tr> </tbody> </table>	zeolite	dr	NaY (58)	59:41	LiY (63)	58.5:41.5	KY (49)	61:39	CsY (41)	60:40	RbY (40)	59.5:40.5	88
zeolite	dr														
NaY (58)	59:41														
LiY (63)	58.5:41.5														
KY (49)	61:39														
CsY (41)	60:40														
RbY (40)	59.5:40.5														
	 <p>(β-cyclodextrin)</p>	 <p>(24) dr 50:50</p>	88												
		 <p>(80) dr 71:29</p>	85												
		 <p>(79) dr 74:26</p>	85												

Table 11. *Continued*


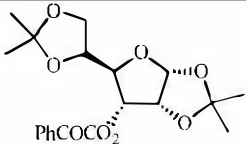
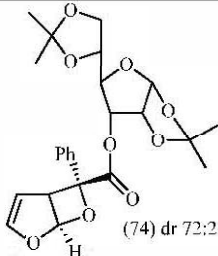


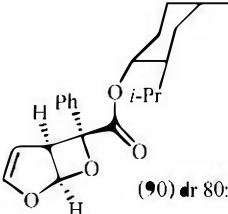

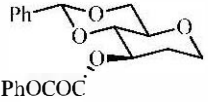
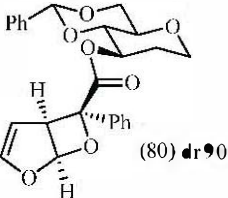
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 <p>(74) dr 72:28</p>	85
		 <p>(90) dr 80:20</p>	83b
		 <p>(80) dr 90:10</p>	85

Table 11. *Continued*


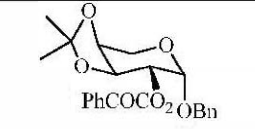
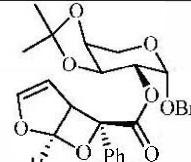

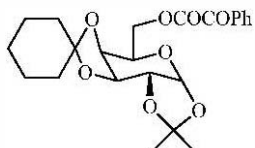
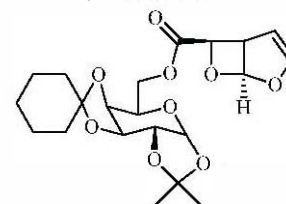

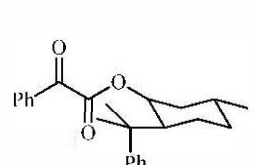
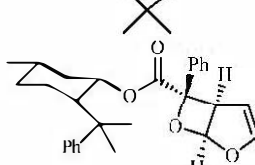

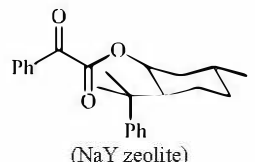
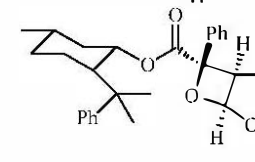
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 (78) dr 71.5:28.5	85
		 (84) dr 53:47	85
		 (88) dr 97.5:2.5	84
	 (NaY zeolite)	 (90) dr 99:1	84

Table 11. *Continued*


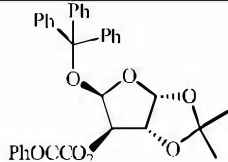
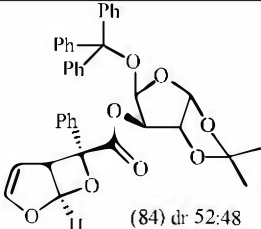

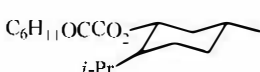
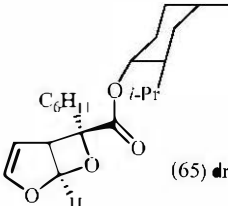

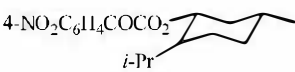
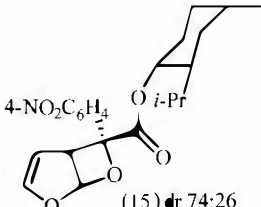
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 <p>(84) dr 52:48</p>	84
		 <p>(65) dr 74:26</p>	83b
		 <p>(15) dr 74:26</p>	83b

Table 11. *Continued*



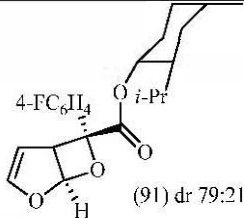


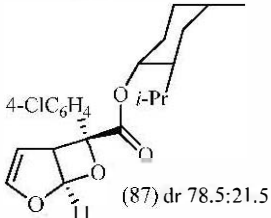

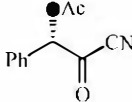
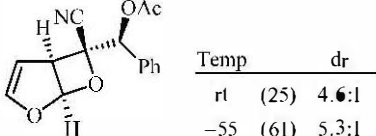

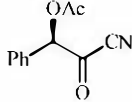
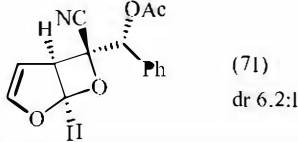
Substrate	Carbonyl compound	Product (yields %)	Ref.
	4-FC ₆ H ₄ COCO ₂ 	 (91) dr 79:21	83b
	4-ClC ₆ H ₄ COCO ₂ 	 (87) dr 78.5:21.5	83b
		 Temp dr rt (25) 4.6:1 -55 (61) 5.3:1	314
		 (71) dr 6.2:1	314

Table 11. *Continued*


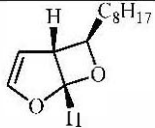


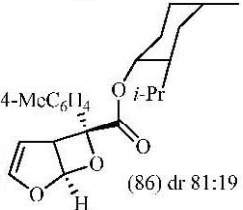


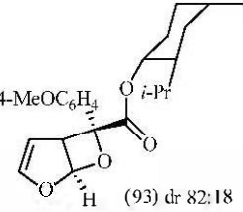
Substrate	Carbonyl compound	Product (yields %)	Ref.
	$C_8H_{17}CHO$	 (100)	317
	$4-MeC_6H_4COCO_2$  <i>i</i> -Pr	 (86) dr 81:19	83b
	$4-MeOC_6H_4COCO_2$  <i>i</i> -Pr	 (93) dr 82:18	83b

Table 11. *Continued*


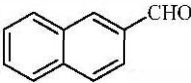
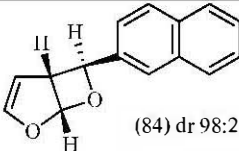

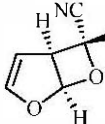

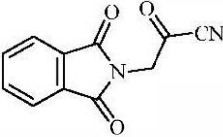
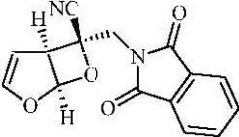

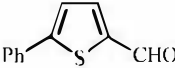
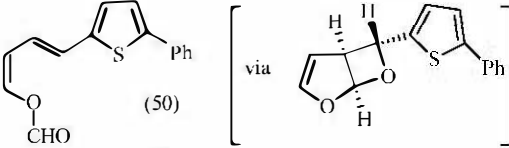
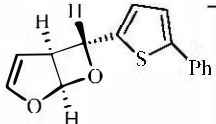

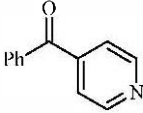
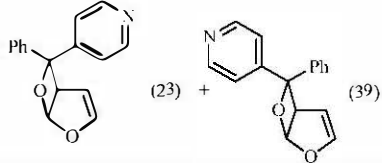
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 (84) dr 98:2	72
	2,4,6-Me ₃ C ₆ H ₂ COCN	 C ₆ H ₂ Me ₃ -2,4,6 (89) dr 16:1	68d 314
		 (30) dr 3.5:1	314
		 (50) [via 	312
		 (23) + (39)	74

Table 11. *Continued*



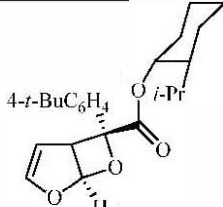

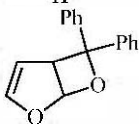

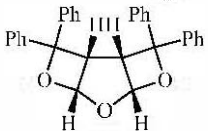
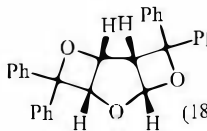

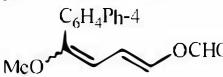
Substrate	Carbonyl compound	Product (yields %)	Ref.
	$4\text{-}t\text{-BuC}_6\text{H}_4\text{COCO}_2$ 	 <p>(83) dr 81:19</p>	83b
	Ph ₂ CO	 <p>(—)</p>	318
	Ph ₂ CO (1 equiv)	 <p>(26.7-29)</p>  <p>(18.2)</p>	73d 252 319 320
	4-PhC ₆ H ₄ CO ₂ Me	 <p>(36)</p>	311

Table 11. *Continued*


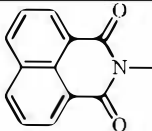
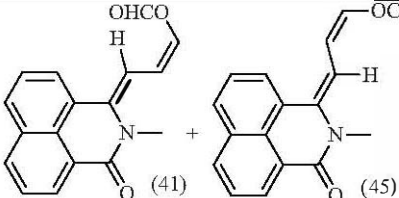
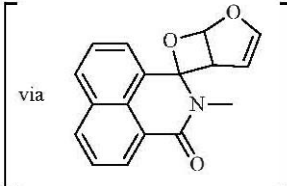

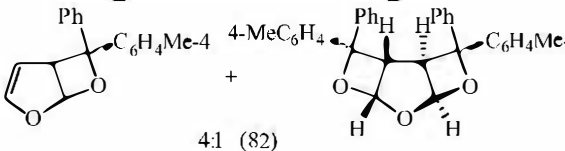

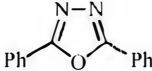
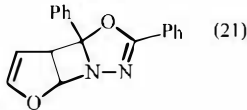
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 <p>(41) + (45)</p> <p>via</p> 	113c
	4-MeC ₆ H ₄ COPh (10 equiv)	 <p>4:1 (82)</p>	309
	 (0.01 equiv)	 <p>(21)</p>	321

Table 11. *Continued*


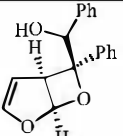

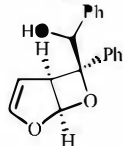

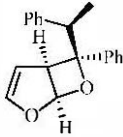

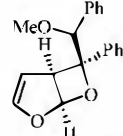

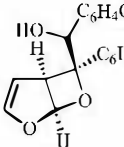
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCHOHPh	 (56) dr 100:0	322
	PhCOCHOHPh (NaY zeolite, ephedrine)	 (20) dr 100:0	322
	PhCOCHMePh	 (43) dr >99:1	323
	PhCOCHOMePh	 (54) dr 86:14	322
	4-Me-C ₆ H ₄ -C(=O)-CH(OH)-C ₆ H ₄ -Me	 (72) dr 100:0	322

Table 11. *Continued*


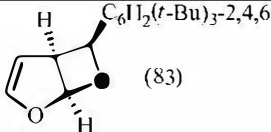

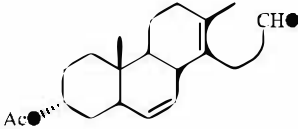
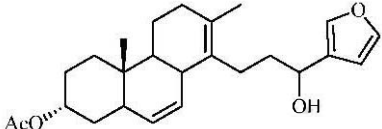
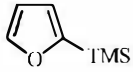
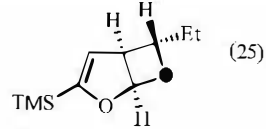
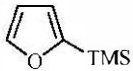
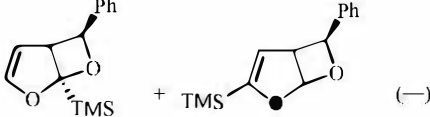
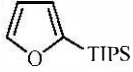
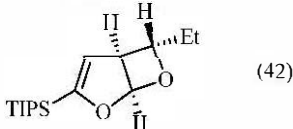
Substrate	Carbonyl compound	Product (yields %)	Ref.
	2,4,6-(<i>t</i> -Bu) ₃ C ₆ H ₂ CHO	 (83)	68b
		 (—)	315
	EtCHO (0.56 equiv)	 (25)	75
	PhCHO (0.56 equiv)	 (—)	75 77
	PhCHO (0.56 equiv)	 (42)	75

Table 11. *Continued*

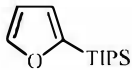
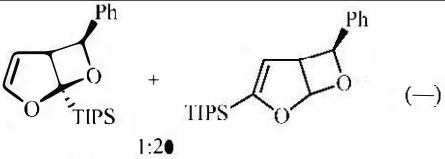
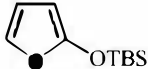
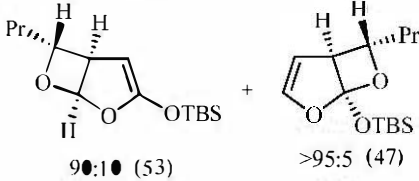
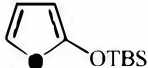
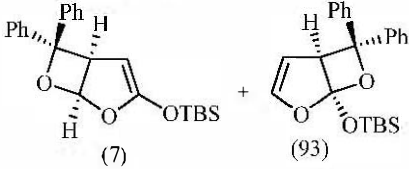
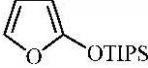
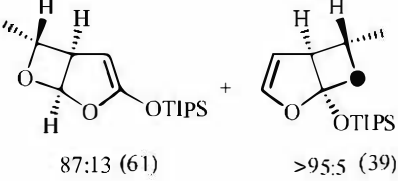
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.56 equiv)	 1:20	75 77
	PrCHO (0.5 equiv)	 90:10 (53) >95:5 (47)	76
	Ph ₂ CO (0.5 equiv)	 (7) (93)	76
	MeCHO (0.5 equiv)	 87:13 (61) >95:5 (39)	76

Table 11. *Continued*

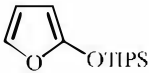
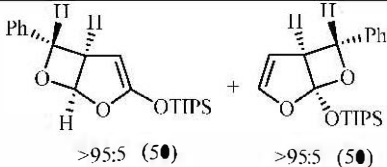
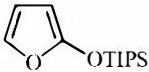
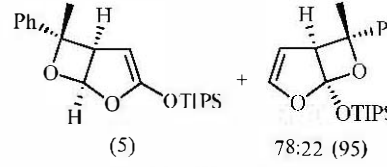
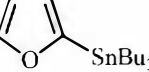
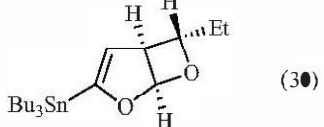
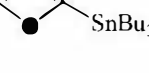
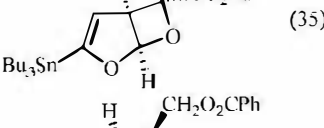


Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.5 equiv)		76
	PhCOMe (0.5 equiv)		76
	EtCHO (0.56 equiv)		75
	BuO ₂ CCHO (0.56 equiv)		75
	PhCO ₂ CH ₂ CHO (0.56 equiv)		316

Table 11. *Continued*

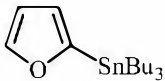
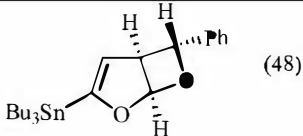


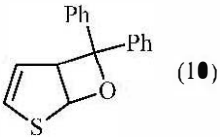

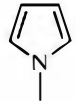
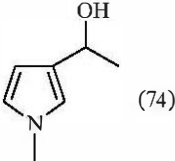
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.56 equiv)	 (48)	75
	Ph ₂ CO (1 equiv)	No reaction	324
	Ph ₂ CO (1 equiv, BF ₃)	 (10)	324
	Ph ₂ CO (1 equiv)	No reaction	325
	MeCHO (1 equiv)	 (74)	302

Table 11. *Continued*

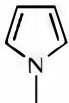
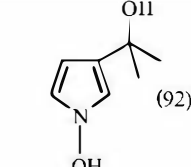
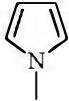
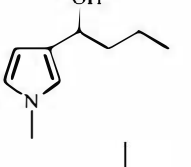
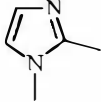
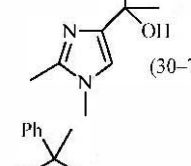
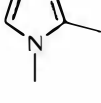
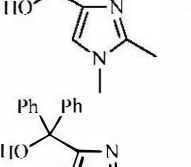
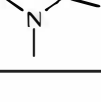
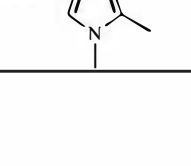
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Me ₂ CO (1 equiv)	 (92)	302
	PrCHO (1 equiv)	 (50)	302
	Me ₂ CO	 (30–70)	303 305
	PhCOMe (1.23 equiv)	 (1.2)	303
	Ph ₂ CO (1.04 equiv)	 (9.7)	303

Table 11. *Continued*

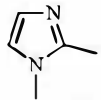
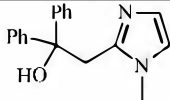
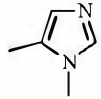
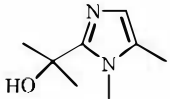
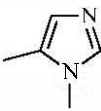
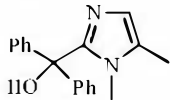
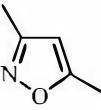
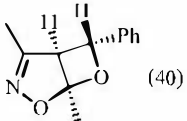
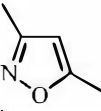
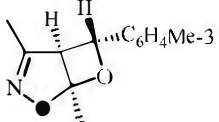
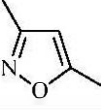
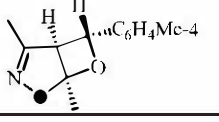
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (0.027 equiv)	 (4)	305
	Me ₂ CO	 (30)	304
	Ph ₂ CO	 (4)	304
	PhCHO (1 equiv)	 (40)	306
	3-MeC ₆ H ₄ CHO (1 equiv)	 (18)	306
	4-MeC ₆ H ₄ CHO (1 equiv)	 (18)	306

Table 11. *Continued*

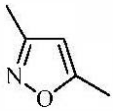
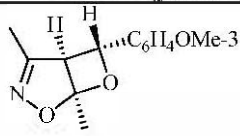
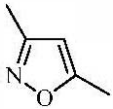
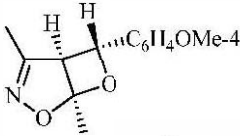
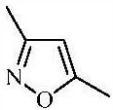
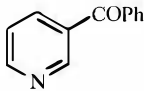
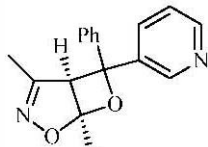
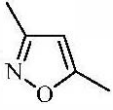
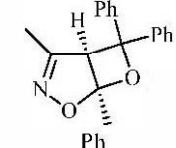
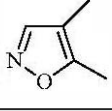
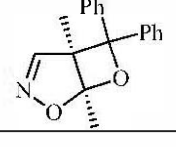
Substrate	Carbonyl compound	Product (yields %)	Ref.
	3-MeOC ₆ H ₄ CHO (1 equiv)	 C ₆ H ₄ OMe-3 (0)	306
	4-MeOC ₆ H ₄ CHO (1 equiv)	 C ₆ H ₄ OMe-4 (25)	306
	 COPh (0.03 equiv)	 Ph (24)	305
	Ph ₂ CO (0.03 equiv)	 Ph (40)	305
	Ph ₂ CO (0.03 equiv)	 Ph (65)	305

Table 11. *Continued*

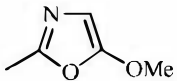
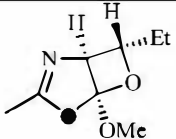
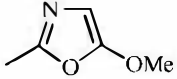
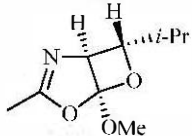
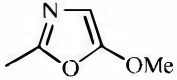
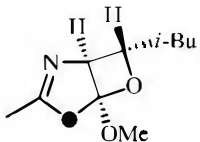
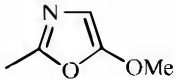
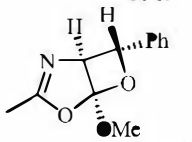
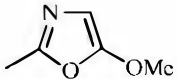
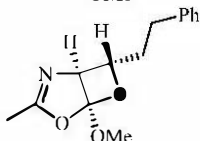
Substrate	Carbonyl compound	Product (yields %)	Ref.
	EtCHO (1.43 equiv)	 (90) dr >98:2	255 326
	<i>i</i> -PrCHO (1.43 equiv)	 (86) >98:2	255 326
	<i>t</i> -BuCHO (1.43 equiv)	 (88) dr >98:2	255 326
	PhCHO (1.43 equiv)	 (87) dr >98:2	255 326
	PhCH ₂ CH ₂ CHO (1.43 equiv)	 (87) dr >98:2	255 326

Table 11. *Continued*

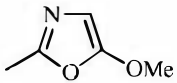
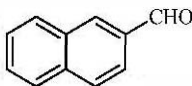
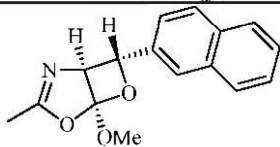
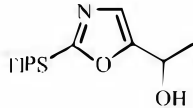
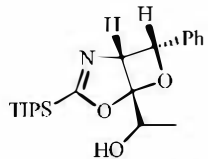
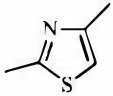
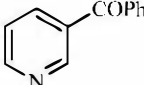
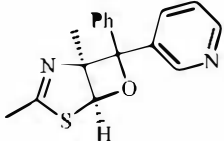
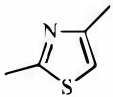
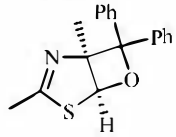
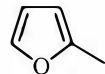
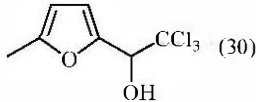
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (1.43 equiv)	 (85) dr >98:2	255 326
	PhCHO (1.5 equiv)	 (64) dr 80:20	327
	 (0.03 equiv)	 (40)	305
	Ph ₂ CO (0.03 equiv)	 (25)	305
	CCl ₃ CHO (1 equiv)	 (30)	309

Table 11. *Continued*

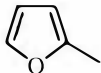
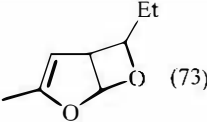
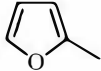
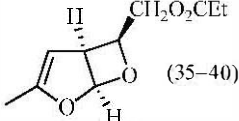
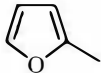
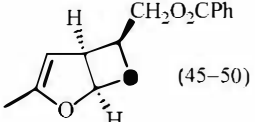
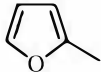
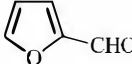
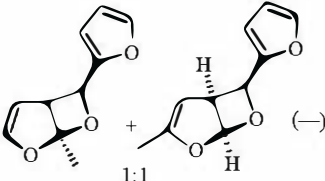
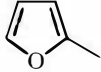
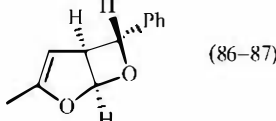
Substrate	Carbonyl compound	Product (yields %)	Ref.
	EtCHO (0.26 equiv)	 (73)	73•
	EtCO ₂ CH ₂ CHO	 (35–40)	316
	PhCO ₂ CH ₂ CHO	 (45–50)	316
	 (0.32 equiv)	 (—)	77
	PhCHO	 (86–87)	53 73•

Table 11. *Continued*

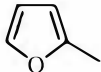
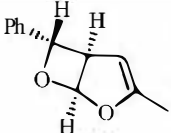
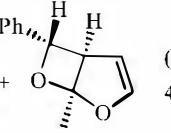
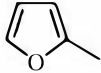
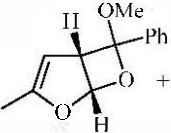
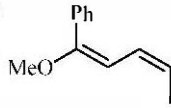
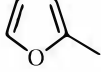
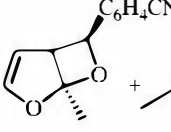
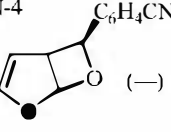
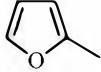
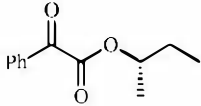
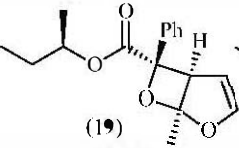
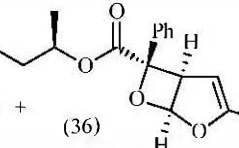
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (0.1 equiv)	 +  (95) 45:55–51:49	77 328
	PhCO ₂ Me (1.64 equiv)	 +  (—)	311
	4-CNC ₆ H ₄ CHO (0.32 equiv)	 +  (—) 1:2	77
		 (19) dr 97:3 +  (36) dr 50:50	84

Table 11. *Continued*

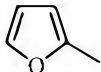
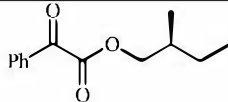
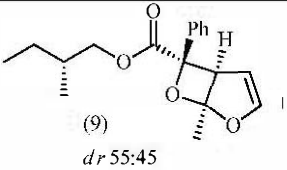
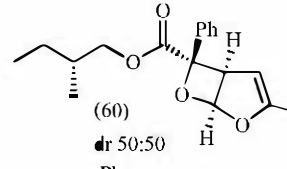
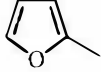
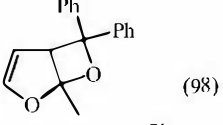
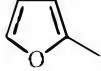
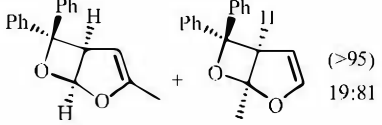
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 <p>(9) dr 55:45</p>  <p>(60) dr 50:50</p>	84
	Ph ₂ CO	 <p>(98)</p>	73c
	Ph ₂ CO (0.1 equiv)	 <p>(>95) 19:81</p>	328

Table 11. *Continued*

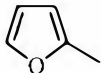
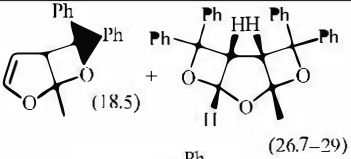
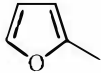
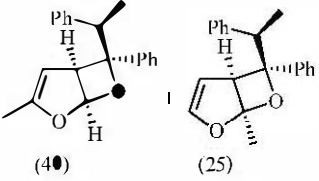
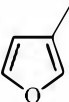
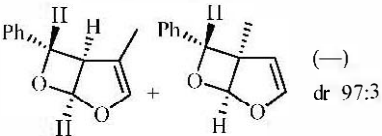

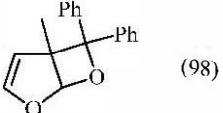
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph_2CO (1 equiv)	 (18.5) + (26.7-29)	252 319
	PhCOCHMePh	 (40) + (25) dr > 99:1 dr > 99:1	323
	PhCHO (0.1 equiv)	 (II) + (I) (—) dr 97:3	328
	Ph_2CO	 (98)	73c

Table 11. *Continued*

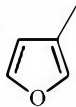
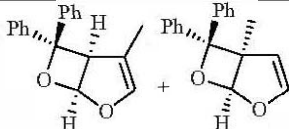
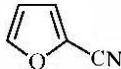
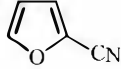
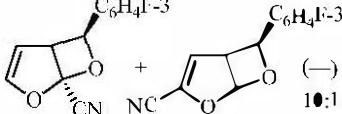

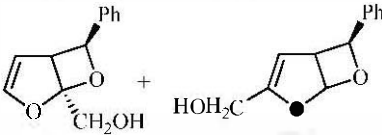
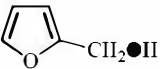
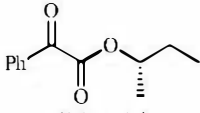
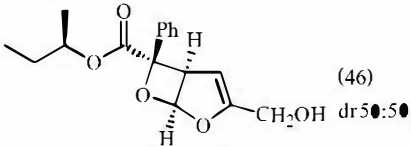
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph_2CO (0.1 equiv)	 (-) 17:83	328
	CCl_3CHO	No reaction	309
	$3\text{-FC}_6\text{H}_4\text{CHO}$ (0.3 equiv)	 (-) 10:1	77
	PhCHO (1.5 equiv)	 (50) (26)	77 94
	 (0.2 equiv)	 (46) dr 50:50	84

Table 11. *Continued*

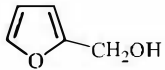
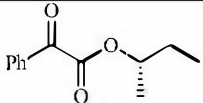
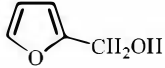
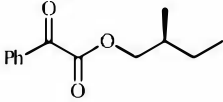
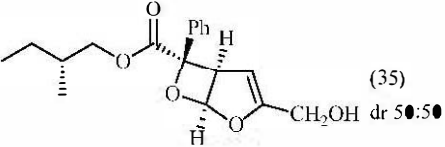
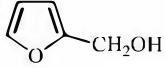
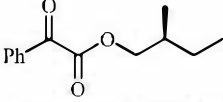
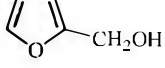
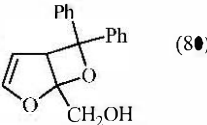
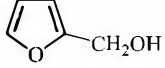
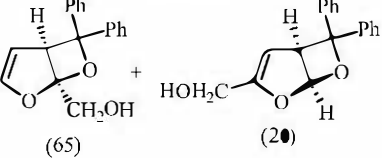
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.2 equiv, NaY zeolite)	No reaction	84
	 (0.2 equiv)	 (35) dr 50:50	84
	 (0.33 equiv, NaY zeolite)	No reaction	84
	Ph ₂ CO	 (80)	73c
	Ph ₂ CO (1.5 equiv)	 (65) + (20)	94

Table 11. *Continued*

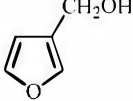
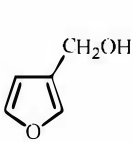
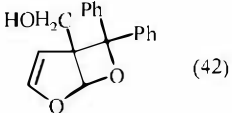
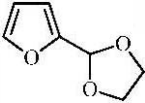
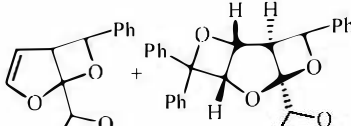

Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (1.5 equiv)	No reaction	101
	Ph ₂ CO (1.5 equiv)	 (42)	101
	Ph ₂ CO (1 equiv)		309
	CCl ₃ CHO	No reaction	309

Table 11. *Continued*

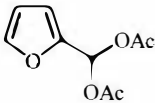
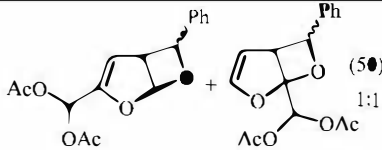
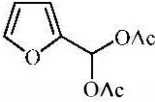
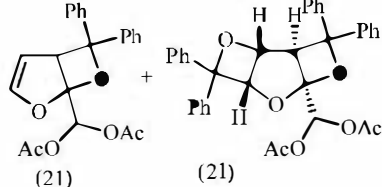
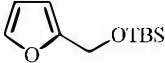
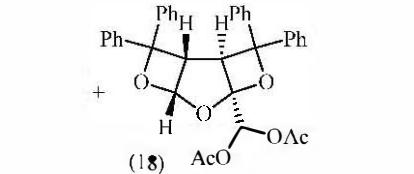
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (1 equiv)	 (50) 1:1	309
	Ph ₂ CO (1 equiv)	 (21)	309
	PhCHO (0.3 equiv)	 (18) 1:1 (→)	77

Table 11. *Continued*

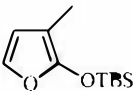
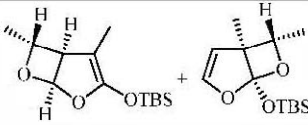
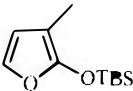
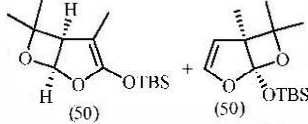
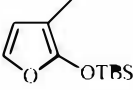
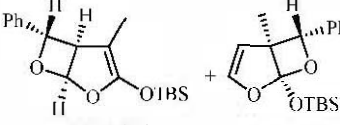
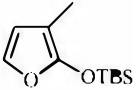
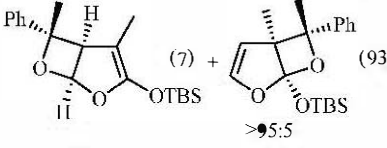
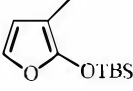
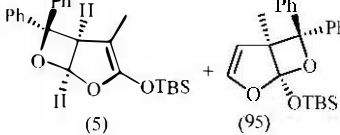
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCHO (0.5 equiv)	 81:19 (54) >95:5 (46)	76
	Me ₂ CO (0.5 equiv)	 (50) (50)	76
	PhCHO (1.5 equiv)	 87:13 (40) >95:5 (60)	76
	PhCOMe (1.5 equiv)	 (7) + (93) >95:5	76
	Ph ₂ CO (1.5 equiv)	 (5) (95)	76

Table 11. *Continued*

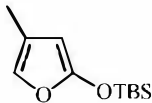
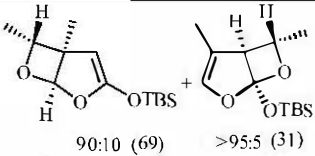
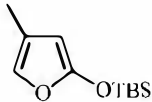
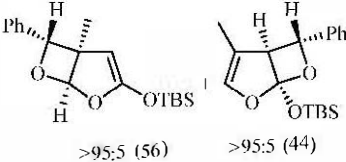
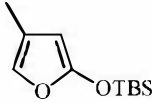
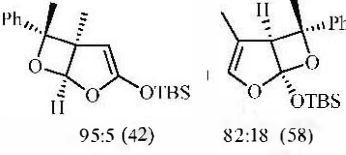
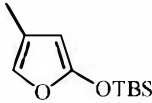
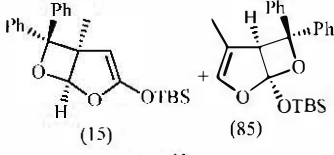
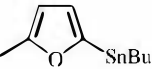
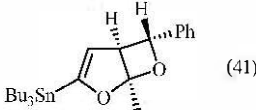
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCHO (1.5 equiv)	 90:10 (69) >95:5 (31)	76
	PhCHO (1.5 equiv)	 >95:5 (56) >95:5 (44)	76
	PhCOMe (1.5 equiv)	 95:5 (42) 82:18 (58)	76
	Ph ₂ CO (1.5 equiv)	 (15) (85)	76
	PhCHO (0.56 equiv)	 (41)	75

Table 11. *Continued*


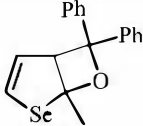
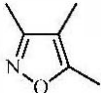
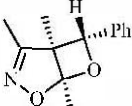
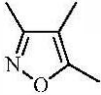
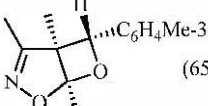
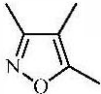
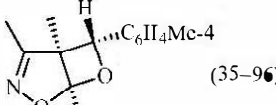
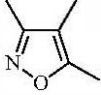
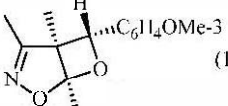
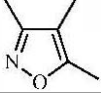
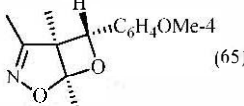
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph_2CO (1 equiv)	 (34)	325
	PhCHO (1 equiv)	 (41-98)	306
	$3\text{-MeC}_6\text{H}_4\text{CHO}$ (1 equiv)	 (65-92)	306
	$4\text{-MeC}_6\text{H}_4\text{CHO}$ (1 equiv)	 (35-96)	306
	$3\text{-MeOC}_6\text{H}_4\text{CHO}$ (1 equiv)	 (19)	306
	$4\text{-MeOC}_6\text{H}_4\text{CHO}$ (1 equiv)	 (65)	306

Table 11. Continued

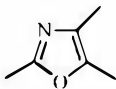
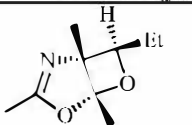
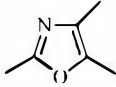
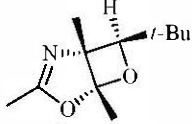
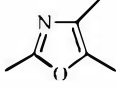
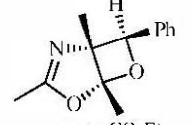
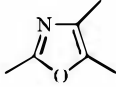
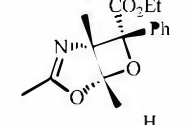
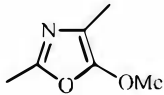
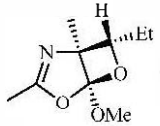
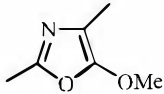
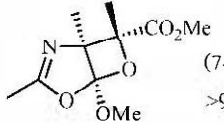
Substrate	Carbonyl compound	Product (yields %)	Ref.
	EtCHO	 (ca. 100) dr >99:1	329
	<i>t</i> -BuCHO	 (ca. 100) dr >99:1	329
	PhCHO	 (ca. 100) dr >99:1	329
	PhCOCO ₂ Et	 (ca. 100) dr 74:26	329
	EtCHO (0.9 equiv)	 (84–90)	255 326
	MeCOCO ₂ Me (0.9 equiv)	 (74) >98:2	326 330

Table 11. *Continued*

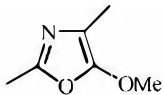
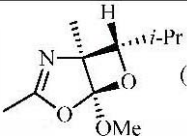
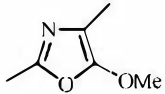
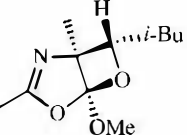
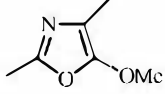
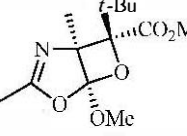
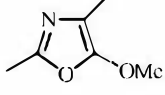
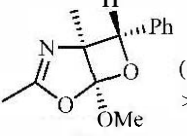
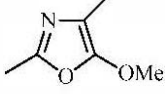
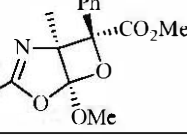
Substrate	Carbonyl compound	Product (yields %)	Ref.
	<i>i</i> -PrCHO (0.9 equiv)	 (90–93)	255 326
	<i>i</i> -BuCHO (0.9 equiv)	 (84)	255 326
	<i>t</i> -BuCOCO ₂ Me (0.9 equiv)	 (74) >98:2	326
	PhCHO (0.9 equiv)	 (82–85) >98:2	255 326
	PhCOCO ₂ Me (0.9 equiv)	 (79–86) 79:21	326 330

Table 11. *Continued*

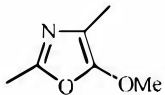
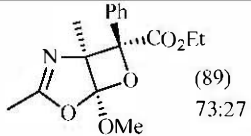
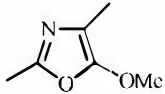
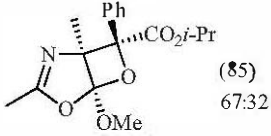
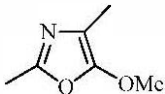
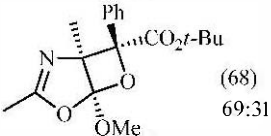
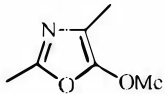
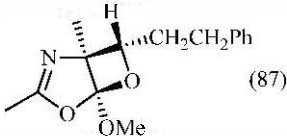
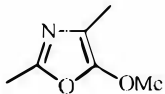
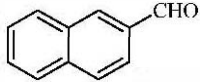
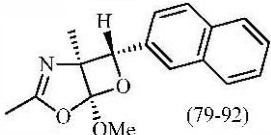
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ Et (0.9 equiv)	 (89) 73:27	326
	PhCOCO ₂ <i>i</i> -Pr (0.9 equiv)	 (85) 67:32	326
	PhCOCO ₂ <i>t</i> -Bu (0.9 equiv)	 (68) 69:31	326
	PhCH ₂ CH ₂ CHO (0.9 equiv)	 (87)	255 326
	 (0.9 equiv)	 (79-92) >98:2	255 326

Table 11. *Continued*

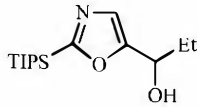
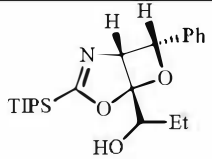
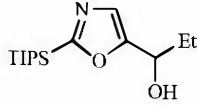
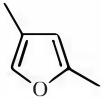
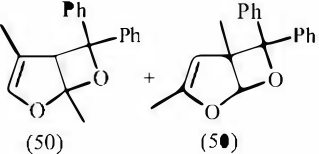
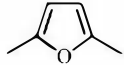
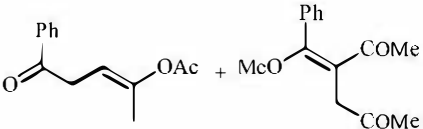
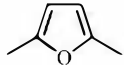
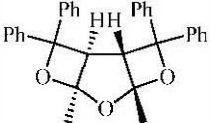
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (1.5 equiv)	 (75) dr 80:20	327
	Ph ₂ CO (1.5 equiv)	No reaction	327
	Ph ₂ CO	 (50) + (50)	73c
	PhCO ₂ Me (0.18 equiv)	 (44)	311
	Ph ₂ CO	 (9.9)	252 319

Table 11. *Continued*

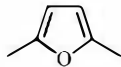
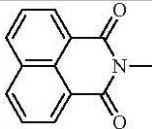
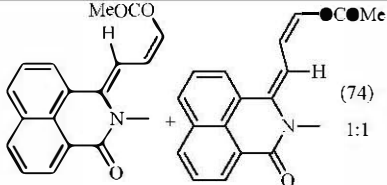
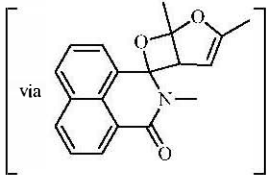

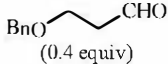
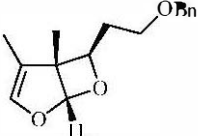

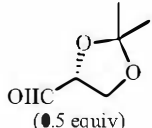
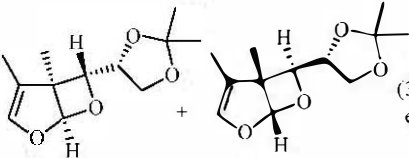
Substrate	Carbonyl compound	Product (yields %)	Ref.
		 <p>(74) 1:1</p> <p>via</p> 	113c
	 <p>(0.4 equiv)</p>	 <p>(63)</p>	331
	 <p>(0.5 equiv)</p>	 <p>(35) er 77:23</p>	332

Table 11. *Continued*

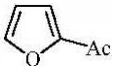
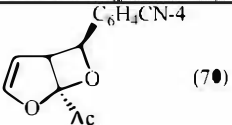
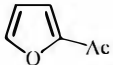
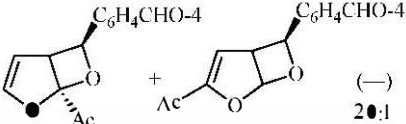
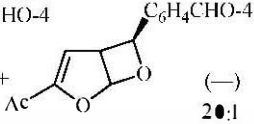
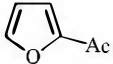
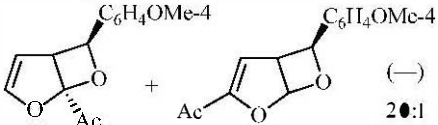
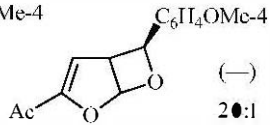
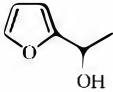
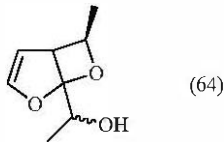
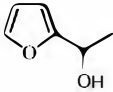
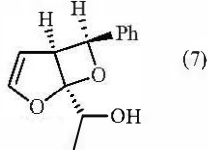
Substrate	Carbonyl compound	Product (yields %)	Ref.
	4-CNC ₆ H ₄ CHO (0.32 equiv)	 (70)	77
	4-OHCC ₆ H ₄ CHO (0.32 equiv)	 +  (—) 20:1	77
	4-MeOC ₆ H ₄ CHO (0.32 equiv)	 +  (—) 20:1	77
	MeCHO (1.5 equiv)	 (64)	97
	PhCHO (1.5 equiv)	 (7)	94

Table 11. *Continued*

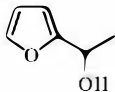
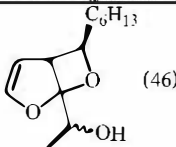
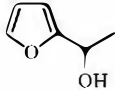
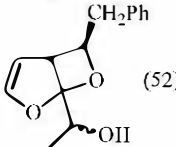
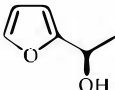
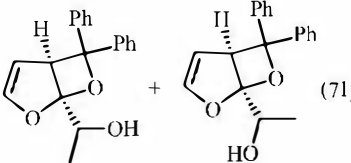

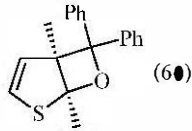

Substrate	Carbonyl compound	Product (yields %)	Ref.
	$C_6H_{13}CHO$ (1.5 equiv)	 (46)	97
	$PhCH_2CHO$ (1.5 equiv)	 (52)	97
	Ph_2CO (1.5 equiv)	 (71)	94
	Ph_2CO (1 equiv)	 (60)	333
	Ph_2CO (1 equiv)	No reaction	333

Table 11. *Continued*

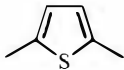
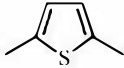
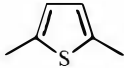
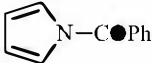
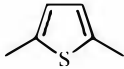
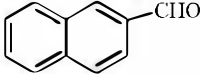
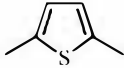
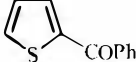
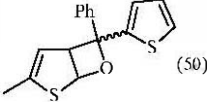
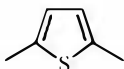
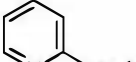
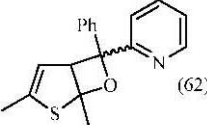
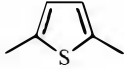
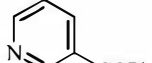
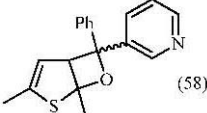
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (1 equiv)	No reaction	334
	PhCOMe (1 equiv)	No reaction	334
	 (1 equiv)	No reaction	334
	 (1 equiv)	No reaction	334
	 (1 equiv)	 (50)	334
	 (1 equiv)	 (62)	334
	 (1 equiv)	 (58)	334

Table 11. *Continued*

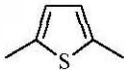
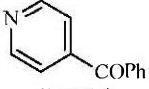
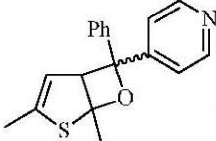
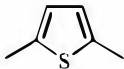
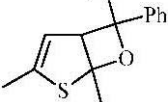
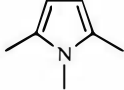
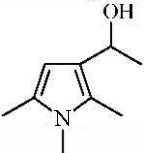
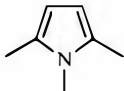
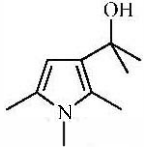
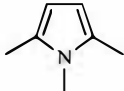
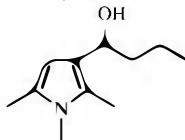
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (1 equiv)	 (60)	334
	Ph ₂ CO	 (62)	73g 335
	MeCHO	 (5)	302
	Me ₂ CO	 (56)	302
	PrCHO	 (15)	302

Table 11. *Continued*

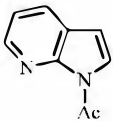
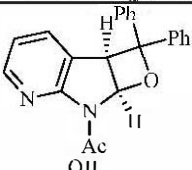



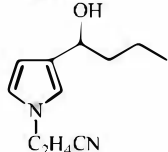
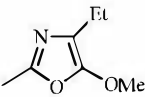
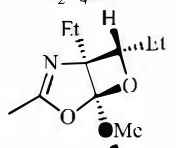
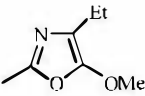
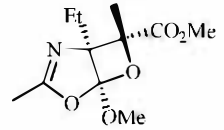
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (3.2 equiv)	 (4)	336
	Me ₂ CO	 (52)	302
	PrCHO	 (85)	302
	EtCHO (0.9 equiv)	 (90-92)	255 326
	MeCOCO ₂ Me (0.9 equiv)	 (66) >98:2	326 330

Table 11. Continued

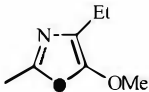
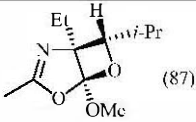
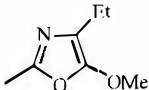
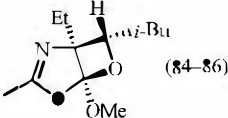
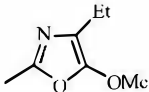
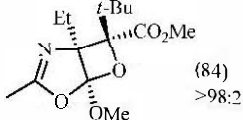
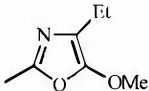
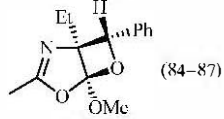
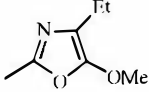
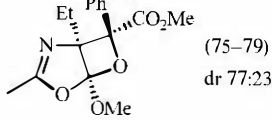
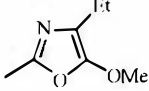
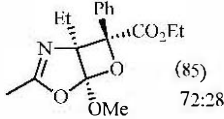
Substrate	Carbonyl compound	Product (yields %)	Ref.
	<i>i</i> -PrCHO (0.9 equiv)	 (87)	255 326
	<i>i</i> -BuCHO (0.9 equiv)	 (84–86)	255 326
	<i>t</i> -BuCOCO ₂ Me (0.9 equiv)	 (84) >98:2	255
	PhCHO (0.9 equiv)	 (84–87)	255 326
	PhCOCO ₂ Me (0.9 equiv)	 (75–79) dr 77:23	255 330
	PhCOCO ₂ Et (0.9 equiv)	 (85) 72:28	255

Table 11. Continued

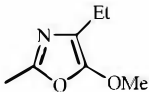
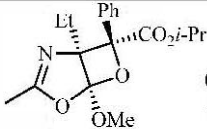
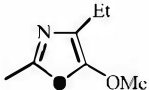
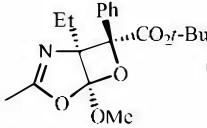
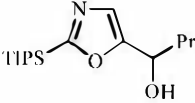
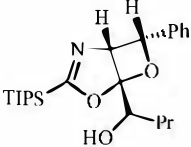
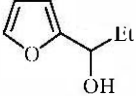
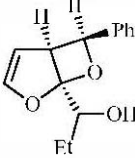
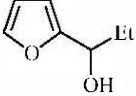
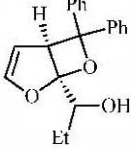
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ <i>i</i> -Pr (0.9 equiv)	 (87) 66:34	255
	PhCOCO ₂ <i>t</i> -Bu (0.9 equiv)	 (63) 67:33	255
	PhCHO (1.5 equiv)	 (71) dr 80:20	327
	PhCHO (1.5 equiv)	 (78)	94
	Ph ₂ CO (1.5 equiv)	 (73)	94

Table 11. *Continued*

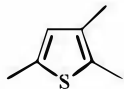
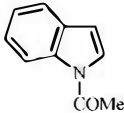
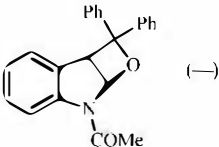
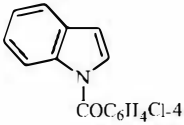
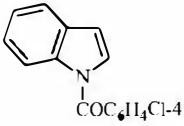
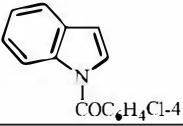
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (1 equiv)	No reaction	333
	Ph ₂ CO	 (—)	337
	EtCHO	No reaction	337
	Me ₂ CO	No reaction	337
	PhCHO	No reaction	337

Table 11. *Continued*

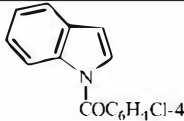
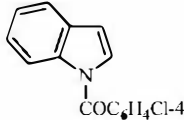
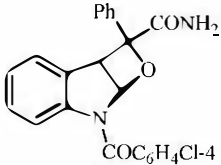
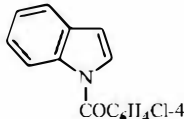
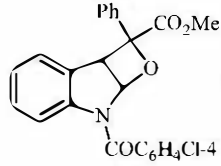
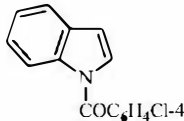
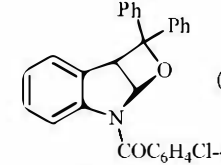
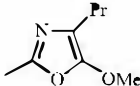
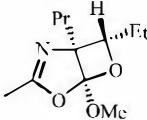
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOMe	No reaction	337
	PhCOCONH ₂	 (33)	337
	PhCOCO ₂ Me	 (33)	337
	Ph ₂ CO	 (83)	337
	EtCHO (0.9 equiv)	 (86-95) >98:2	255 326

Table 11. Continued

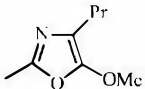
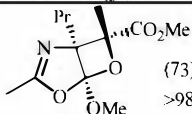
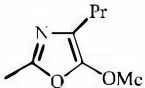

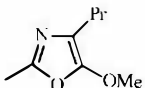
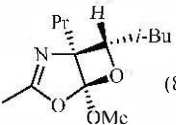
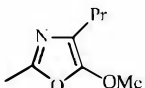
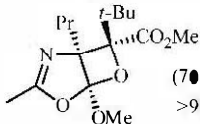
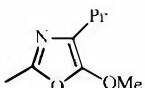
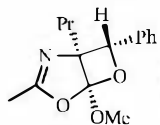
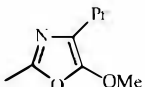
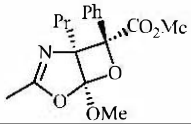
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCOCO ₂ Me (0.9 equiv)	 (73) >98:2	255 330
	<i>i</i> -PrCHO	 (85–86)	255 326
	<i>i</i> -BuCHO (0.9 equiv)	 (80–83)	255 326
	<i>t</i> -BuCOCO ₂ Me (0.9 equiv)	 (70) >98:2	255
	PhCHO (0.9 equiv)	 (86–87) >98:2	255 326
	PhCOCO ₂ Me (0.9 equiv)	 (78–79) dr 75:25	255 330

Table 11. *Continued*

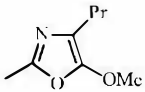
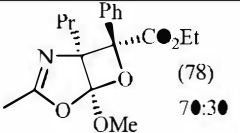
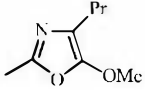
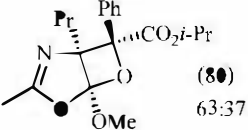
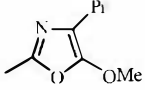
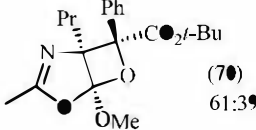
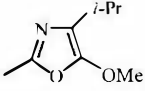
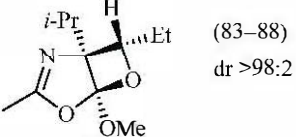
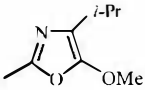
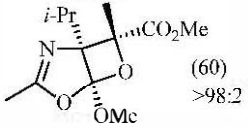
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ Et (0.9 equiv)	 (78) 70:30	255
	PhCOCO ₂ <i>i</i> -Pr (0.9 equiv)	 (80) 63:37	255
	PhCOCO ₂ <i>t</i> -Bu (0.9 equiv)	 (70) 61:39	255
	EtCHO (0.9 equiv)	 (83–88) dr >98:2	255 326
	MeCOCO ₂ Me (0.9 equiv)	 (60) >98:2	255 330

Table 11. Continued

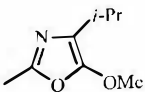
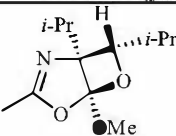
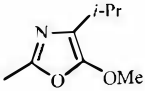
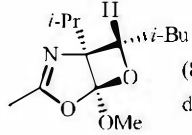
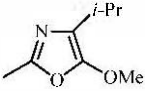
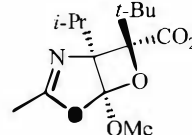
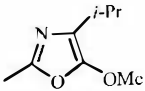
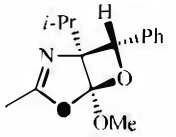
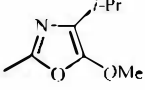
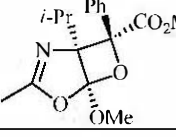
Substrate	Carbonyl compound	Product (yields %)	Ref.
	<i>i</i> -PrCHO (0.9 equiv)	 (81–83) dr > 98:2	255 326
	<i>i</i> -BuCHO (0.9 equiv)	 (81–87) dr 81:19	255 326
	<i>t</i> -BuCOCO ₂ Me (0.9 equiv)	 (69) 49:51	255
	PhCHO (0.9 equiv)	 (80–85) dr 73:27	255 326
	PhCOCO ₂ Me (0.9 equiv)	 (79–85) 71:29	255 330

Table 11. *Continued*

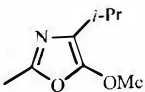
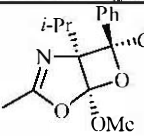
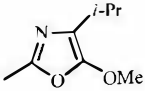
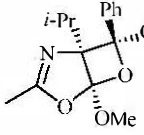
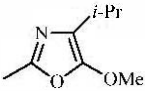
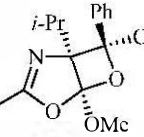
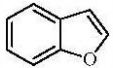
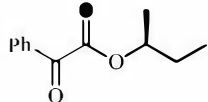
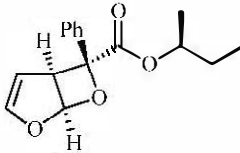
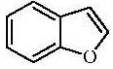
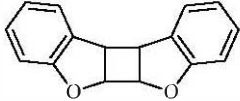
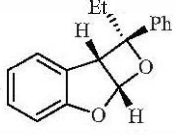
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ Et (0.9 equiv)	 (75) 67:33	255
	PhCOCO ₂ <i>i</i> -Pr (0.9 equiv)	 (90) 51:49	255
	PhCOCO ₂ <i>t</i> -Bu (0.9 equiv)	 (68) 53:47	255
		 (20) dr 79:21	322
	PhCOEt (4.3 equiv)	 +  (-)	219

Table 11. *Continued*

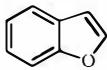
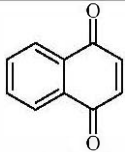
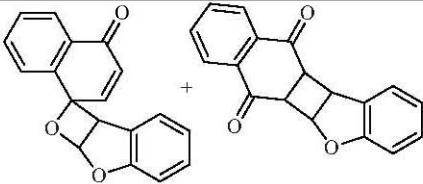
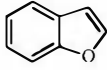
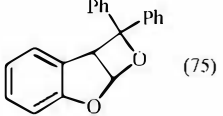
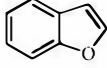
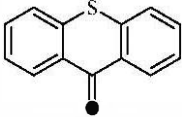
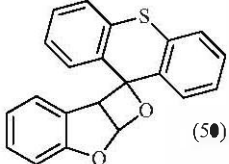
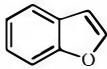
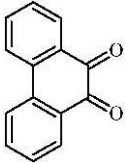
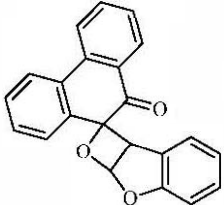
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 1.32:1 (65)	288 338
	Ph_2CO (0.7 equiv)	 (75)	339
	 (0.13 equiv)	 (50)	339
	 (0.25 equiv)	 (80)	211

Table 11. *Continued*

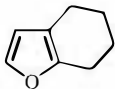
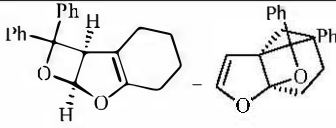
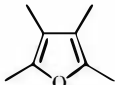
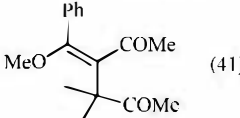
Substrate	Carbonyl compound	Product (yields %)	Ref.																		
	Ph ₂ CO	 <div style="display: flex; justify-content: space-around; width: 100%;"> I II </div> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th data-bbox="965 380 1021 397">Temp</th> <th data-bbox="1029 380 1053 397">I</th> <th data-bbox="1061 380 1085 397">II</th> </tr> </thead> <tbody> <tr> <td data-bbox="973 408 1005 425">60</td> <td data-bbox="1029 408 1061 425">(13)</td> <td data-bbox="1085 408 1117 425">(66)</td> </tr> <tr> <td data-bbox="973 442 1005 459">20</td> <td data-bbox="1029 442 1061 459">(16)</td> <td data-bbox="1085 442 1117 459">(61)</td> </tr> <tr> <td data-bbox="973 476 1005 492">0</td> <td data-bbox="1029 476 1061 492">(16)</td> <td data-bbox="1085 476 1117 492">(61)</td> </tr> <tr> <td data-bbox="973 509 1005 526">-45</td> <td data-bbox="1029 509 1061 526">(26)</td> <td data-bbox="1085 509 1117 526">(59)</td> </tr> <tr> <td data-bbox="973 543 1005 560">-75</td> <td data-bbox="1029 543 1061 560">(28)</td> <td data-bbox="1085 543 1117 560">(52)</td> </tr> </tbody> </table>	Temp	I	II	60	(13)	(66)	20	(16)	(61)	0	(16)	(61)	-45	(26)	(59)	-75	(28)	(52)	99b
Temp	I	II																			
60	(13)	(66)																			
20	(16)	(61)																			
0	(16)	(61)																			
-45	(26)	(59)																			
-75	(28)	(52)																			
	PhCO ₂ Me (0.4 equiv)	 (41)	311																		

Table 11. *Continued*

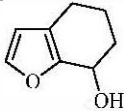
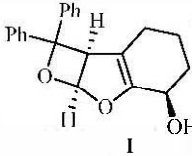
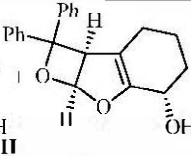
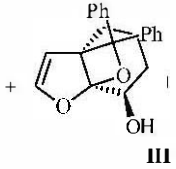
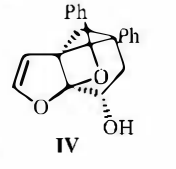
Substrate	Carbonyl compound	Product (yields %)	Ref.																														
	Ph ₂ CO (0.5 equiv)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>I</p> </div> <div style="text-align: center;">  <p>II</p> </div> </div> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;">  <p>III</p> </div> <div style="text-align: center;">  <p>IV</p> </div> </div> <table border="1" style="margin-top: 10px; width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">Temp</th> <th style="text-align: center;">I</th> <th style="text-align: center;">II</th> <th style="text-align: center;">III</th> <th style="text-align: center;">IV</th> </tr> </thead> <tbody> <tr> <td>60</td> <td style="text-align: center;">(3)</td> <td style="text-align: center;">(7)</td> <td style="text-align: center;">(37)</td> <td style="text-align: center;">(28)</td> </tr> <tr> <td>20</td> <td style="text-align: center;">(4)</td> <td style="text-align: center;">(12)</td> <td style="text-align: center;">(36)</td> <td style="text-align: center;">(30)</td> </tr> <tr> <td>.25</td> <td style="text-align: center;">(5)</td> <td style="text-align: center;">(23)</td> <td style="text-align: center;">(28)</td> <td style="text-align: center;">(36)</td> </tr> <tr> <td>46</td> <td style="text-align: center;">(7)</td> <td style="text-align: center;">(28)</td> <td style="text-align: center;">(23)</td> <td style="text-align: center;">(39)</td> </tr> <tr> <td>-75</td> <td style="text-align: center;">(7)</td> <td style="text-align: center;">(31)</td> <td style="text-align: center;">(13)</td> <td style="text-align: center;">(33)</td> </tr> </tbody> </table>	Temp	I	II	III	IV	60	(3)	(7)	(37)	(28)	20	(4)	(12)	(36)	(30)	.25	(5)	(23)	(28)	(36)	46	(7)	(28)	(23)	(39)	-75	(7)	(31)	(13)	(33)	99a 99b
Temp	I	II	III	IV																													
60	(3)	(7)	(37)	(28)																													
20	(4)	(12)	(36)	(30)																													
.25	(5)	(23)	(28)	(36)																													
46	(7)	(28)	(23)	(39)																													
-75	(7)	(31)	(13)	(33)																													

Table 11. *Continued*

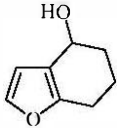
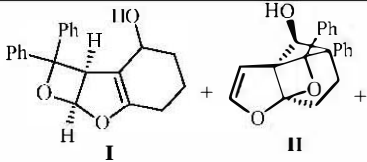
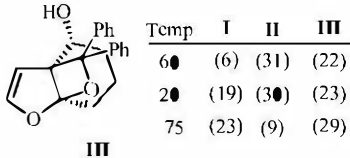
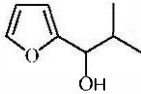
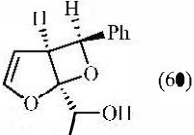
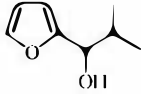
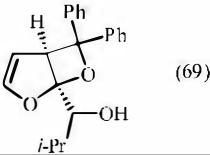
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (0.5 equiv)	 	99 ^o
	PhCHO (1.5 equiv)		94
	Ph ₂ CO (1.5 equiv)		94

Table 11. *Continued*

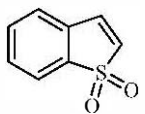
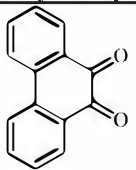
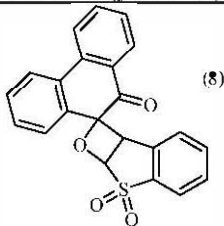
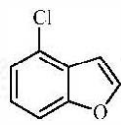
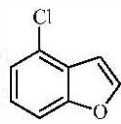
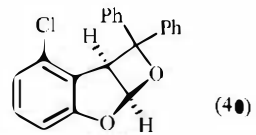
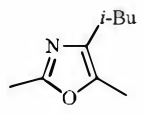
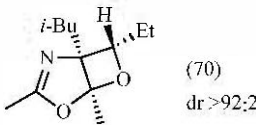
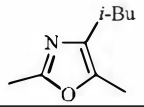
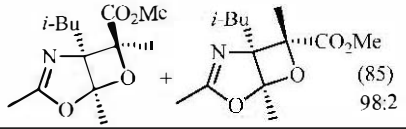
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.25 equiv)	 (8)	211
	PhCHO (1.5 equiv)	No reaction	340
	Ph ₂ CO (1.5 equiv)	 (40)	340
	EtCHO (1 equiv)	 (70) dr >92:2	341
	MeCOCO ₂ Me (1 equiv)	 (85) 98:2	341

Table 11. Continued

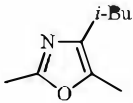
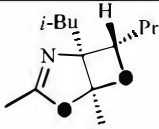
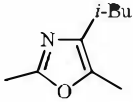
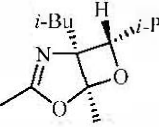
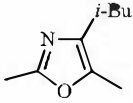
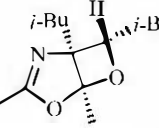
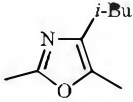
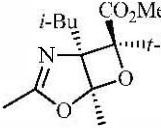
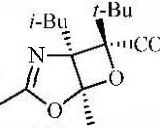
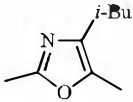
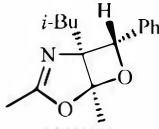
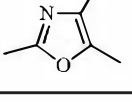
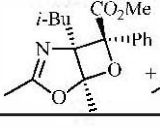
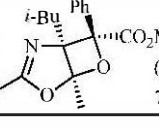
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PrCHO (1 equiv)	 (68) dr >98:2	341
	<i>i</i> -PrCHO (1 equiv)	 (67) dr >98:2	341
	<i>t</i> -BuCHO (1 equiv)	 (68) dr >98:2	341
	<i>t</i> -BuCOCOMe (1 equiv)	 +  (79) 98:2	341
	PhCHO (1 equiv)	 (62) dr >98:2	341
	PhCOCOMe (1 equiv)	 +  (86) 71:29	341

Table 11. Continued

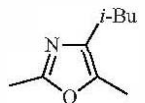
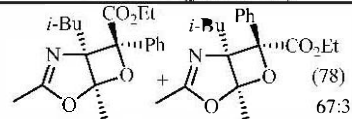
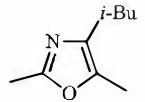
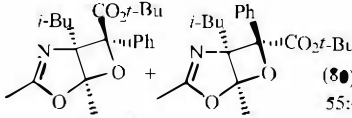
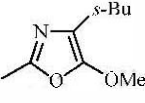
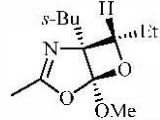
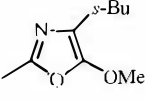
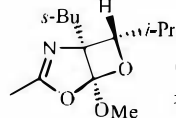
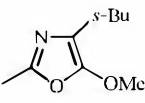
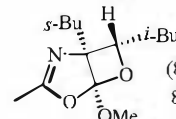
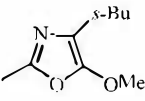

Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ Et (1 equiv)	 (78) 67:33	341
	PhCOCO ₂ <i>t</i> -Bu (1 equiv)	 (80) 55:45	341
	EtCHO (0.9 equiv)	 (87) dr 52:48 → 98:2	255 326
	<i>i</i> -PrCHO (0.9 equiv)	 (83) >98:2	255
	<i>i</i> -BuCHO (0.9 equiv)	 (83) 89:11	255
	PhCHO (0.9 equiv)	 (81) 85:15	255

Table 11. *Continued*

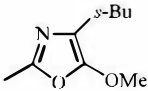
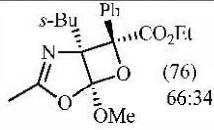
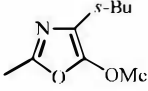
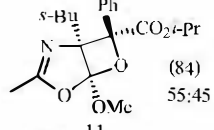
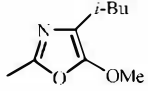
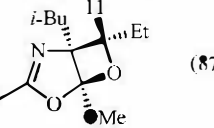
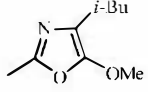
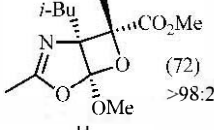
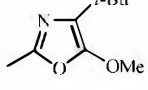
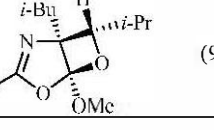
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ Et (0.9 equiv)	 (76) 66:34	255
	PhCOCO ₂ <i>i</i> -Pr (0.9 equiv)	 (84) 55:45	255
	EtCHO (1 equiv)	 (87)	326
	MeCOCO ₂ Me (0.9 equiv)	 (72) >98:2	255 330
	<i>i</i> -PrCHO (0.9 equiv)	 (91)	326

Table 11. *Continued*

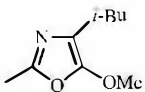
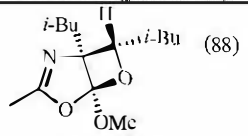
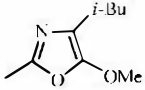
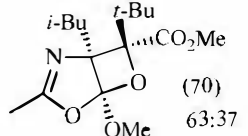
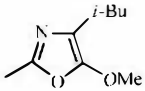
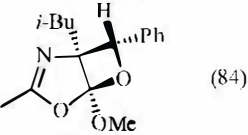
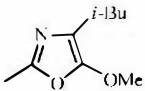
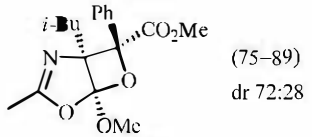
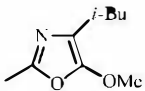
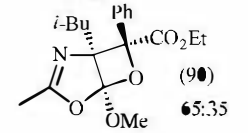
Substrate	Carbonyl compound	Product (yields %)	Ref.
	<i>i</i> -BuCHO (1 equiv)	 (88)	326
	<i>t</i> -BuC2CO ₂ Me (0.9 equiv)	 (70) 63:37	255
	PhCHO (1 equiv)	 (84)	326
	PhCOCO ₂ Me (0.9 equiv)	 (75–89) dr 72:28	255 330
	PhCOCO ₂ Et (0.9 equiv)	 (90) 65:35	255

Table 11. *Continued*

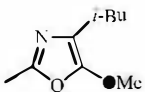
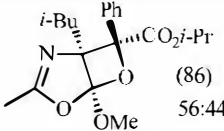
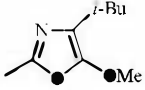
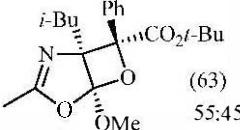
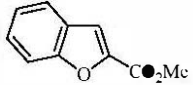
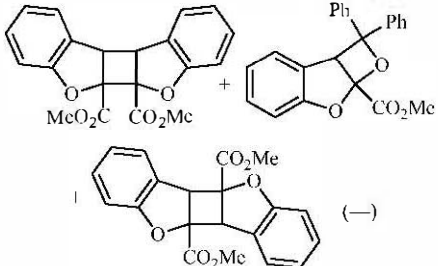
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCOCO ₂ <i>i</i> -Pr (0.9 equiv)	 (86) 56:44	255
	PhCOCO ₂ <i>t</i> -Bu (0.9 equiv)	 (63) 55:45	255
	Ph ₂ CO (0.3 equiv)	 (+) (−)	219 342

Table 11. *Continued*

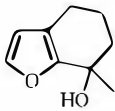
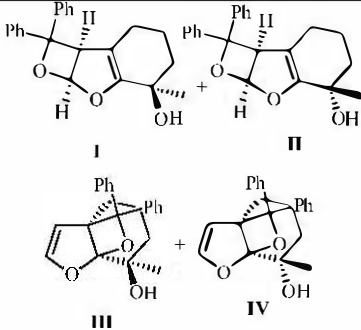
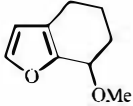
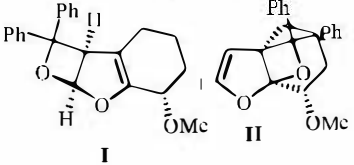
Substrate	Carbonyl compound	Product (yields %)	Ref.																														
	Ph ₂ CO	 <table border="1" data-bbox="906 554 1169 728"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> <th>III</th> <th>IV</th> </tr> </thead> <tbody> <tr> <td>60</td> <td>(4)</td> <td>(3)</td> <td>(39)</td> <td>(12)</td> </tr> <tr> <td>20</td> <td>(5)</td> <td>(4)</td> <td>(55)</td> <td>(18)</td> </tr> <tr> <td>0</td> <td>(6)</td> <td>(7)</td> <td>(58)</td> <td>(23)</td> </tr> <tr> <td>-46</td> <td>(10)</td> <td>(16)</td> <td>(38)</td> <td>(30)</td> </tr> <tr> <td>-75</td> <td>(9)</td> <td>(9)</td> <td>(22)</td> <td>(29)</td> </tr> </tbody> </table>	Temp	I	II	III	IV	60	(4)	(3)	(39)	(12)	20	(5)	(4)	(55)	(18)	0	(6)	(7)	(58)	(23)	-46	(10)	(16)	(38)	(30)	-75	(9)	(9)	(22)	(29)	99b
Temp	I	II	III	IV																													
60	(4)	(3)	(39)	(12)																													
20	(5)	(4)	(55)	(18)																													
0	(6)	(7)	(58)	(23)																													
-46	(10)	(16)	(38)	(30)																													
-75	(9)	(9)	(22)	(29)																													
	Ph ₂ CO	 <table border="1" data-bbox="1125 750 1292 944"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>60</td> <td>(20)</td> <td>(52)</td> </tr> <tr> <td>20</td> <td>(15)</td> <td>(32)</td> </tr> <tr> <td>0</td> <td>(16)</td> <td>(33)</td> </tr> <tr> <td>-45</td> <td>(30)</td> <td>(50)</td> </tr> <tr> <td>-75</td> <td>(34)</td> <td>(51)</td> </tr> </tbody> </table>	Temp	I	II	60	(20)	(52)	20	(15)	(32)	0	(16)	(33)	-45	(30)	(50)	-75	(34)	(51)	99b												
Temp	I	II																															
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-75	(34)	(51)																															

Table 11. *Continued*

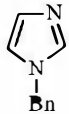
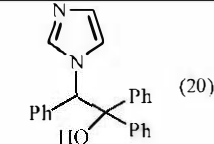
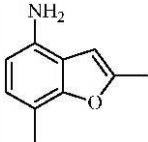
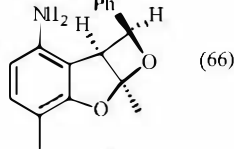
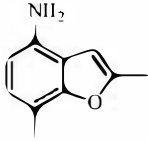
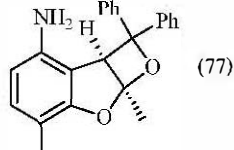
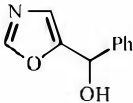
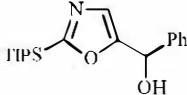
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO	 (20)	304
	PhCHO (1.5 equiv)	 (66)	340
	Ph ₂ CO (1.5 equiv)	 (77)	340
	Ph ₂ CO (1.5 equiv)	No reaction	327
	PhCHO (1.5 equiv)	No reaction	327

Table 11. *Continued*

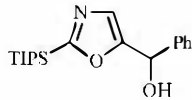
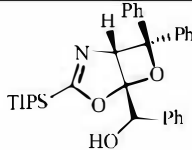
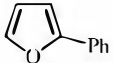
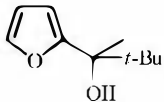
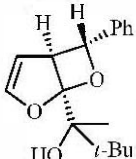
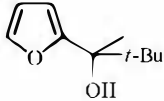
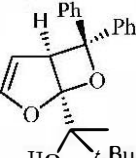
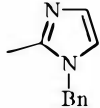
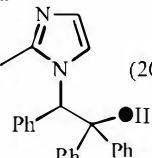
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (1.5 equiv)	 (54) dr 84:16	327
	PhCO ₂ CH ₂ CHO	No reaction	316
	PhCHO (1.5 equiv)	 (50) dr 71:29	98
	Ph ₂ CO (1.5 equiv)	 (49) dr 85.5:14.5	98
	Ph ₂ CO	 (20)	305

Table 11. *Continued*

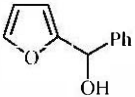
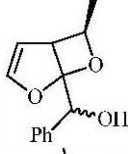
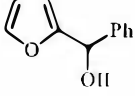
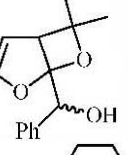
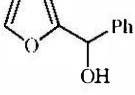
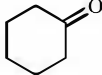
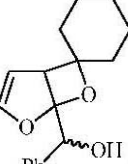
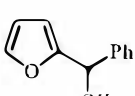
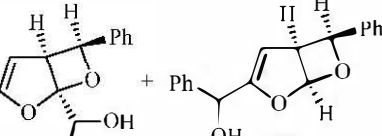
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCHO (1.5 equiv)	 (58)	97
	Me ₂ CO (1.5 equiv)	 (33–47)	97
	 (1.5 equiv)	 (30)	97
	PhCHO (1.5 equiv)	 (25) + (43)	94

Table 11. *Continued*

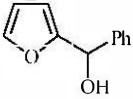
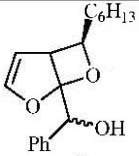
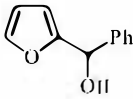
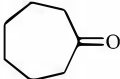
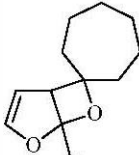
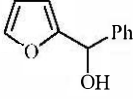
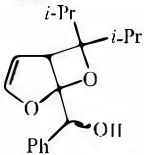
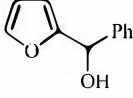
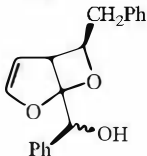
Substrate	Carbonyl compound	Product (yields %)	Ref.
	$\text{C}_6\text{H}_{13}\text{CHO}$ (1.5 equiv)	 (56)	97
	 (1.5 equiv)	 (40)	97
	$(i\text{-Pr})_2\text{CO}$ (1.5 equiv)	 (45)	97
	PhCH_2CHO (1.5 equiv)	 (64)	97

Table 11. *Continued*

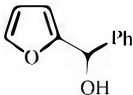
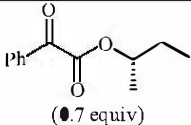
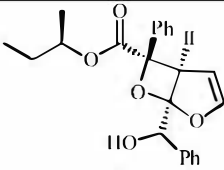
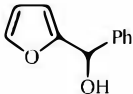
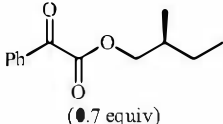
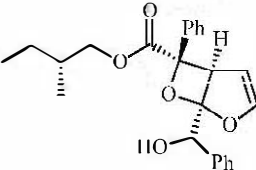
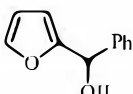
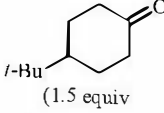
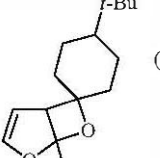
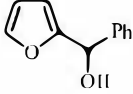
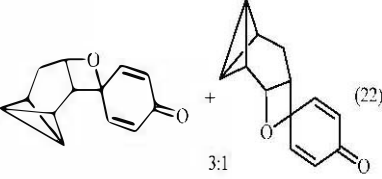
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 <p>(0.7 equiv)</p>	 <p>(65) dr 93:7</p>	84
	 <p>(0.7 equiv)</p>	 <p>(63) dr 98.5:1.5</p>	84
	 <p>(1.5 equiv)</p>	 <p>(25)</p>	97
	<p>Ph₂CO (1.5 equiv)</p>	 <p>(22) 3:1</p>	94

Table 11. *Continued*

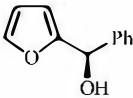
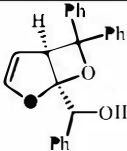
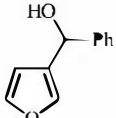
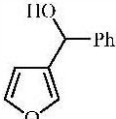
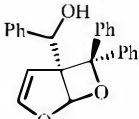
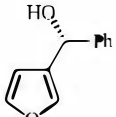
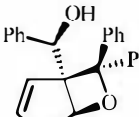
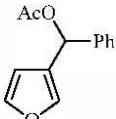
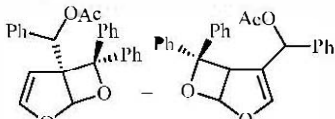
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (1.5 equiv)	 (73) dr >99:1	94
	PhCHO (1.5 equiv)	No reaction	101
	Ph ₂ CO (1.5 equiv)	 (58)	101
	Ph ₂ CO (1.5 equiv)	 (60) dr 99.5:0.5	101
	Ph ₂ CO (1.5 equiv)	 (—) dr 50:50	101

Table 11. *Continued*

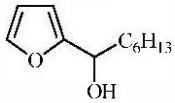
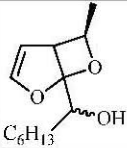
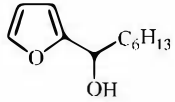
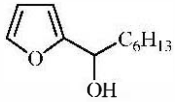
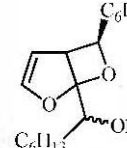
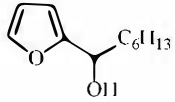
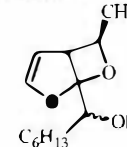
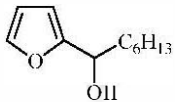
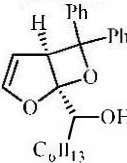
Substrate	Carbonyl compound	Product (yields %)	Ref.
	MeCHO (1.5 equiv)	 (42)	97
	PhCHO (1.5 equiv)	No reaction	94
	C ₆ H ₁₃ CHO (15 equiv)	 (68)	97
	PhCH ₂ CHO (1.5 equiv)	 (48)	97
	Ph ₂ CO (1.5 equiv)	 (61)	94

Table 11. Continued

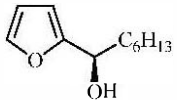
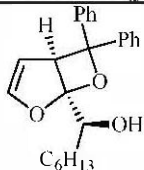
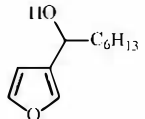
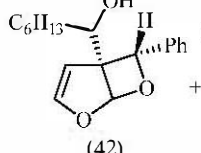
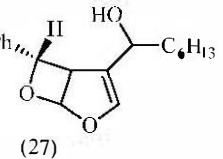
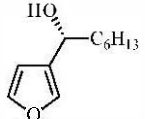
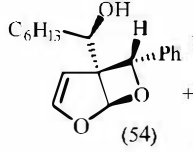
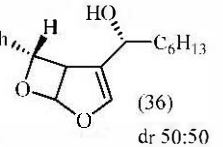
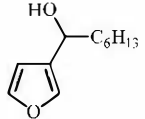
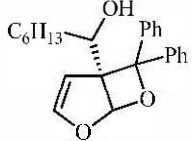
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (1.5 equiv)	 (61) dr > 99:1	94
	PhCHO (1.5 equiv)	 (42) +  (27)	101
	PhCHO (1.5 equiv)	 (54) +  (36) dr 50:50 dr 71.5:28.5	101
	Ph ₂ CO (1.5 equiv)	 (73)	101

Table 11. *Continued*

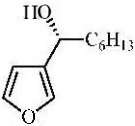
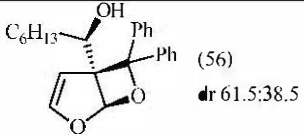
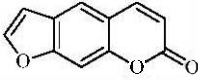
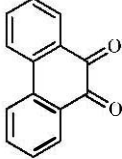
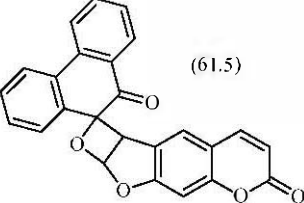
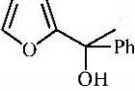
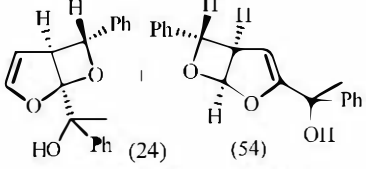
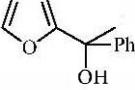
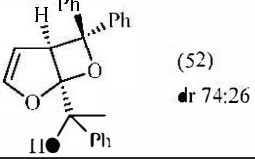
Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph ₂ CO (1.5 equiv)	 (56) dr 61.5:38.5	101
	 (1 equiv)	 (61.5)	211
	PhCHO (1.5 equiv)	 (24) (54) dr 100:0 dr 50:50	98
	Ph ₂ CO (1.5 equiv)	 (52) dr 74:26	98

Table 11. *Continued*

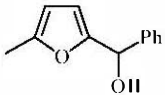
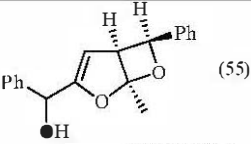
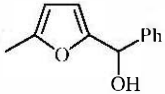
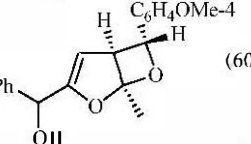
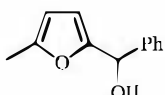
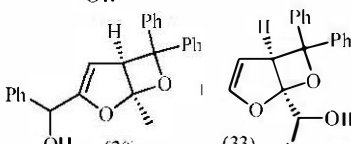
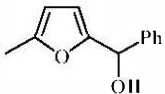
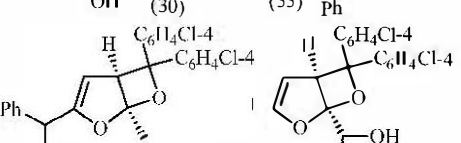
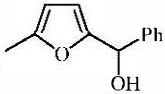
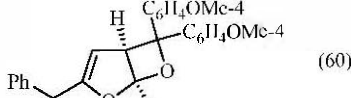
Substrate	Carbonyl compound	Product (yields %)	Ref.
	PhCHO (1.5 equiv)	 (55)	95
	4-MeOC ₆ H ₄ CHO (1.5 equiv)	 (60)	95
	Ph ₂ CO (1.5 equiv)	 (30) (33)	95
	(4-ClC ₆ H ₄) ₂ CO (1.5 equiv)	 (12) (30)	95
	(4-MeOC ₆ H ₄) ₂ CO (1.5 equiv)	 (60)	95

Table 11. *Continued*

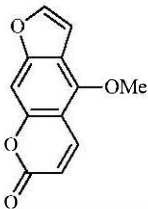
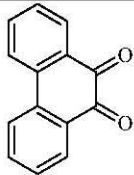
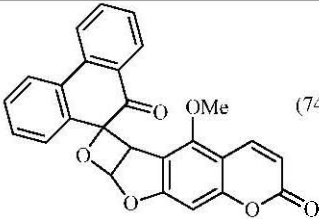
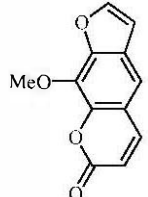
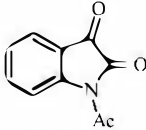
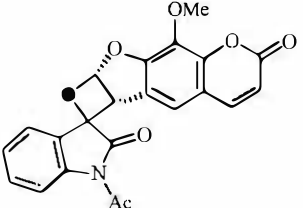
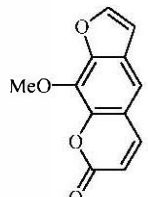
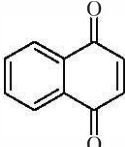
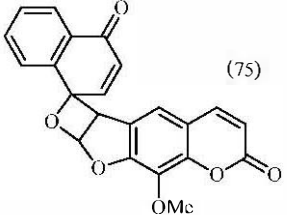
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 <p>(1 equiv)</p>	 <p>(74.5)</p>	211
	 <p>(0.5 equiv)</p>	 <p>(95)</p>	52
	 <p>(1 equiv)</p>	 <p>(75)</p>	288 338

Table 11. *Continued*

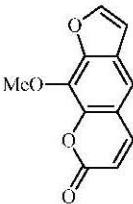
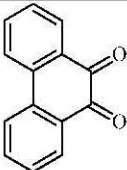

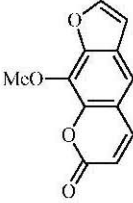
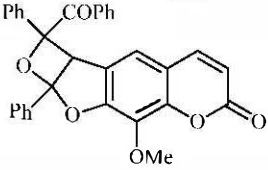
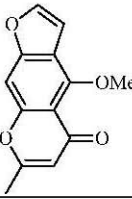
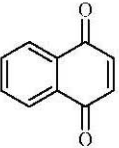
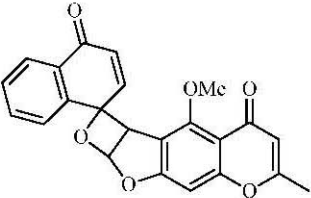
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (1 equiv)	 (66)	211
	PhCOCOPh (1 equiv)	 (94)	211
	 (1 equiv)	 (65)	288 338

Table 11. *Continued*

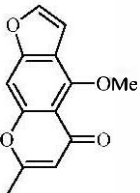
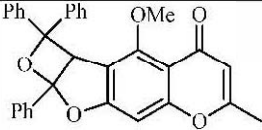
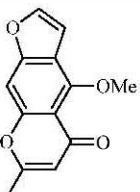
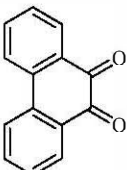
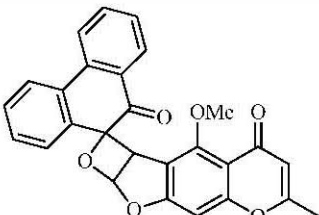
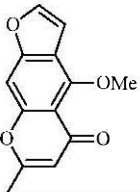
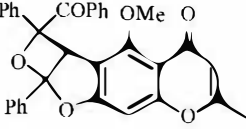
Substrate	Carbonyl compound	Product (yields %)	Ref.
	<p>Ph₂CO (1 equiv)</p>	 <p>(72)</p>	211
	 <p>(1 equiv)</p>	 <p>(69)</p>	211
	<p>PhCOCOPh (1 equiv)</p>	 <p>(56)</p>	211

Table 11. *Continued*

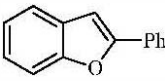
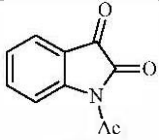
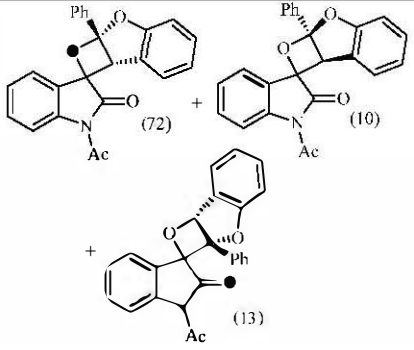
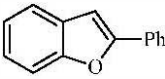
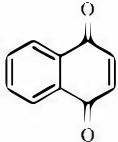
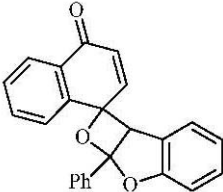
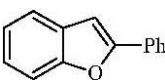
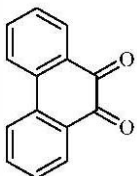
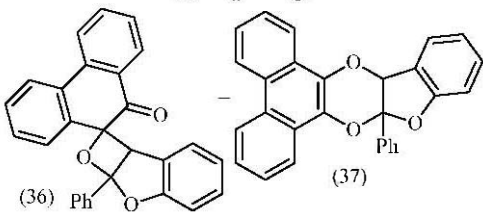
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)		52
	 (0.5 equiv)		288 338
	 (0.5 equiv)		211

Table 11. *Continued*

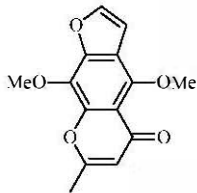
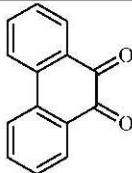
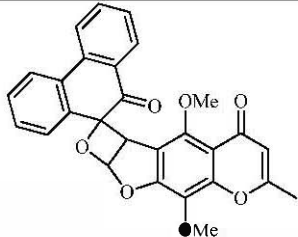
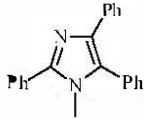
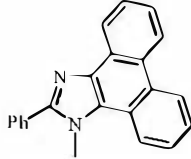
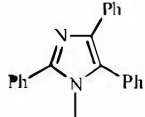
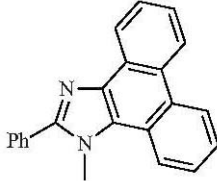
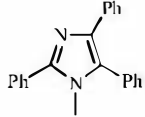
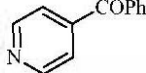
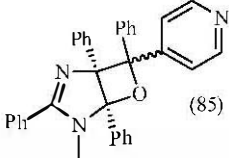
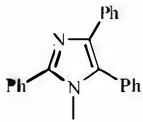
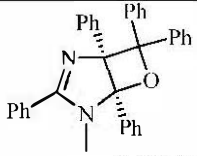
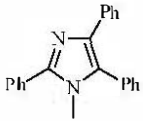
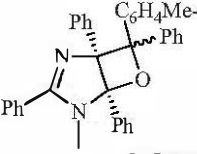
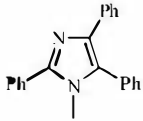
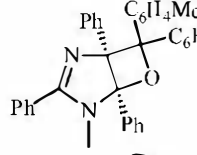
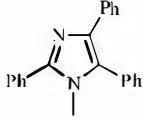
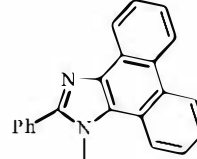
Substrate	Carbonyl compound	Product (yields %)	Ref.
	 (0.5 equiv)	 (70)	211
	PhCHO (11.9 equiv)	 (18)	343
	PhCOMe (8.7 equiv)	 (16)	343
	 (2.8 equiv)	 (85)	343

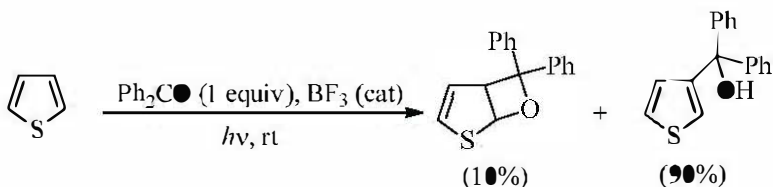
Table 11. *Continued*

Substrate	Carbonyl compound	Product (yields %)	Ref.
	Ph_2CO (5.7 equiv)	 (64)	343
	$4\text{-MeC}_6\text{H}_4\text{COPh}$ (5.7 equiv)	 (59)	343
	$(4\text{-MeC}_6\text{H}_4)_2\text{CO}$ (5.7 equiv)	 (53)	343
	$(4\text{-MeOC}_6\text{H}_4)_2\text{CO}$ (5.7 equiv)	 (54)	343

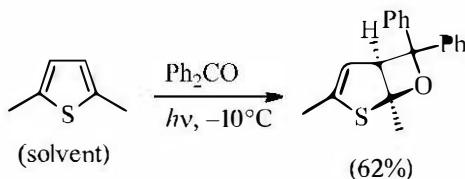
Substrates that possess lower aromaticity are more reactive than heterocycles that are more highly stabilized by aromaticity. The aromatic character in heterocyclic compounds is not always easy to gauge.

Considering only furan, pyrrole, and thiophene, the experimental resonance energies (ERE) are 16.2, 21.6, and 29.1 kcal mol⁻¹, respectively [344]. The Bird (I) and *D* indices give the same order (I: furan, 43; pyrrole, 59; thiophene, 56 [345]; *D*: furan, 0.71, pyrrole, 0.79; thiophene, 0.92 [346]), while the aromatic stabilization energies (ASE) reported are 6.29, 5.26, and 10.90 kcal mol⁻¹, respectively [347]. Assuming an aromaticity order in which thiophene is the most aromatic compound and furan possesses the lowest aromatic stabilization, the observed reactivity is in agreement with the expectation.

Thiophene does not react with benzophenone under the usual Paternò-Büchi reaction conditions [324]. However, thiophene will react with benzophenone in the presence of BF₃, giving the corresponding oxetane adduct in very low yield (10%) (Scheme 77) [324]. It seems likely that the benzophenone-BF₃ complex gives an exciplex whose HSOM has a lower energy than that of the benzophenone triplet [324].



Scheme 77

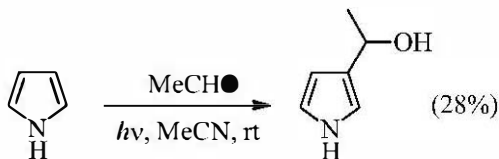


Scheme 78

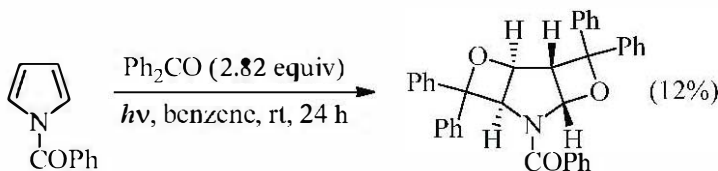
However, 2,5-dimethylthiophene reacts with benzophenone at -10° , giving the corresponding oxetane adduct in 62% yield (Scheme 78) [73g, 335]. This difference in reactivity can be rationalized by considering that, if the reaction occurs as a result of the interaction between the HOMO of the excited carbonyl compound with the LUMO of the alkene, the presence of the methyl groups modify the HOMO and LUMO energies [from -0.24582 and -0.02567 a.u. for thiophene, to -0.22254 and -0.01860 a.u. for 2,5-dimethylthiophene, calculated at the DFT/B3LYP/6-311G+(d,p) level]. The energy levels of the frontier orbitals apparently do not allow interaction of the HOMO of thiophene and the LUMO of the triplet benzophenone, thereby preventing the reaction from occurring. The interaction between the LUMO of 2,5-dimethylthiophene and the HOMO of triplet benzophenone leads to an effective reaction.

The same reaction has been attempted using other aromatic aldehydes and ketones. However, benzaldehyde, 1-naphthaldehyde, and acetophenone do not react [334]. 3,4-Dimethylthiophene and 2,3,5-trimethylthiophene react with benzophenone to afford polymeric materials [333].

The same behavior is observed when pyrrole is irradiated in the presence of a carbonyl compound. Pyrrole reacts with acetaldehyde, acetone, and butanal to give the corresponding pyrrole-3-methanol derivatives in low yields (Scheme 79) [302].



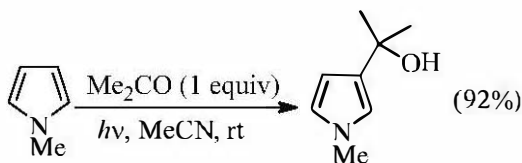
Scheme 79



Scheme 80

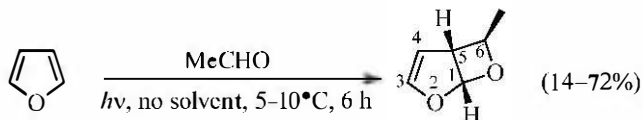
When *N*-benzoylpyrrole is used as the substrate, only low yields of the bisoxetane adduct are observed (Scheme 80) [307, 308].

Good yields of the corresponding pyrrole-3-methanol derivatives are obtained when *N*-methylpyrrole is used as the alkene in the Paternò–Büchi reaction (Scheme 81) [302]. This behavior is in agreement with the same substituent effects observed in the case of thiophene. A 2-*O*-silyl derivative of pyrrole reacts with benzophenone and naphthoquinone to give the corresponding oxetanes [489].

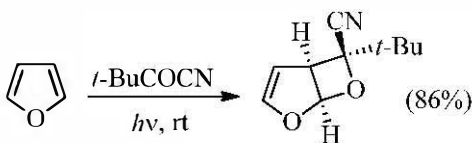


Scheme 81

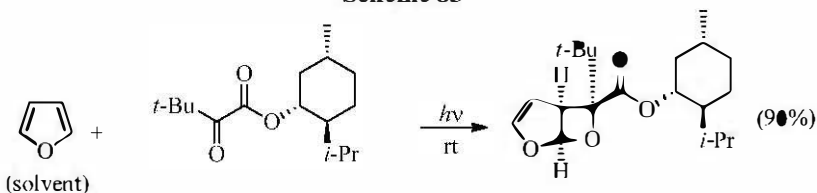
Selenophene does not react when irradiated in the presence of benzophenone; however, 1-methylselenophene gives the corresponding oxetane cycloadduct in low yield (34%) [325]. Selenophene shows a *D* value higher than thiophene (0.97) [346]. As pointed out above, among the 5-membered ring heteroaromatics, furan is the heterocycle showing the least aromatic stabilization and therefore is expected to be the more reactive substrate in the Paternò–Büchi reaction. In fact, furan reacts with aliphatic aldehydes [68d, 72, 73a, 73b, 73f, 83a, 309, 310, 315, 317], α -cyano esters [199] and -ketones [314], α -diketones [105d, 146], α -keto esters [68d, 73f, 83b], and α, β -unsaturated carbonyl compounds [73b]. Schemes 82 [72, 73b], 83 [314], and 84 [83b] detail some of the most relevant results. In all the reported examples, the *exo* stereochemistry of the substituent at C-6 is favored.



Scheme 82



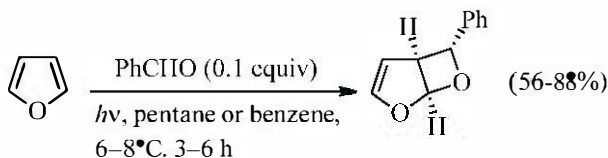
Scheme 83



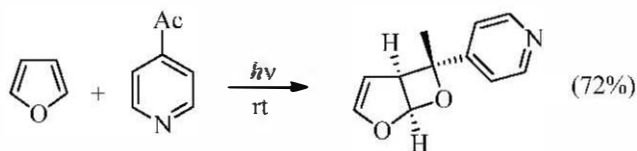
Scheme 84

The reaction of furan with acetone and other aliphatic ketones seems to be inefficient for preparative purposes (e.g., 1.7% yield of the oxetane in the case of acetone and 27% yield with cyclohexanecarboxaldehyde) [73b].

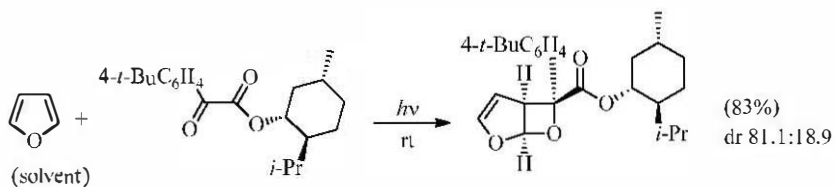
Furan also reacts with aromatic aldehydes [68b, 68d, 72, 73a, 311, 316], esters [311], amides [113c], ketones [73b, 73d, 252, 309, 318, 319, 320], diketones [52], α -keto esters [84,85,88], α -cyano ketones [68d, 314], α -hydroxy ketones [322], heteroaromatic aldehydes [73b, 74, 311, 312], and heteroaromatic ketones [74] (Schemes 85 [68b, 68d, 73a, 311, 316], 86 [74], 87 [83b], and 88 [73d, 252, 319, 320]). In some cases, the metathesis product generated by oxetane ring opening is obtained (Scheme 89) [311].



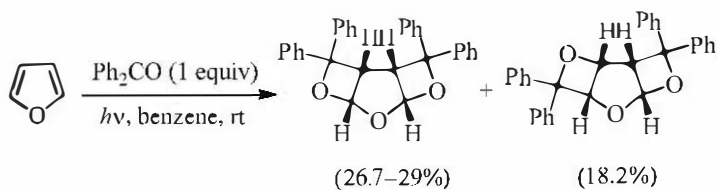
Scheme 85



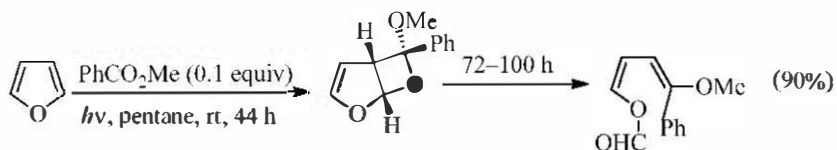
Scheme 86



Scheme 87



Scheme 88

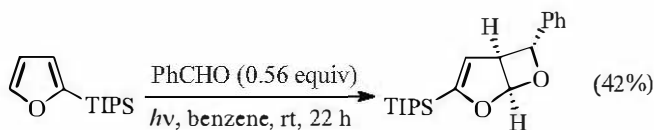


Scheme 89

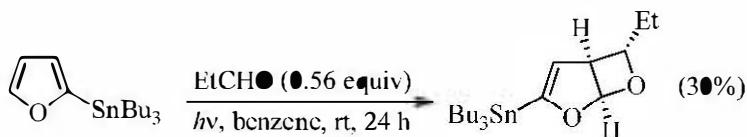
Aromatic α -cyano ketones also react with furan [314]. It is noteworthy that in the case of aromatic compounds, the yields of the oxetane are generally acceptable. In some cases, the high reactivity of the substrates allows the formation of products derived from attack of the carbonyl compounds on both carbon-carbon double bonds of furan. This result is observed when benzophenone is used in benzene as the solvent (Scheme 88) [73d, 252, 319, 320]. The reaction between furan and aromatic aldehydes can be used for didactic purposes to show chemical kinetics and possible synthetic uses of photochemistry [348].

The reaction of furan with chiral phenylglyoxylates gives the corresponding adduct with good yields and modest stereoselectivity (Scheme 87) [83b, 84, 85, 88].

The presence of substituents on the furan modifies both the reactivity and the regiochemistry of the reaction. Silyl- and stannyl-substituted furans react with aliphatic and aromatic carbonyl compounds in relatively low yields (Schemes 90 [75], 91 [75], 92 [76], 93 [76], and 94 [76]).

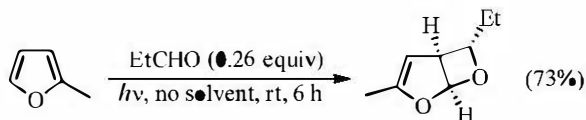


Scheme 90

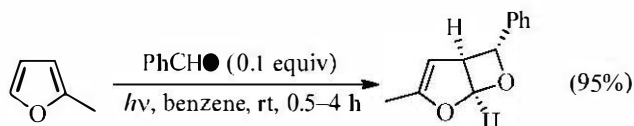


Scheme 91

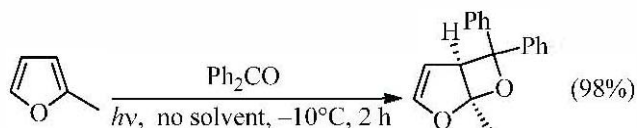
compound used in the reaction (Schemes 95 and 96) [53, 73a, 73c, 77, 84, 252, 309, 311, 316, 319, 323, 328].



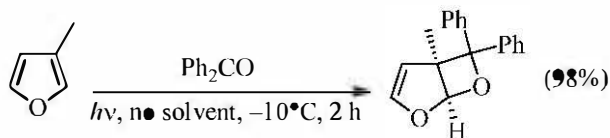
Scheme 95



Scheme 96



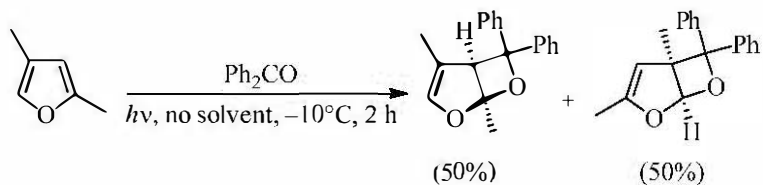
Scheme 97



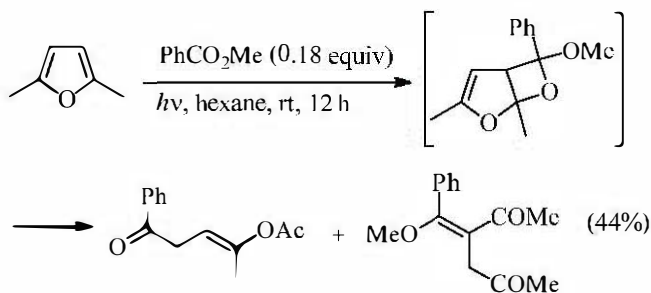
Scheme 98

In contrast, 3-methylfuran reacts mainly on the most substituted side of the molecule because the more stable biradical intermediate is formed (Scheme 98) [73c, 328].

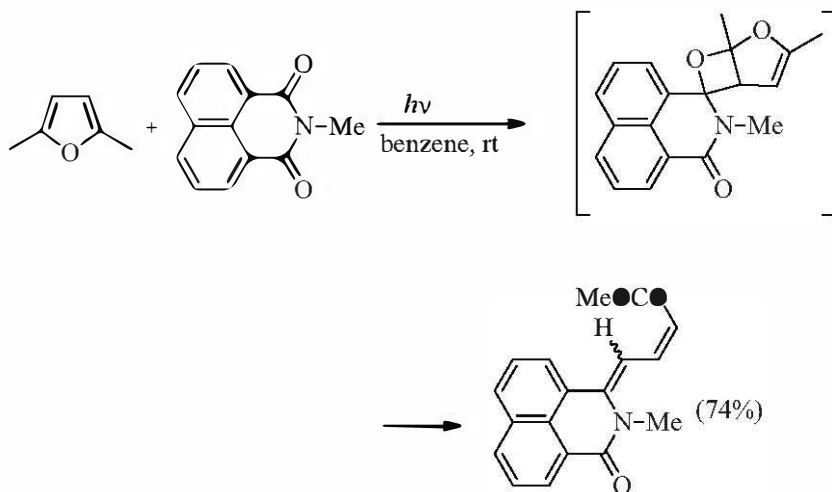
2,4-Dimethylfuran reacts with benzophenone to give a 1:1 mixture of the regioisomeric adducts (Scheme 99) [73c]. On the other hand, 2,5-dimethylfuran gives the ring metathesis product on reaction with methyl benzoate (Scheme 100) [311], and a bisadduct when the reaction is performed with benzophenone in benzene [252, 319]. The same result is obtained using 2-methyl-benzo[*de*]isoquinoline-1,3-dione as the substrate (Scheme 101) [113c]. 3,4-Dimethylfuran reacts with aliphatic aldehydes to give the corresponding adducts in variable yields (35-63%) [331, 332].



Scheme 99

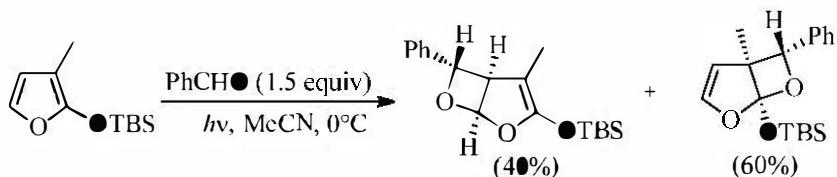


Scheme 100

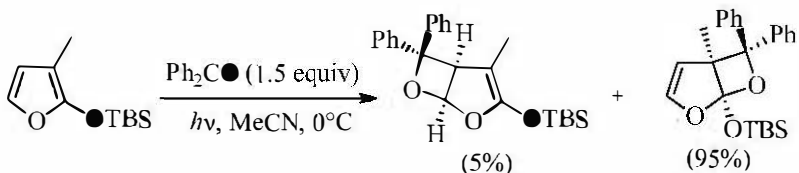


Scheme 101

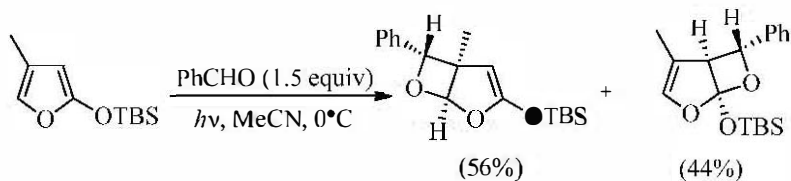
When both a methyl and an \bullet -silyl group are present in the furan, different behavior is observed. Thus, 2-*tert*-butyldimethylsilyloxy-3-methylfuran reacts with aliphatic carbonyl compounds with low selectivity [76]. The regioselectivity increases when using benzaldehyde, giving a 60:40 regioisomeric mixture where the attack on the most hindered side of the molecule is favored (Scheme 102) [76]. Aromatic ketones give mainly the product resulting from attack on the most hindered side of the molecule (Scheme 103) [76].



Scheme 102

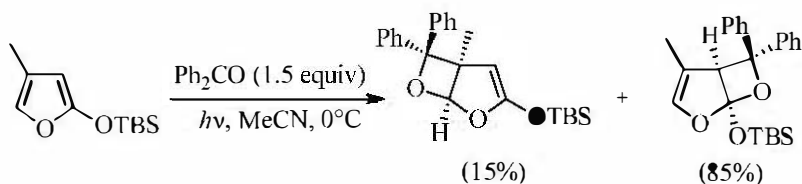


Scheme 103



Scheme 104

When the reaction is performed in the presence of $\text{MeCH}\bullet$ and $\text{PhCH}\bullet$, 2-*tert*-butyldimethylsilyloxy-4-methylfuran gives rise to a mixture where the prevalent product is that resulting from attack on the side bearing the methyl group, while in the presence of aromatic ketones, the main product is that resulting from attack on the side of the molecule bearing the silyloxy group (Schemes 104–105) [76].

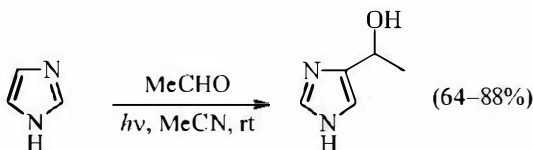


Scheme 105

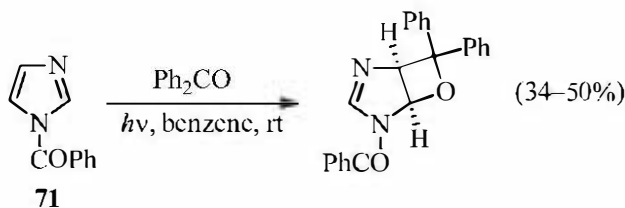
With regard to furylmethanol derivatives, the reactivity and, in particular, the stereoselectivity has been discussed above (cfr. Scheme 42). These reactions do not occur when using 2-cyanofuran and trichloroacetaldehyde as

reagents [309], while the cycloaddition is successful when 3-fluorobenzaldehyde is used as the carbonyl partner [77]. The reaction occurs on the most hindered side of the furan ring. 2-Furyl methyl ketone reacts with 4-cyanobenzaldehyde and some other substituted benzaldehydes to give the corresponding adducts with high regioselectivity (the reaction occurs on the side of the furan bearing the acetyl group) [77].

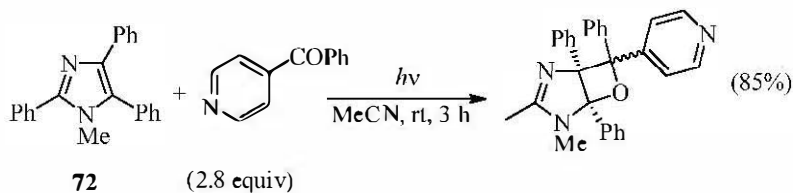
Imidazole reacts with acetaldehyde, but the corresponding oxetane opens spontaneously to recapture the aromaticity of the imidazole ring (Scheme 106) [302–305]. In contrast, both **71** and **72** allow isolation of the oxetane (Schemes 107 [304, 305] and 108 [343]).



Scheme 106

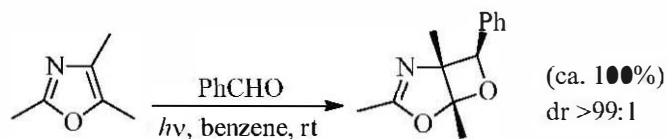


Scheme 107

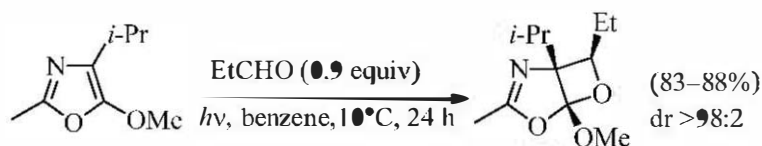


Scheme 108

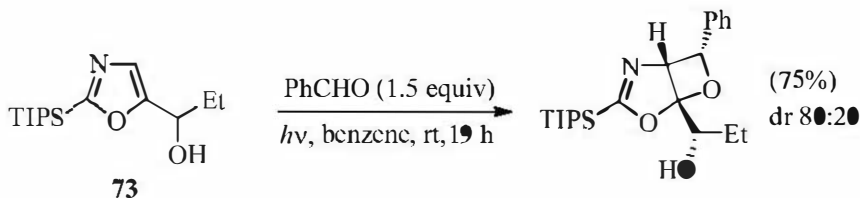
Isoxazole reacts with aromatic carbonyl compounds, but the yields of the oxetanes thus obtained are very low [306]. Results indicating the formation of the oxetanes in reasonable yields are obtained using 3,5-dimethylisoxazole, 3,4,5-trimethylisoxazole [305, 306], and 4,5-dimethylisoxazole [305]. Thiazole does not react with benzophenone [305], while 2,4-dimethylthiazole reacts with benzophenone, allowing the formation of the oxetane adduct, although in low yields [305]. 4-Methylisothiazole reacts with the methyl group [305].



Scheme 109



Scheme 110

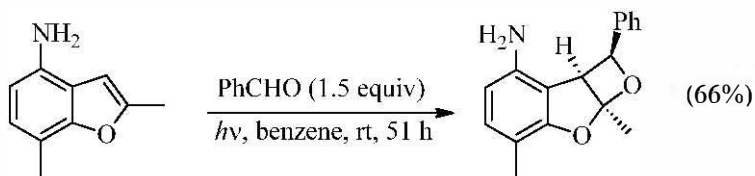


Scheme 111

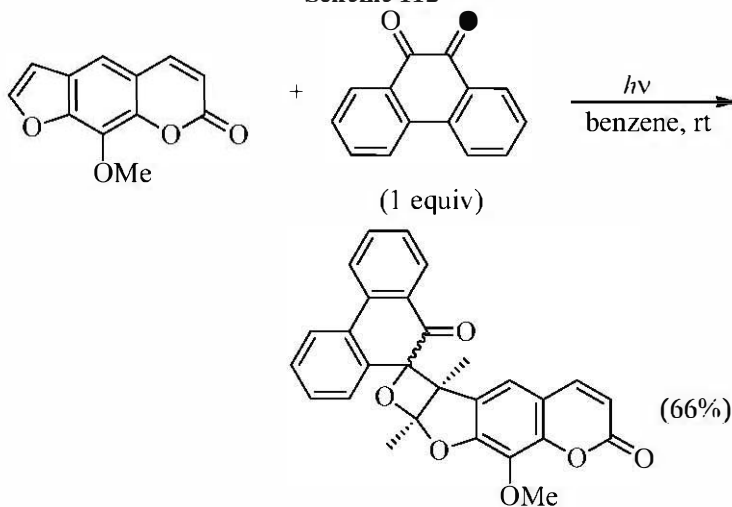
2,4,5-Trisubstituted oxazole derivatives give the Paternò–Büchi products in good yield and with high *exo* stereoselectivity (Schemes 109 [329] and 110 [255, 326]).

It is interesting to note that when oxazole **73** is irradiated in the presence of benzaldehyde, good *endo* stereoselectivity is observed in the oxetane product (Scheme 111) [327].

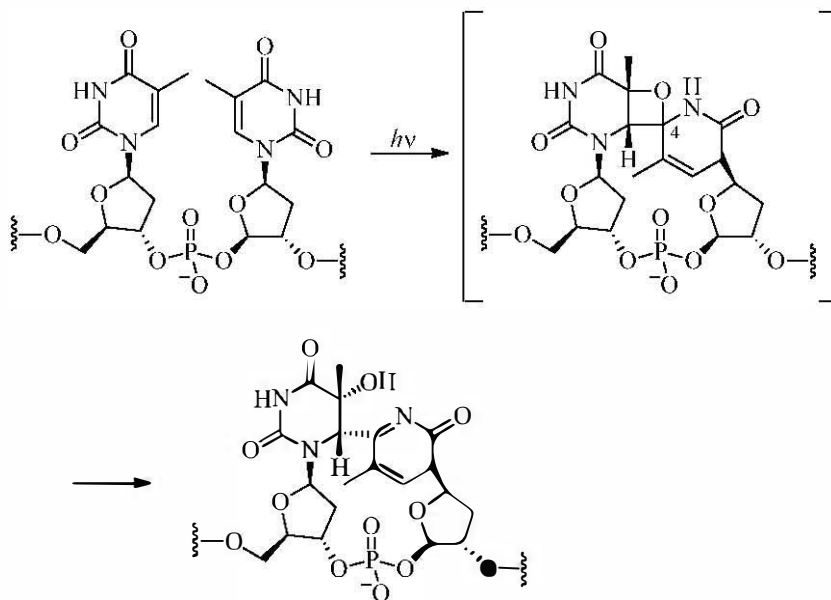
N-Benzoyl indole derivatives react with benzophenone to give the corresponding adducts in low to good yields depending on the carbonyl compounds used in the reaction [337]. The cycloaddition of several carbonyl compounds with benzofuran and other derivatives affords the corresponding oxetanes (Schemes 112 [340] and 113 [211]). Benzofuran does not react with 2,3-dimethylmaleic anhydride [210].



Scheme 112



Scheme 113



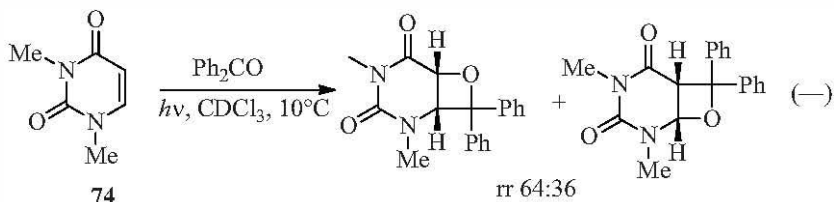
Scheme 114

Reactions with Six-Membered Heterocycles. As discussed above, the reactivity of heterocyclic compounds in Paternò–Büchi reaction is related to the aromaticity of the particular heterocycle. Compounds showing high aromatic character do not react. Therefore, reports on the reactivity of pyridine and pyridine derivatives cannot be found. The Paternò–Büchi reaction of six-membered heterocycles is restricted to the least aromatic compound, pyrimidine (*D* for pyridine: 0.92; pyrazine: 0.88, pyridazine: 0.88; pyrimidine: 0.87) [346].

A (6+4)–photoproduct is obtained as an adduct of two pyrimidines on adjacent sites on the same DNA strand. It is the second major lesion induced in DNA by UV radiation. (6+4)–Photoproducts are believed to be severely mutagenic. This process occurs via an initial intramolecular Paternò–Büchi-type cycloaddition to form an oxetane intermediate. Subsequent C4–C8 bond cleavage gives the observed (6+4) photoproducts (Scheme 114). The (6+4)–

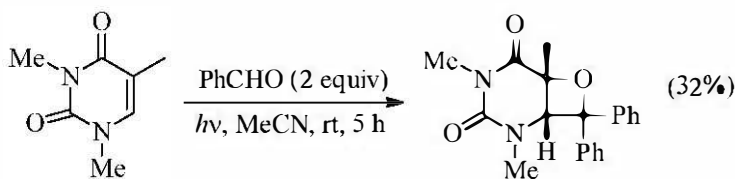
photoproduct is one of the major mutagenic classes of DNA photoproducts and is involved in the etiology of skin cancer.

Most of the research studies in this field have been conducted in NMR tubes, and the identification of the products has been performed on the basis of NMR spectra without isolation of the products. Therefore, most of the studies in this field have only speculative value and little preparative value. For example, the pyrimidine derivative **74**, when irradiated in the presence of benzophenone in CD₃CN, gives a 64:36 regioisomeric mixture of the oxetane adducts (Scheme 115) [54, 349].

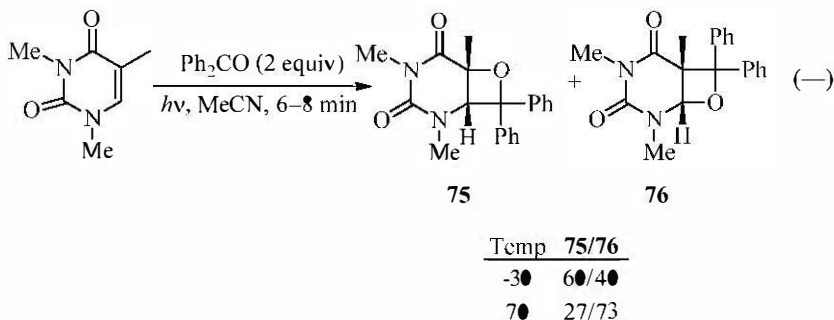


Scheme 115

When a methyl group is present at C5 of the pyrimidine substrate, the Paternò-Büchi reaction with benzaldehyde in MeCN furnishes only one regioisomeric oxetane in low yield (Scheme 116) [350]. When benzophenone is used as the carbonyl compound, both regioisomers are observed (Scheme 117). Furthermore, an interesting temperature effect is observed: at -30°C, a 60:40 mixture of **75** and **76** is obtained, while by irradiating the components at 70°C, a 27:73 regioisomeric mixture is observed [351].



Scheme 116

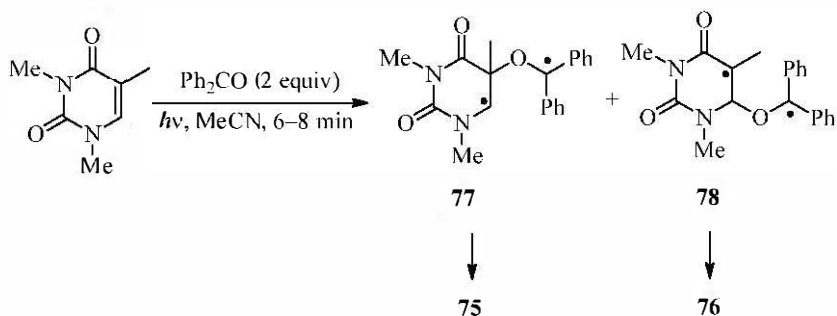


Scheme 117

This behavior is confirmed by determination of the composition of the reaction mixture performed via NMR [54, 349, 352]. However, only **75** is claimed as the reaction product in some reports [350]. A very similar regioisomeric mixture (**71:29**) is observed when the methyl group is at C-6 [54].

A change of the selectivity-determining step is postulated by consideration of a non-linear Eyring plot. Two different cases can be assumed: a situation wherein the rate of conformational changes of the triplet intermediates are slower than ISC at low temperature, and a case wherein the rate of conformational changes exceeds the ISC process [351]. When the conformational interchange is faster than the ISC process, the population of high potential energy conformations decreases, while the population of a lower potential energy conformer increases.

In a computational approach to this reaction [54], the biradical intermediates **77** and **78** are studied (Scheme 118). Compound **78** is more stable than **77**, and the formation of **77** is faster than **78**. Thus, **76** can be considered the thermodynamic product, while **75** is the kinetic one.



Scheme 118

Because of the energy barriers between the two stable conformers of each of the biradical intermediates **77** and **78**, the equilibrium is more favorable for the formation of the oxetane **76** than that for oxetane **75** at a higher temperature [349c]. Triplet benzophenones with short lifetimes give rise to a less efficient Paternò-Büchi reaction [349a].

A oxetane is also obtained in the reaction between benzophenone and benzophenone-derived drugs and thymidine [353]. In laser flash photolysis experiments, the use of enantiopure ketoprofen in a Paternò-Büchi reaction with thymidine shows that thymidine gives a higher quenching constant of the triplet-triplet transition of ketoprofen when *R*-ketoprofen is used than when the *S*-enantiomer is employed. This quenching is related to the formation of the C–O bond, the first step of oxetane formation [354].

Table 12 collects all the results obtained in the Paternò-Büchi reaction on six-membered heterocycles.

Table 12. Intermolecular reactions with six-membered heterocyclic compounds.

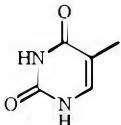
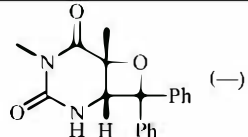
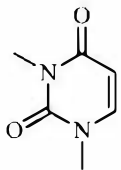
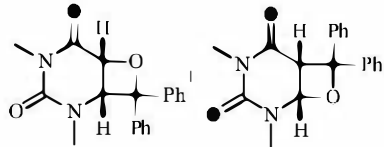
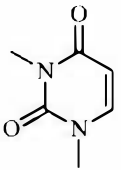
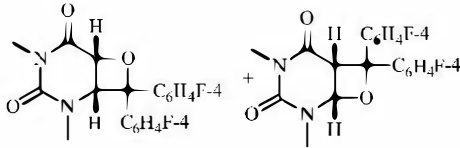
Substrate	Carbonyl compound	Product (Yields %)	Ref.												
	Ph ₂ CO (1 equiv)	 (—)	355												
	Ph ₂ CO (1 equiv)	 <table border="1" data-bbox="813 554 1197 683"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(51) 64:36</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(39) 65:35</td> </tr> <tr> <td>C₆D₆-CD₃CN</td> <td>-</td> <td>(29) 58:42</td> </tr> </tbody> </table>	Solvent	Temp	rr	CD ₃ CN	10	(51) 64:36	CD ₃ CN	25	(39) 65:35	C ₆ D ₆ -CD ₃ CN	-	(29) 58:42	54 349a 349b 349c
Solvent	Temp	rr													
CD ₃ CN	10	(51) 64:36													
CD ₃ CN	25	(39) 65:35													
C ₆ D ₆ -CD ₃ CN	-	(29) 58:42													
	(4-FC ₆ H ₄) ₂ CO (1 equiv)	 <table border="1" data-bbox="790 840 1157 963"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(64) 63:37</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(49) 63:27</td> </tr> <tr> <td>C₆D₆-CD₃CN</td> <td>-</td> <td>(32) 49:51</td> </tr> </tbody> </table>	Solvent	Temp	rr	CD ₃ CN	10	(64) 63:37	CD ₃ CN	25	(49) 63:27	C ₆ D ₆ -CD ₃ CN	-	(32) 49:51	54 349a 349b 349c
Solvent	Temp	rr													
CD ₃ CN	10	(64) 63:37													
CD ₃ CN	25	(49) 63:27													
C ₆ D ₆ -CD ₃ CN	-	(32) 49:51													

Table 12. Continued

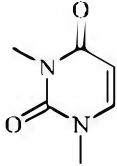
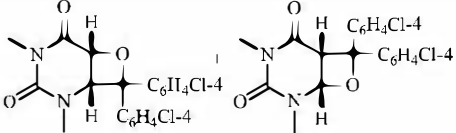
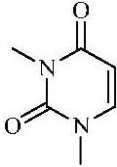
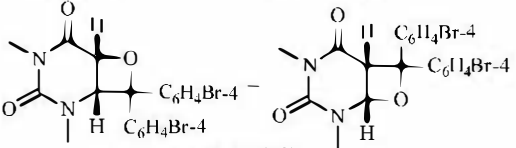
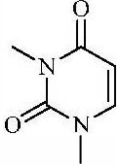
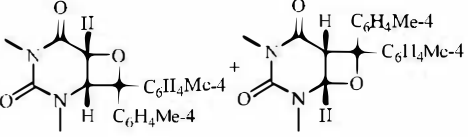
Substrate	Carbonyl compound	Product (Yields %)	Ref.												
	(4-ClC ₆ H ₄) ₂ CO (1 equiv)	 <table border="1" data-bbox="778 386 1157 498"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(70) 56:44</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(49) 54:46</td> </tr> <tr> <td>C₆H₆-CD₃CN</td> <td>-</td> <td>(35) 43:57</td> </tr> </tbody> </table>	Solvent	Temp	rr	CD ₃ CN	10	(70) 56:44	CD ₃ CN	25	(49) 54:46	C ₆ H ₆ -CD ₃ CN	-	(35) 43:57	54 349a 349b 349c
Solvent	Temp	rr													
CD ₃ CN	10	(70) 56:44													
CD ₃ CN	25	(49) 54:46													
C ₆ H ₆ -CD ₃ CN	-	(35) 43:57													
	(4-BrC ₆ H ₄) ₂ CO (1 equiv)	 <p style="text-align: center;">53:47 (28)</p>	349a												
	(4-MeC ₆ H ₄) ₂ CO (2 equiv)	 <table border="1" data-bbox="821 845 1141 964"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(38) 75:25</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(13) 77:23</td> </tr> <tr> <td>C₆D₆-CD₃CN</td> <td>-</td> <td>(14) 71:29</td> </tr> </tbody> </table>	Solvent	Temp	rr	CD ₃ CN	10	(38) 75:25	CD ₃ CN	25	(13) 77:23	C ₆ D ₆ -CD ₃ CN	-	(14) 71:29	54 349c
Solvent	Temp	rr													
CD ₃ CN	10	(38) 75:25													
CD ₃ CN	25	(13) 77:23													
C ₆ D ₆ -CD ₃ CN	-	(14) 71:29													

Table 12. *Continued*

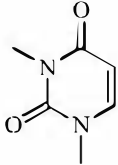
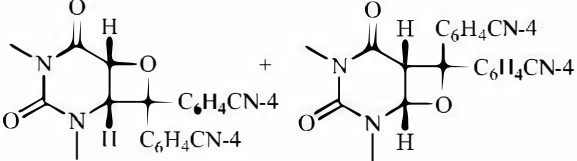
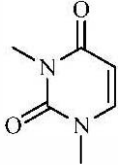
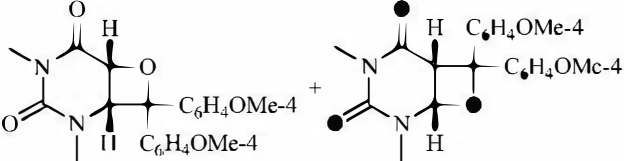
Substrate	Carbonyl compound	Product (Yields %)	Ref.																
	(4-CN-C ₆ H ₄) ₂ CO (1 equiv)	 <table border="1" data-bbox="735 418 1107 555"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th colspan="2">rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(75)</td> <td>39:61</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(51)</td> <td>38:62</td> </tr> <tr> <td>C₆H₆-CD₃CN</td> <td>-</td> <td>(39)</td> <td>32:68</td> </tr> </tbody> </table>	Solvent	Temp	rr		CD ₃ CN	10	(75)	39:61	CD ₃ CN	25	(51)	38:62	C ₆ H ₆ -CD ₃ CN	-	(39)	32:68	349a 349b 349c
Solvent	Temp	rr																	
CD ₃ CN	10	(75)	39:61																
CD ₃ CN	25	(51)	38:62																
C ₆ H ₆ -CD ₃ CN	-	(39)	32:68																
	(4-MeOC ₆ H ₄) ₂ CO (1 equiv)	 <table border="1" data-bbox="740 757 1112 893"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th colspan="2">rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(19)</td> <td>>95:5</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(7)</td> <td>>95:5</td> </tr> <tr> <td>C₆H₆-CD₃CN</td> <td>-</td> <td>(7)</td> <td>>95:5</td> </tr> </tbody> </table>	Solvent	Temp	rr		CD ₃ CN	10	(19)	>95:5	CD ₃ CN	25	(7)	>95:5	C ₆ H ₆ -CD ₃ CN	-	(7)	>95:5	54 349a 349b 349c
Solvent	Temp	rr																	
CD ₃ CN	10	(19)	>95:5																
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Table 12. *Continued*

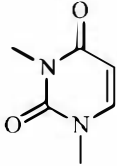
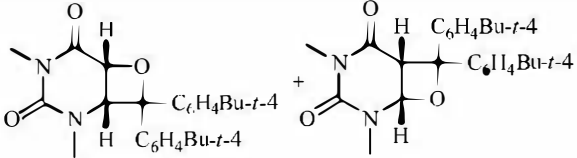
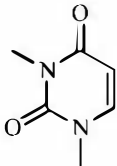
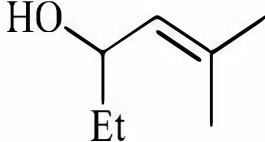
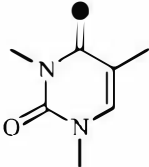
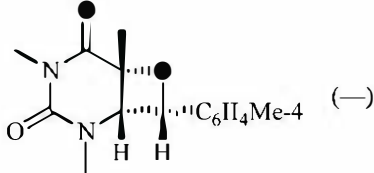
Substrate	Carbonyl compound	Product (Yields %)	Ref.																
	<p>(4-<i>t</i>-BuC₆H₄)₂CO (2 equiv)</p>	 <table border="1" data-bbox="762 431 1141 565"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th colspan="2">rr</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>10</td> <td>(60)</td> <td>70:30</td> </tr> <tr> <td>CD₃CN</td> <td>25</td> <td>(21)</td> <td>76:24</td> </tr> <tr> <td>C₆D₆-CD₃CN</td> <td>-</td> <td>(16)</td> <td>63:17</td> </tr> </tbody> </table>	Solvent	Temp	rr		CD ₃ CN	10	(60)	70:30	CD ₃ CN	25	(21)	76:24	C ₆ D ₆ -CD ₃ CN	-	(16)	63:17	<p>54 349b 349c</p>
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	<p>PhCHO (2 equiv)</p>		<p>350a 350b 356</p>																
	<p>4-MeC₆H₄CHO (2 equiv)</p>		<p>350a 356</p>																

Table 12. *Continued*

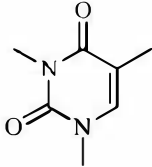
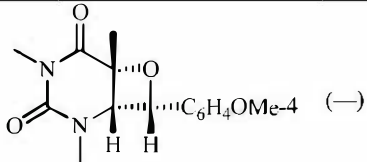
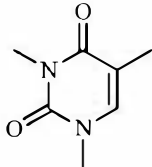
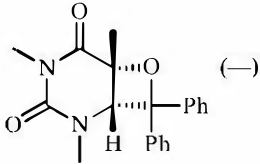
Substrate	Carbonyl compound	Product (Yields %)	Ref.
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	Ph ₂ CO (2 equiv)		350a 350b 356

Table 12. *Continued*

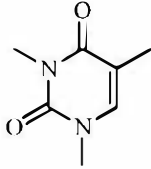
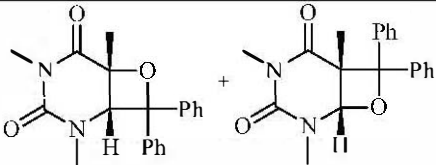
Substrate	Carbonyl compound	Product (Yields %)	Ref.																																							
	Ph ₂ CO (2 equiv)	 I II	351 357																																							
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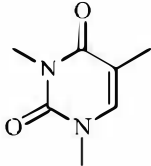
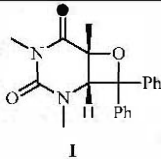
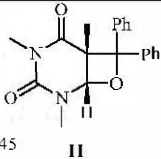
Substrate	Carbonyl compound	Product (Yields %)	Ref.																																																																																						
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Table 12. Continued

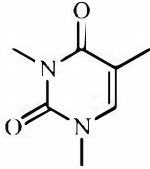
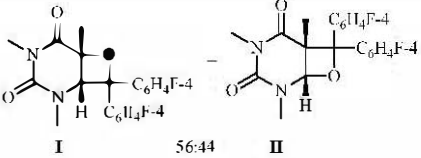
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Table 12. *Continued*

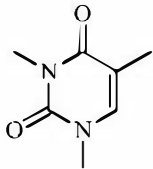
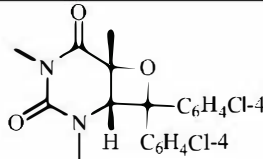
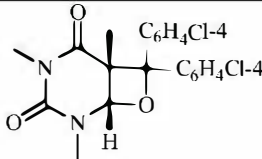
Substrate	Carbonyl compound	Product (Yields %)		Ref.
	(4-ClC ₆ H ₄) ₂ CO (1 equiv)	 I	 II	54 349a 349b 349c
		38:64	(77)	
		Solvent: C ₆ D ₆ -D ₃ CN	Temp	I/II
Temp	time [min]	I/II		
-30	15	49:51 (61)		-27.4 (75.6) 54:46
-20	15	48:52 (54)		-21.4 (68.5) 52:48
0	5	45:55 (57)		-11.5 (69.6) 46:54
20	10	43:57 (66)		-0.9 (74.7) 42:58
40	15	35:65 (80)		9.9 (75.0) 39:61
50	20	32:68 (77)		20.1 (74.4) 34:66
60	5	31:69 (32)		25 (26) 8:92
				30.0 (63.4) 30:70
				40.0 (67.4) 26:74
				49.5 (62.8) 21:79
				60.0 (63.5) 17:83
				69.1 (59.8) 14:86

Table 12. *Continued*

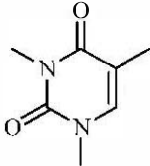
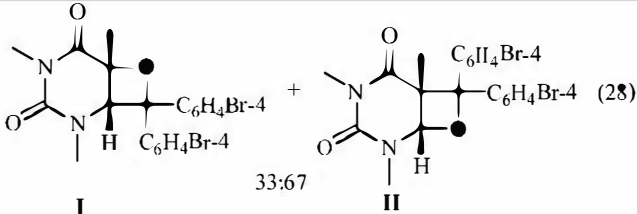
Substrate	Carbonyl compound	Product (Yields %)	Ref.																								
	(4-BrC ₆ H ₄) ₂ CO (1 equiv)	 I + II (28) 33:67	349a																								
		<table border="1"> <thead> <tr> <th data-bbox="805 490 869 517">Temp</th> <th data-bbox="885 490 1029 517">I/II</th> </tr> </thead> <tbody> <tr> <td data-bbox="805 528 869 551">-27.4</td> <td data-bbox="885 528 1029 551">(37.6) 50:50</td> </tr> <tr> <td data-bbox="805 562 869 584">-21.4</td> <td data-bbox="885 562 1029 584">(37.5) 46:54</td> </tr> <tr> <td data-bbox="805 595 869 618">-11.5</td> <td data-bbox="885 595 1029 618">(44.4) 40:60</td> </tr> <tr> <td data-bbox="805 629 869 651">-0.9</td> <td data-bbox="885 629 1029 651">(38.6) 36:64</td> </tr> <tr> <td data-bbox="805 663 869 685">9.9</td> <td data-bbox="885 663 1029 685">(38.5) 31:69</td> </tr> <tr> <td data-bbox="805 696 869 719">20.1</td> <td data-bbox="885 696 1029 719">(32.8) 30:70</td> </tr> <tr> <td data-bbox="805 730 869 752">30.0</td> <td data-bbox="885 730 1029 752">(29.2) 25:75</td> </tr> <tr> <td data-bbox="805 763 869 786">40.0</td> <td data-bbox="885 763 1029 786">(26.7) 23:77</td> </tr> <tr> <td data-bbox="805 797 869 819">49.5</td> <td data-bbox="885 797 1029 819">(22.4) 18:82</td> </tr> <tr> <td data-bbox="805 831 869 853">60.0</td> <td data-bbox="885 831 1029 853">(14.5) 14:86</td> </tr> <tr> <td data-bbox="805 864 869 887">69.1</td> <td data-bbox="885 864 1029 887">(11.4) 10:90</td> </tr> </tbody> </table>	Temp	I/II	-27.4	(37.6) 50:50	-21.4	(37.5) 46:54	-11.5	(44.4) 40:60	-0.9	(38.6) 36:64	9.9	(38.5) 31:69	20.1	(32.8) 30:70	30.0	(29.2) 25:75	40.0	(26.7) 23:77	49.5	(22.4) 18:82	60.0	(14.5) 14:86	69.1	(11.4) 10:90	
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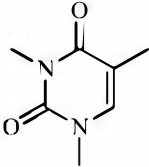
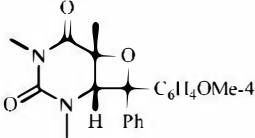
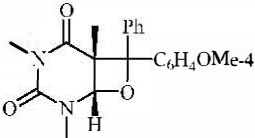
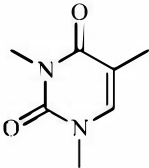
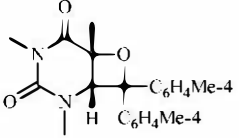
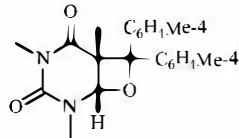
Substrate	Carbonyl compound	Product (Yields %)	Ref.																					
	PhCOC ₆ H ₄ OMe-4 (2 equiv)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>I</p> </div> <div style="text-align: center;">  <p>II</p> </div> </div> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Solvent</th> <th colspan="2">I/II</th> </tr> </thead> <tbody> <tr> <td>CD₃CN</td> <td>(96)</td> <td>44:56</td> </tr> <tr> <td>4:1 CD₃CN/D₂O</td> <td>(94)</td> <td>33:67</td> </tr> <tr> <td>3:2 CD₃CN/D₂O</td> <td>(89)</td> <td>28:72</td> </tr> <tr> <td>2:3 CD₃CN/D₂O</td> <td>(86)</td> <td>17:83</td> </tr> <tr> <td>1:3 CD₃CN/D₂O</td> <td>(28)</td> <td>7:93</td> </tr> <tr> <td>Benzene</td> <td>(100)</td> <td>32:68</td> </tr> </tbody> </table>	Solvent	I/II		CD ₃ CN	(96)	44:56	4:1 CD ₃ CN/D ₂ O	(94)	33:67	3:2 CD ₃ CN/D ₂ O	(89)	28:72	2:3 CD ₃ CN/D ₂ O	(86)	17:83	1:3 CD ₃ CN/D ₂ O	(28)	7:93	Benzene	(100)	32:68	352
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Table 12. Continued

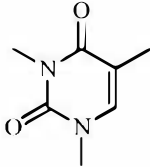
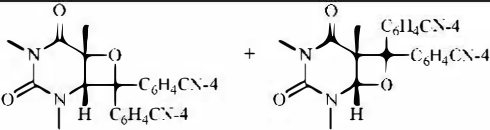
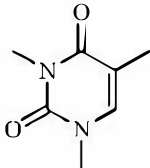
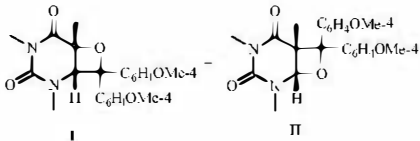
Substrate	Carbonyl compound	Product (Yields %)	Ref.																																																																																										
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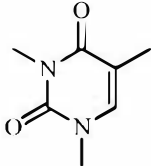
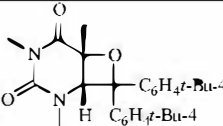
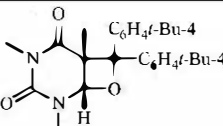
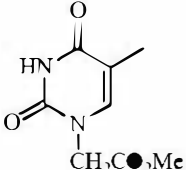
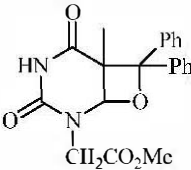
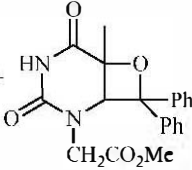
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				60	10	30:70																																																																																									
				70	10	26:74																																																																																									
	Ph ₂ CO (2 equiv)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>(19)</p> </div> <div style="text-align: center;">+</div> <div style="text-align: center;">  <p>(36)</p> </div> </div>		358																																																																																											

Table 12. *Continued*

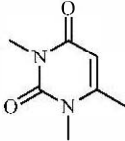
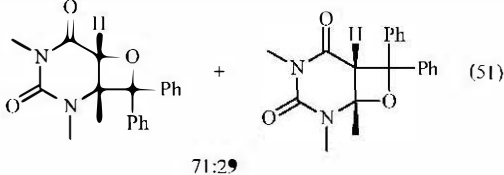
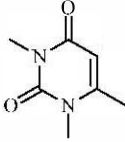
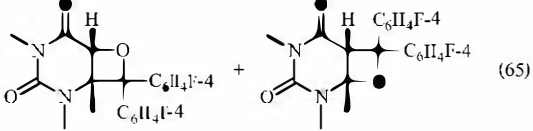
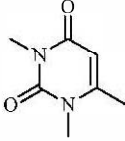
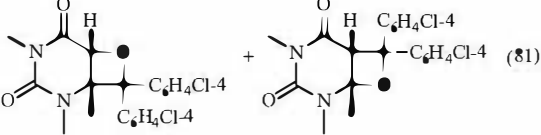
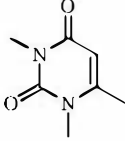
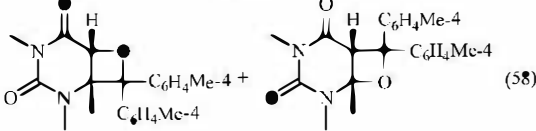
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Ph ₂ CO (2 equiv)	 71:29	54
	(4-FC ₆ H ₄) ₂ CO (2 equiv)	 64:36	54
	(4-ClC ₆ H ₄) ₂ CO (2 equiv)	 59:41	54
	(4-MeC ₆ H ₄) ₂ CO (2 equiv)	 82:18	54

Table 12. *Continued*

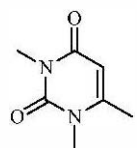
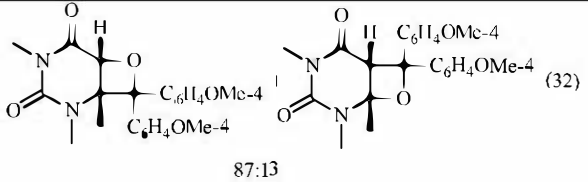
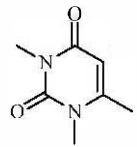
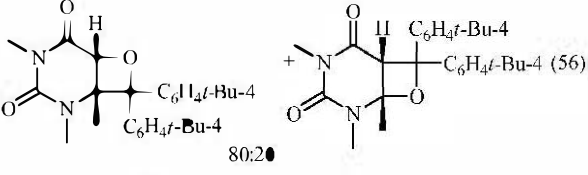
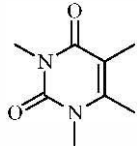
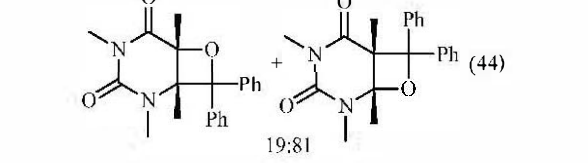
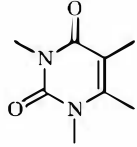
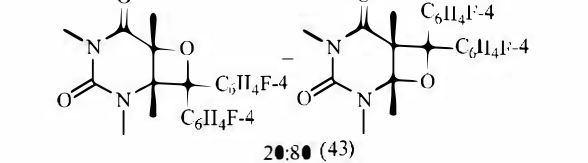
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	(4-MeOC ₆ H ₄) ₂ CO (2 equiv)		54
	(4- <i>t</i> -BuC ₆ H ₄) ₂ CO (2 equiv)		54
	Ph ₂ CO (2 equiv)		54
	(4-FC ₆ H ₄) ₂ CO (2 equiv)		54

Table 12. Continued

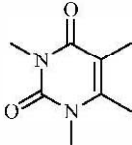
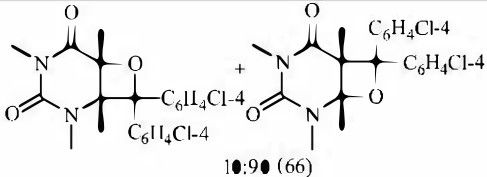
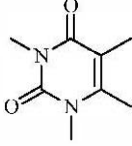
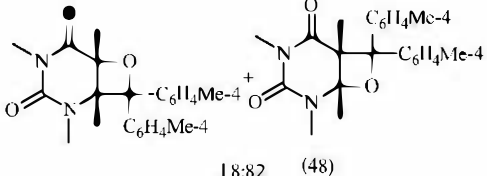
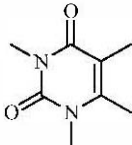
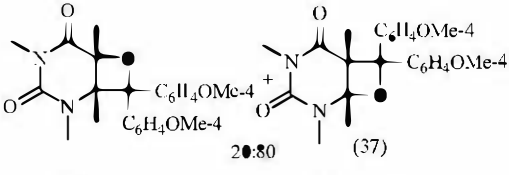
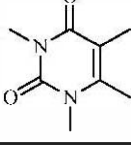
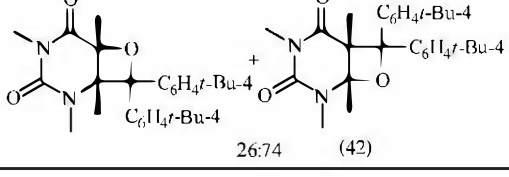
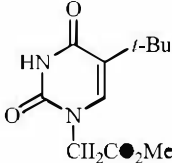
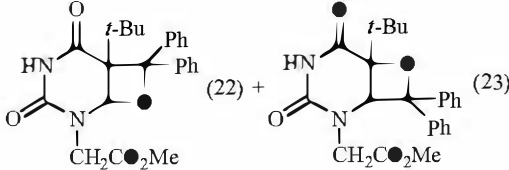
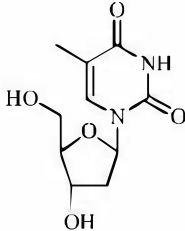
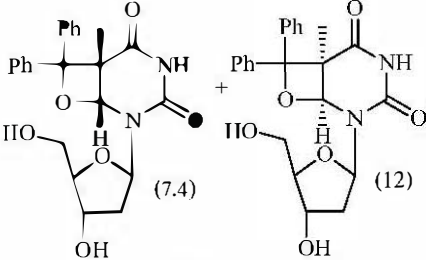
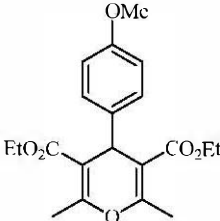
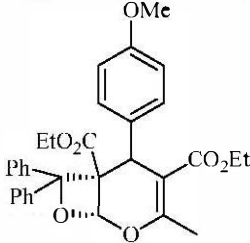
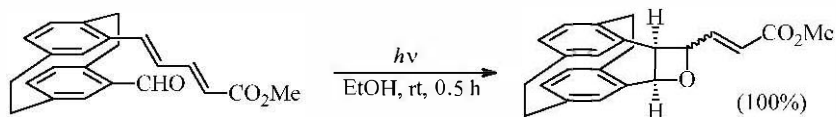
Substrate	Carbonyl compound	Product (Yields %)	Ref.
	(4-ClC ₆ H ₄) ₂ CO (2 equiv)	 10:90 (66)	54
	(4-MeC ₆ H ₄) ₂ CO (2 equiv)	 18:82 (48)	54
	(4-MeOC ₆ H ₄) ₂ CO (2 equiv)	 20:80 (37)	54
	(4- <i>t</i> -BuC ₆ H ₄) ₂ CO (2 equiv)	 26:74 (42)	54

Table 12. *Continued*

Substrate	Carbonyl compound	Product (Yields %)	Ref.
	Ph ₂ CO (2 equiv)		358
	Ph ₂ CO (2 equiv)		353 354
	Ph ₂ CO (0.05 equiv)	 (—)	359

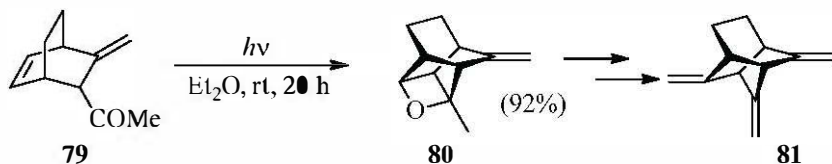
Intramolecular Reactions

An intramolecular Paternò–Büchi reaction on a paracyclophane derivative is reported to give the corresponding adduct in quantitative yield (Scheme 119) [360].

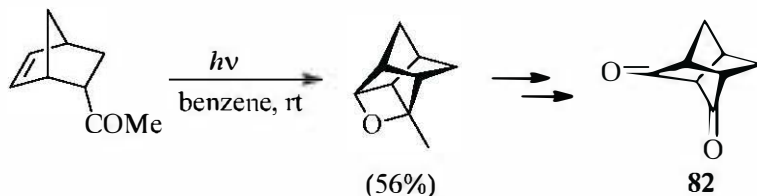


Scheme 119

An intramolecular Paternò–Büchi reaction of **79** to give oxetane **80** is used in the synthesis of 2,7,9-trimethylenetricyclo[4.3.0.0^{3,8}]nonane **8** (Scheme 120) [361].

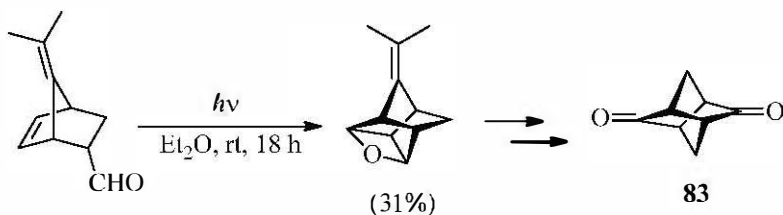


Scheme 120

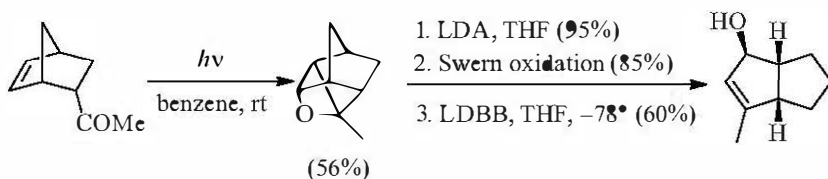


Scheme 121

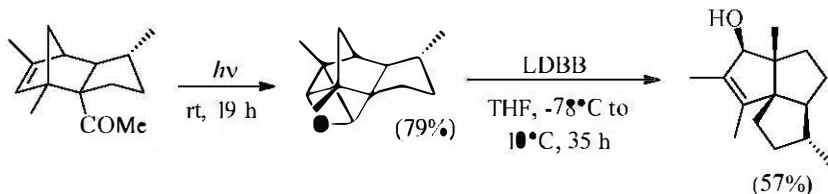
The same synthetic scheme is used in the synthesis of 2,7,9-trimethylenetricyclo[4.3.0.0^{3,8}]non-4-ene [362]. The preparation of some stelladiones such as tricyclo[3.3.0.0^{3,7}]octane-2,4-dione **82** or tricyclo[3.3.0.0^{3,7}]octane-2,6-dione **83** is carried out by using the same approach (Schemes 121–122) [363]. This type of intramolecular Paternò–Büchi reaction is the key step used in the synthesis of diquinanes and triquinanes (Schemes 123 [364] and 124 [365]).



Scheme 122

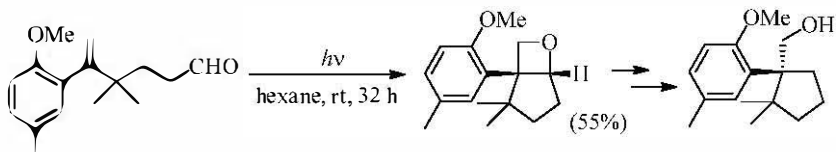


Scheme 123



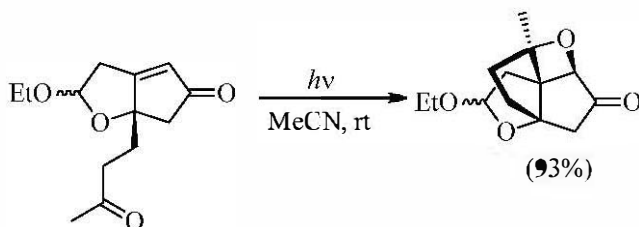
Scheme 124

The synthesis of 1,13-herbertenediol is performed using an intramolecular Paternò–Büchi reaction between an aldehydic group and an α -alkyl-substituted styrene moiety (Scheme 125) [366].



Scheme 125

An intramolecular, stereoselective Paternò–Büchi reaction is the key step in the synthesis of some derivatives of *R*-(+)-sclareolide [367]. A synthesis of the scaffold of merrilactone A also involves an intramolecular [2+2] cycloaddition to give the corresponding adduct (Scheme 126) [368]. The reaction of a carbonyl group with an electron-poor alkene has been reported in another case [490].

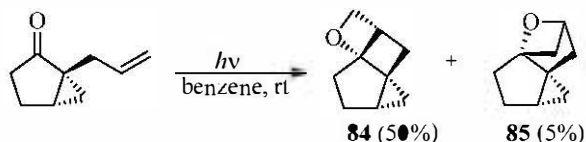


Scheme 126

On the other hand, an approach to the synthesis of thromboxane analogs using an intramolecular reaction of a ketone with an enol ether allows one to obtain the expected oxetane derivative in only 11% yield [369].

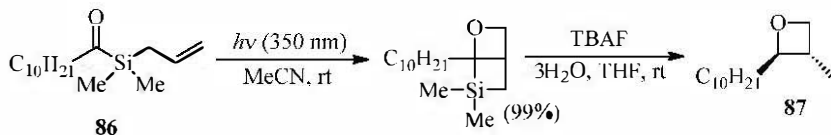
Intramolecular reactions on allyl cyclopentanone derivatives has been reported [370]. In this case, both *linear* (**84**) and *crossed* (**85**) oxetanes are obtained (Scheme 127). Using 2-allylcyclopentanone, nearly equal amounts of

these isomers are obtained. However, the use of the more rigid starting material (such as that in the Scheme 127) allows the preferential formation of the *linear* isomer.



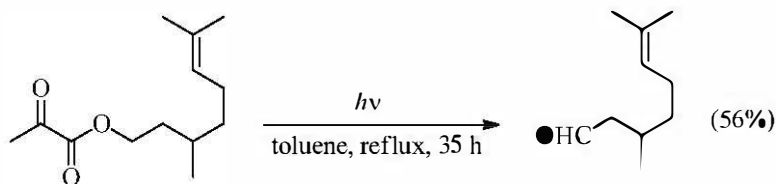
Scheme 127

Compound **86** gives a quantitative yield of the corresponding oxetane through an intramolecular Paternò–Büchi reaction. The oxetane thus obtained is converted into **87** via fluoride desilylation (Scheme 128) [371].

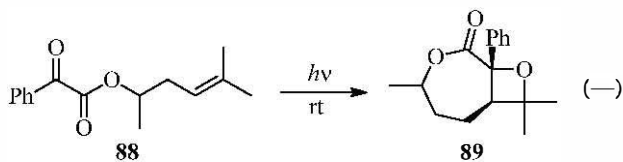


Scheme 128

When alkenyl glyoxylates are used as substrates in attempted Paternò–Büchi reactions, a Norrish type II reaction is the main pathway occurring in most cases (Scheme 129) [372]. A few exceptions are observed, however. For example, the reaction of compound **88** gives oxetane adduct **89** (Scheme 130). [372, 373]

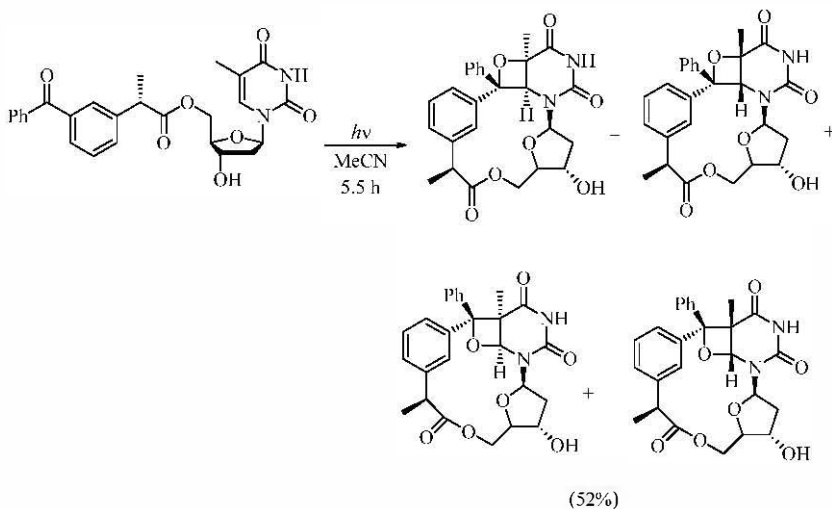


Scheme 129



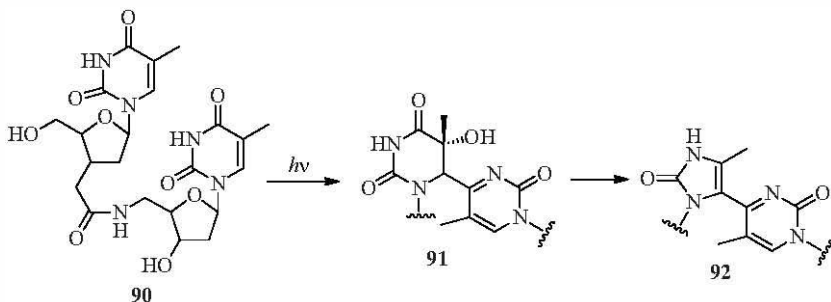
Scheme 130

Enamine derivatives reacts with imine to give a aza-Paternò-Büchi reaction [487]. An intramolecular reaction between thymidine esterified by ketoprofen is reported to give a mixture of the corresponding oxetane adducts (Scheme 131) [374].



Scheme 131

The irradiation of **90** gives **92** derived from the (6+4)-photoadduct **91** (Scheme 132) [375].



Scheme 132

All the reactions performed in this field are collected in Table 13.

Limitations Attributable to the Properties of the Carbonyl Compounds

Carbonyl compounds able to react with an alkene to give the corresponding oxetane must be able to access an $n \rightarrow \pi^*$ singlet or triplet state [23]. This is the most important limitation of the carbonyl compounds. Furthermore, the reaction fails when there is not a good correlation between the HOMO of the alkene and the LUMO of the excited state of the carbonyl compounds. Carbonyl compounds that usually react through the excited singlet state such as naphthyl-substituted aldehydes and ketones are unreactive toward less reactive alkenes [23, 299]. Some substituents on the carbonyl compounds seem to prevent the reaction. The presence of a double bond allows a [2+2] cycloaddition reaction between the alkenes. Furthermore, the presence of nitrile [116c, 290a, 290b], amino [23], and hydroxy groups [144] sometimes inhibits the reaction.

Table 13. Intramolecular reactions

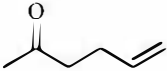

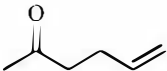
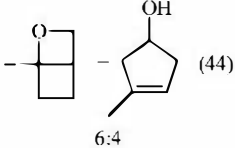
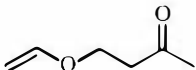
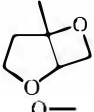
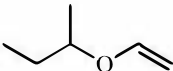
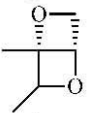
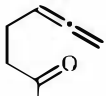
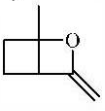
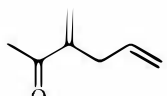
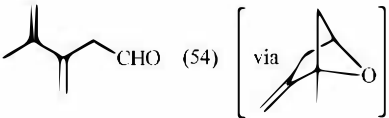


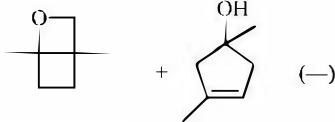
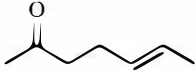
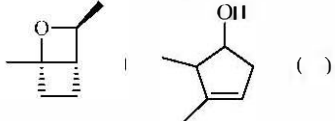


Substrate	Product (yields %)	Ref.
	 (—)	22
	 (44) 6:4	376
	 (63)	69
	 (40)	377
	 (91)	378
	 (54) [via 	379
	 (—)	376
	 (—)	376 380
	 (30)	381

Table 13. *Continued*

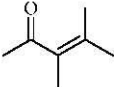

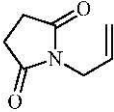
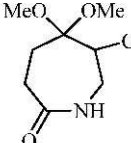
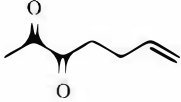
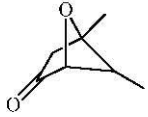
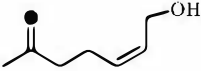
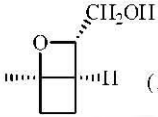
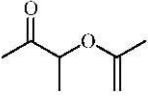
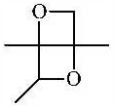
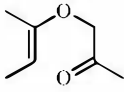
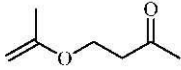

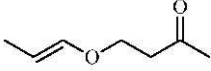
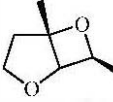
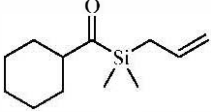
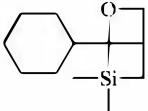


Substrate	Product (yields %)	Ref.
	 (—)	106a
	 (70)	382
	 (—)	383 384
	 (10)	385
	 +  (—)	386
	 (72)	69
	 (64)	69
	 (52)	371
	 ()	387

Table 13. Continued


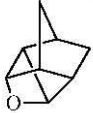
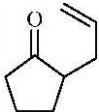





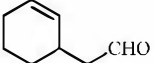
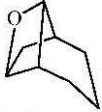
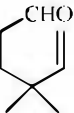


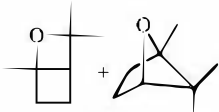
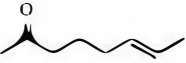

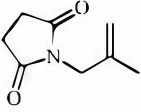

Substrate	Product (yields %)	Ref.
	 (57)	364a
	 (32) +  (22) +  (14)	370a
	 (18) +  (8)	
	 (40)	388
	 (—)	389
	 (56)	376
	 (—)	390
	 (ca. 100)	382

Table 13. Continued

Substrate	Product (yields %)	Ref.
		382
		391
		385
		385
		371
		392
		346a 346b 346c 346d
		393

Table 13. Continued

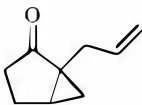
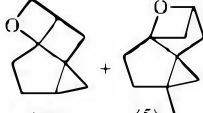
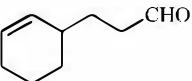
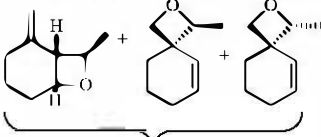
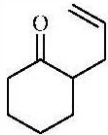
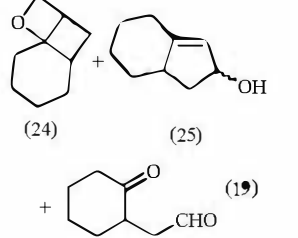
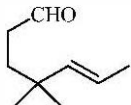
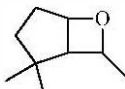
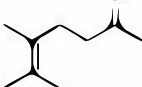
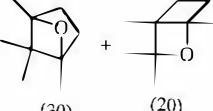
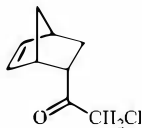

Substrate	Product (yields %)	Ref.
	 (50) + (5)	370b
	 (7.6)	394
	 (8.5) + (47) + (27)	370
	 (24)	395
	 (30) + (20)	396
	 (43)	397

Table 13. *Continued*

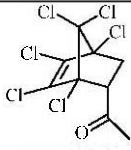
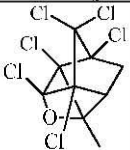
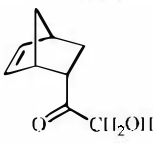
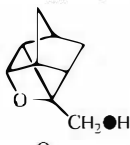
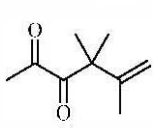
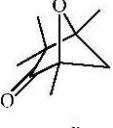
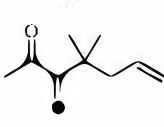
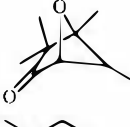
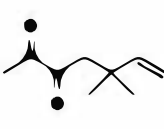
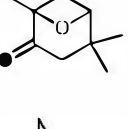

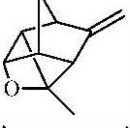
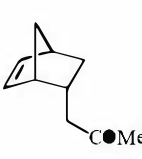
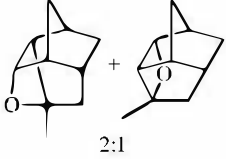


Substrate	Product (yields %)	Ref.
	 (55)	398
	 (47)	397
	 (94-100)	383 384
	 (—)	383 384
	 (—)	384
	 (68)	246
	 (64) 2:1	399
	 (—)	364a

Table 13. Continued

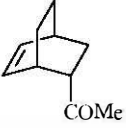


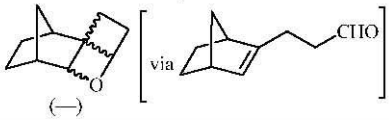
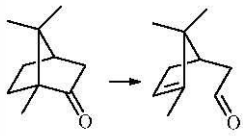
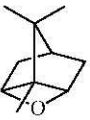
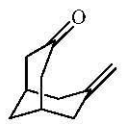
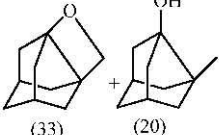
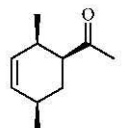
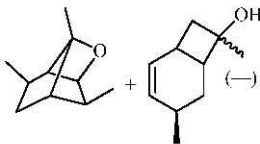
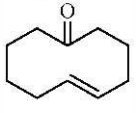
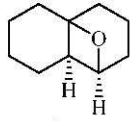
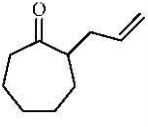
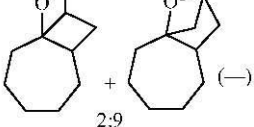
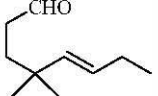
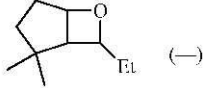
Substrate	Product (yields %)	Ref.
	 (88)	364a 393
		400
	 (1)	401
		402
		403
	 (27)	404
		405
		395

Table 13. Continued

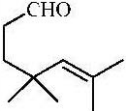
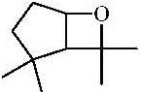
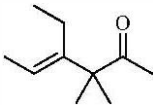
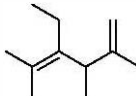

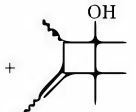
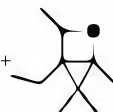


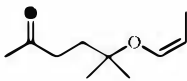

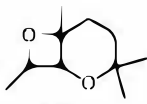
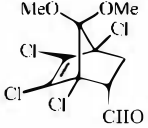
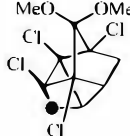
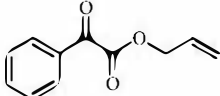


Substrate	Product (yields %)	Ref.
	 (—)	395
	 +  +  +  (0.05)	406
	 (0.04)	406
	 (9) +  (31)	369
	 (24)	398
	PhCHO + CH ₂ =CHCHO (—)	373
	 (31)	363

Table 13. Continued

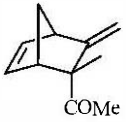

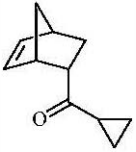

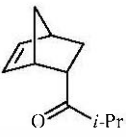

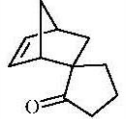

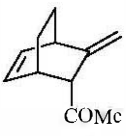
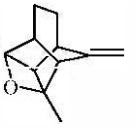
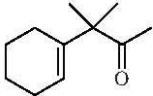
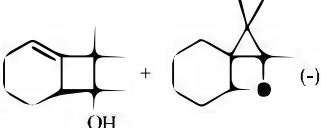
Substrate	Product (yields %)	Ref.
	 (61)	246
	 (—)	364a
	 (81)	364a 364c
	 (44)	136
	 (92)	361
	 (—)	407

Table 13. *Continued*

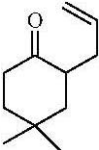
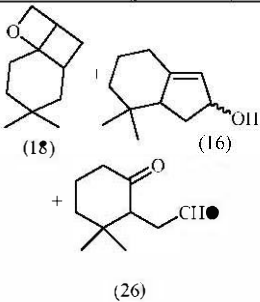
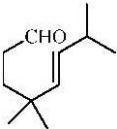
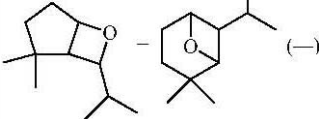
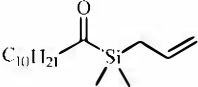
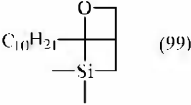
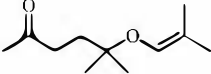
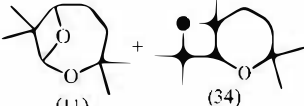
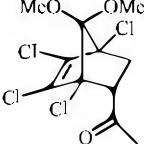
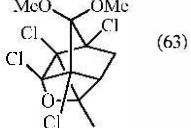

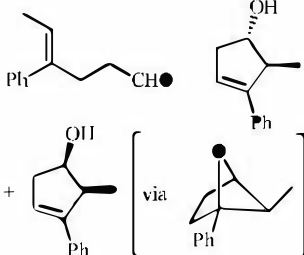
Substrate	Product (yields %)	Ref.
	 <p>(18) (16) (26)</p>	370a
	 <p>(-)</p>	389
	 <p>(99)</p>	371
	 <p>(11) (34)</p>	369
	 <p>(63)</p>	398
	 <p>(CH₂) (via)</p>	408

Table 13. Continued

Substrate	Product (yields %)	Ref.															
		409															
		370b															
		364a															
		410															
	<table border="1"> <thead> <tr> <th>Solvent</th> <th>I</th> <th>II</th> <th>III</th> <th>IV</th> </tr> </thead> <tbody> <tr> <td>pentane</td> <td>(7)</td> <td>(14)</td> <td>(20)</td> <td>(43)</td> </tr> <tr> <td>isopropanol</td> <td>(2)</td> <td>(2)</td> <td>(20)</td> <td>(4)</td> </tr> </tbody> </table>	Solvent	I	II	III	IV	pentane	(7)	(14)	(20)	(43)	isopropanol	(2)	(2)	(20)	(4)	
Solvent	I	II	III	IV													
pentane	(7)	(14)	(20)	(43)													
isopropanol	(2)	(2)	(20)	(4)													
		407															

Table 13. *Continued*

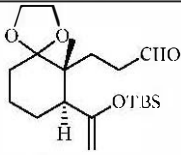
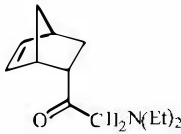
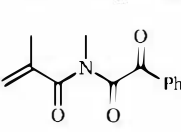
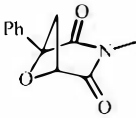


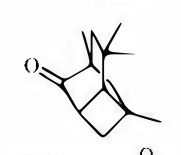

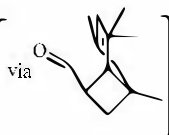
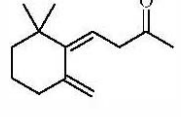
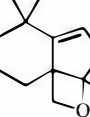
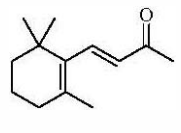
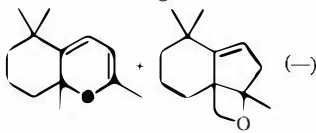
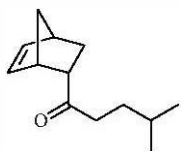

Substrate	Product (yields %)	Ref.
	No reaction	224
	No reaction	397
	 (94)	411
	 (—)	364a
	 (—) [via ]	409
	 (—)	412
	 (—)	412
	 (—)	364a

Table 13. Continued

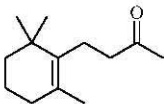
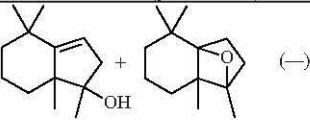
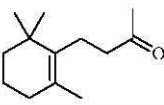
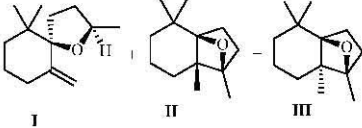
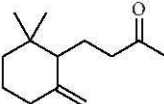
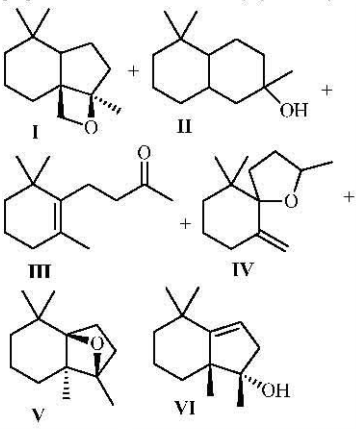
Substrate	Product (yields %)	Ref.																																																		
	 (—)	413																																																		
		396 410																																																		
	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>pentane</td> <td>25</td> <td>(16)</td> <td>(48)</td> <td>(22)</td> </tr> <tr> <td>1,2,3-triacetoxypropane</td> <td>60</td> <td>(13)</td> <td>(12)</td> <td>(9)</td> </tr> <tr> <td>diethyl ether</td> <td>20</td> <td>(14)</td> <td>(59)</td> <td>(21)</td> </tr> <tr> <td>diglycine</td> <td>13</td> <td>(23)</td> <td>(46)</td> <td>(19)</td> </tr> <tr> <td>ethylen glycol</td> <td>25</td> <td>(2)</td> <td>(46)</td> <td>(0)</td> </tr> <tr> <td>glycerol</td> <td>0</td> <td>(4)</td> <td>(28)</td> <td>(0)</td> </tr> <tr> <td>acetonitrile</td> <td>30</td> <td>(9)</td> <td>(72)</td> <td>(19)</td> </tr> <tr> <td>ethanol</td> <td>18</td> <td>(17)</td> <td>(46)</td> <td>(0)</td> </tr> <tr> <td>2-propanol</td> <td>25</td> <td>(16)</td> <td>(66)</td> <td>(18)</td> </tr> </tbody> </table>	Solvent	Temp	I	II	III	pentane	25	(16)	(48)	(22)	1,2,3-triacetoxypropane	60	(13)	(12)	(9)	diethyl ether	20	(14)	(59)	(21)	diglycine	13	(23)	(46)	(19)	ethylen glycol	25	(2)	(46)	(0)	glycerol	0	(4)	(28)	(0)	acetonitrile	30	(9)	(72)	(19)	ethanol	18	(17)	(46)	(0)	2-propanol	25	(16)	(66)	(18)	
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		410																																																		
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Solvent	I	II	III	IV	V	VI																																														
pentane	(16)	(6)	(3)	(3)	(10)	(5)																																														
isopropanol	(25)	(8)	(5)	(3)	(9)	(8)																																														

Table 13. Continued

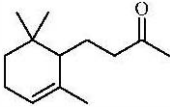
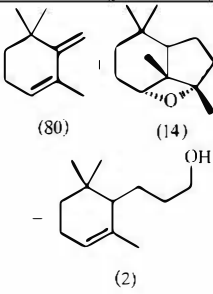
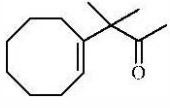
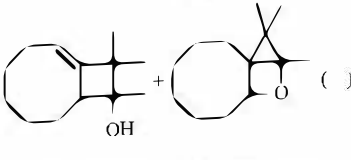
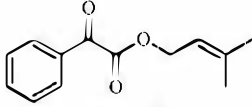
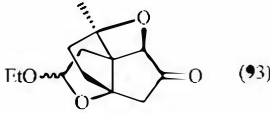
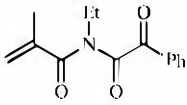
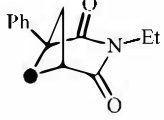
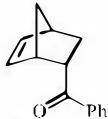
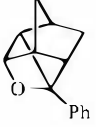

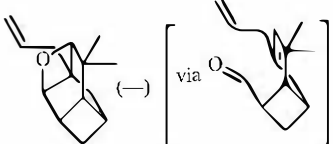
Substrate	Product (yields %)	Ref.
	 <p>(80) (14)</p> <p>(2)</p>	410
	 <p>()</p>	407
 <p>Et •</p> <p>CH₂CH₂C • Me</p>	<p>PhCHO + (CH₃)₂C=CHCHO (—)</p>  <p>(93)</p>	373
	 <p>(89)</p>	411
	 <p>()</p>	364a
	 <p>(—) [via O]</p>	409

Table 13. Continued

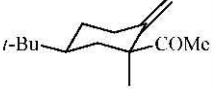

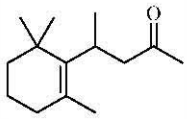
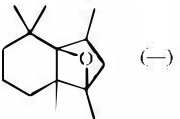
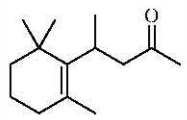
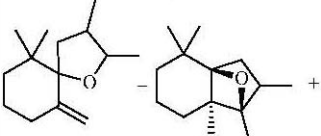

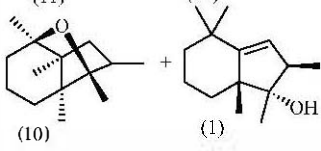
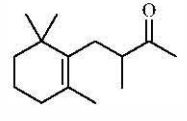
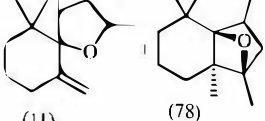
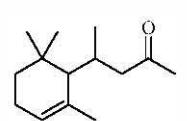
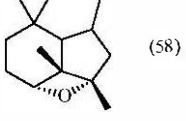
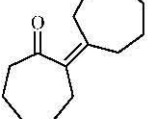
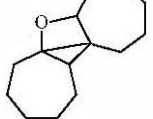
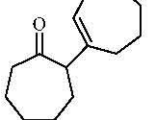
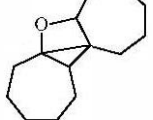
Substrate	Product (yields %)	Ref.
	 (13)	414
	 (–)	413
		410
		
		410
	 (58)	410
	 (32)	415
	 (32)	415

Table 13. *Continued*

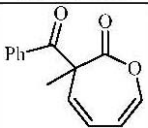
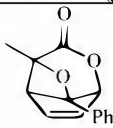
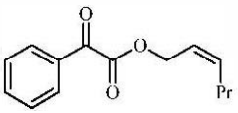
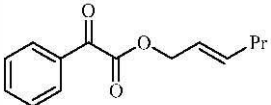
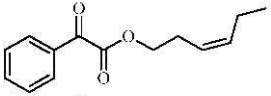
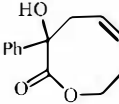
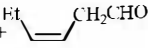
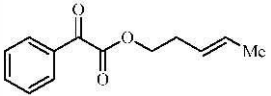
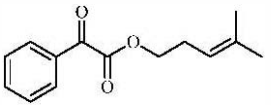
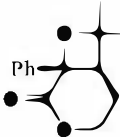
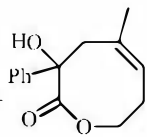
Substrate	Product (yields %)	Ref.
	 (30)	416
	PhCHO + PrCH=CHCHO (—)	373
	PhCHO + PrCH=CHCHO (—)	373
	 + PhCHO +  (—)	373
	PhCHO + EtCH=CHCHO (—)	373
	 I +  II	373
	Solvent	I/II
	DCM	1.4
	benzene	1.1
	2-propanol	—
	methanol	1.7
	acetonitrile	1.9

Table 13. Continued

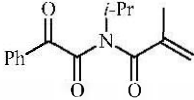
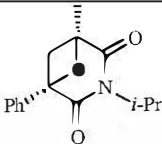
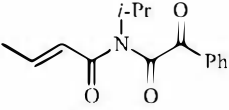
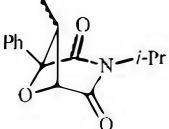


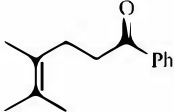
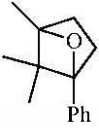

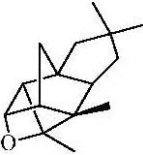


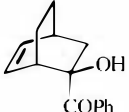
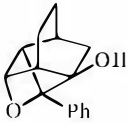
Substrate	Product (yields %)	Ref.
	 react. cond. _____ solid state (68) benzene (96)	36a 411
	 (48)	411
	 (ca. 100)	393 417
	 (ca. 100)	396
	 (90)	418
	 (79)	365
	 (—)	419

Table 13. Continued

Substrate	Product (yields %)	Ref.																
		373																
		36a																
	<table border="1"> <thead> <tr> <th>react. cond.</th> <th>Temp</th> <th>syn/anti</th> <th>cr (svn)</th> </tr> </thead> <tbody> <tr> <td>benzene</td> <td>-</td> <td>(100)</td> <td>2.1 -</td> </tr> <tr> <td>solid state</td> <td>0</td> <td>(84)</td> <td>3.7 67.5:32.5</td> </tr> <tr> <td>solid state</td> <td>-78</td> <td>(89)</td> <td>6.7 99.5:0.5</td> </tr> </tbody> </table>	react. cond.	Temp	syn/anti	cr (svn)	benzene	-	(100)	2.1 -	solid state	0	(84)	3.7 67.5:32.5	solid state	-78	(89)	6.7 99.5:0.5	
react. cond.	Temp	syn/anti	cr (svn)															
benzene	-	(100)	2.1 -															
solid state	0	(84)	3.7 67.5:32.5															
solid state	-78	(89)	6.7 99.5:0.5															
		417																
		415																
		366																
		166																
	No reaction	397																

Table 13. Continued

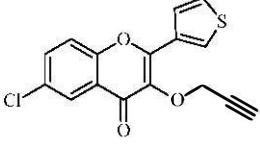
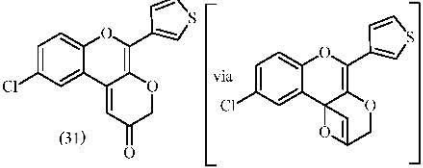
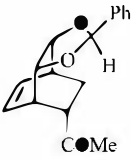
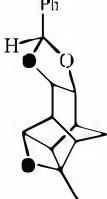
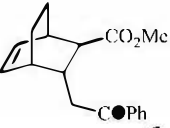
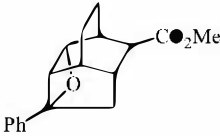
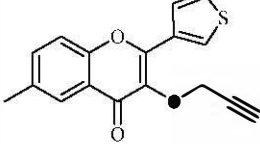
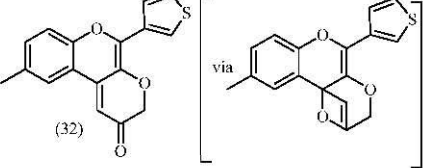
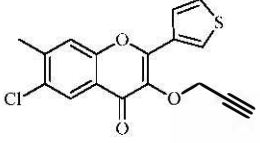
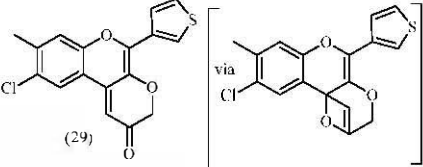
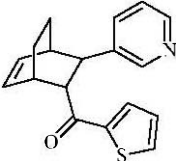
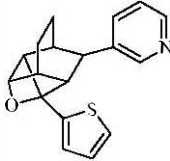
Substrate	Product (yields %)	Ref.
		420
		361
		421
		420
		420
		417

Table 13. Continued

Substrate	Product (yields %)	Ref.								
	 (ca. 100)	417								
	 <table border="0"> <tr> <td>react. cond.</td> <td></td> </tr> <tr> <td>benzene</td> <td>(100)</td> </tr> <tr> <td>solid state</td> <td>(—)</td> </tr> <tr> <td>MeCN</td> <td>(30)</td> </tr> </table>	react. cond.		benzene	(100)	solid state	(—)	MeCN	(30)	36a 36b 36c
react. cond.										
benzene	(100)									
solid state	(—)									
MeCN	(30)									
	 <table border="0"> <tr> <td>react. cond.</td> <td></td> </tr> <tr> <td>benzene</td> <td>(100)</td> </tr> <tr> <td>solid state</td> <td>(—)</td> </tr> </table>	react. cond.		benzene	(100)	solid state	(—)	36a		
react. cond.										
benzene	(100)									
solid state	(—)									
	 (ca. 100)	417								
	 (ca. 100)	417								
	 (—)	364a 422								

Table 13. Continued

Substrate	Product (yields %)	Ref.												
		364a 422												
	 <table border="1"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>-20</td> <td>(91)</td> <td>(6)</td> </tr> <tr> <td>-30</td> <td>(92)</td> <td>(4)</td> </tr> </tbody> </table>	Temp	I	II	-20	(91)	(6)	-30	(92)	(4)	87			
Temp	I	II												
-20	(91)	(6)												
-30	(92)	(4)												
	 <table border="1"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>(10)</td> <td>(19)</td> <td>(42)</td> </tr> <tr> <td>-65</td> <td>(5)</td> <td>(40)</td> <td>(29)</td> </tr> </tbody> </table>	Temp	I	II	III	rt	(10)	(19)	(42)	-65	(5)	(40)	(29)	410
Temp	I	II	III											
rt	(10)	(19)	(42)											
-65	(5)	(40)	(29)											
	 <table border="1"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>(10)</td> <td>(19)</td> <td>(42)</td> </tr> <tr> <td>-65</td> <td>(5)</td> <td>(40)</td> <td>(29)</td> </tr> </tbody> </table>	Temp	I	II	III	rt	(10)	(19)	(42)	-65	(5)	(40)	(29)	396
Temp	I	II	III											
rt	(10)	(19)	(42)											
-65	(5)	(40)	(29)											
	 <table border="1"> <thead> <tr> <th>Temp</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>(10)</td> <td>(19)</td> <td>(42)</td> </tr> <tr> <td>-65</td> <td>(5)</td> <td>(40)</td> <td>(29)</td> </tr> </tbody> </table>	Temp	I	II	III	rt	(10)	(19)	(42)	-65	(5)	(40)	(29)	
Temp	I	II	III											
rt	(10)	(19)	(42)											
-65	(5)	(40)	(29)											

Table 13. Continued

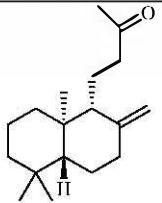
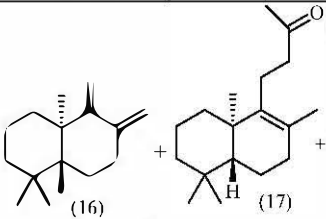
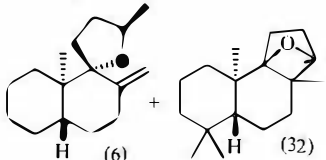
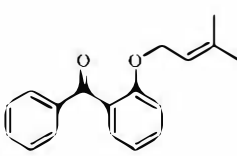
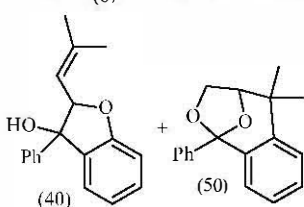
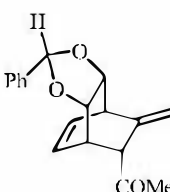
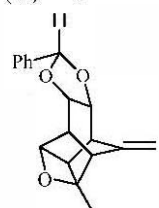
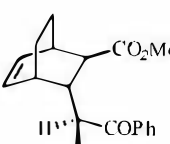
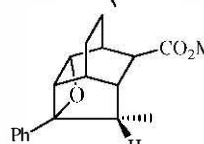
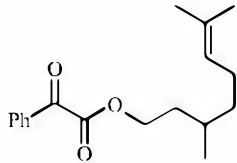
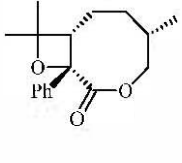
Substrate	Product (yields %)	Ref.
		396
		
		423
		362
		421
		372 373

Table 13. Continued

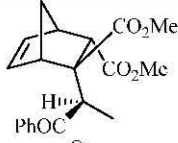
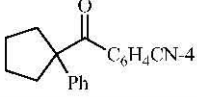
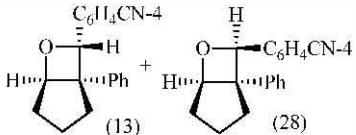
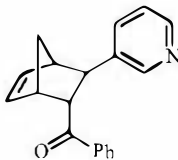
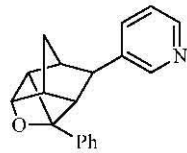
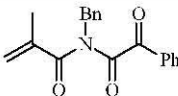
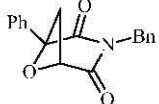
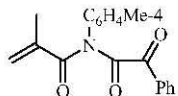
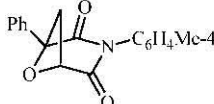
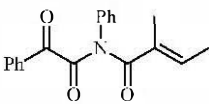
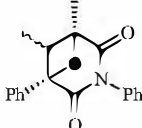
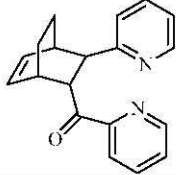
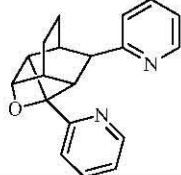
Substrate	Product (yields %)	Ref.
	No reaction	421
	 (13) (28)	87
	 (ca. 100)	417
	 react. cond. _____ benzene (>99) solid state (50)	86a 411
	 (50)	411
	 react. cond. _____ benzene (76) <i>syn/anti</i> 2.1 solid state (0) -	86a
	 (ca. 100)	417

Table 13. Continued

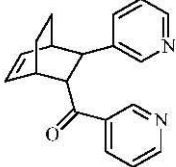
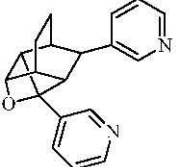
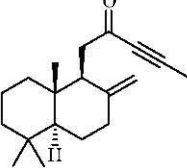
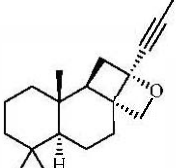
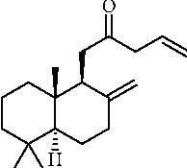
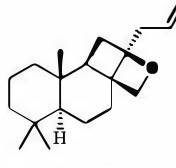
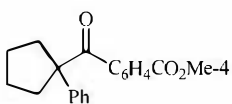
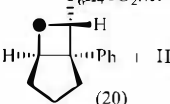
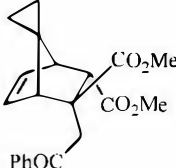
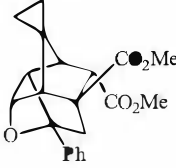
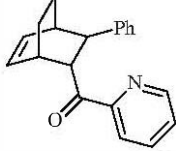
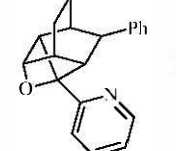
Substrate	Product (yields %)	Ref.
	 (ca. 100)	417
	 (80)	367
	 (82)	367
	 (20)	87
	 (53)	421
	 (ca. 100)	417

Table 13. Continued

Substrate	Product (yields %)	Ref.																
	(ca. 100)	417																
	(ca. 100)	417																
	(ca. 100)	417																
	(ca. 100)	417																
	(ca. 100)	417																
	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>react. cond.</td> <td></td> </tr> <tr> <td>benzene</td> <td>(100)</td> </tr> <tr> <td>solid state</td> <td>(—)</td> </tr> </table>	react. cond.		benzene	(100)	solid state	(—)	86a										
react. cond.																		
benzene	(100)																	
solid state	(—)																	
	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>react. cond.</td> <td>Temp</td> <td><i>syn/anti</i></td> <td>er (<i>syn</i>)</td> </tr> <tr> <td>solid state</td> <td>15</td> <td>(100)</td> <td>60</td> </tr> <tr> <td>solid state</td> <td>-78</td> <td>(100)</td> <td>60</td> </tr> <tr> <td>benzene</td> <td>-</td> <td>(100)</td> <td>2.1</td> </tr> </table>	react. cond.	Temp	<i>syn/anti</i>	er (<i>syn</i>)	solid state	15	(100)	60	solid state	-78	(100)	60	benzene	-	(100)	2.1	86a
react. cond.	Temp	<i>syn/anti</i>	er (<i>syn</i>)															
solid state	15	(100)	60															
solid state	-78	(100)	60															
benzene	-	(100)	2.1															

Table 13. Continued

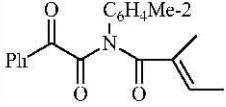
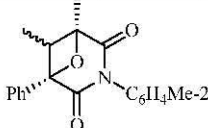
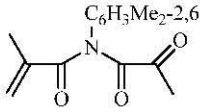
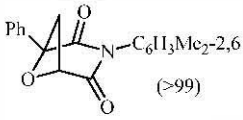
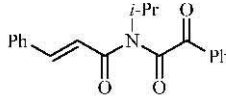
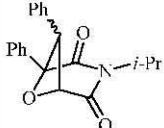
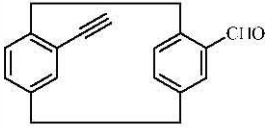
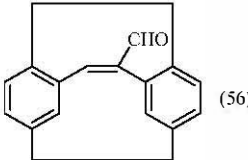
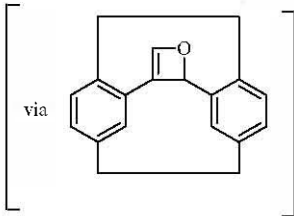
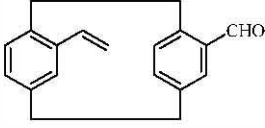
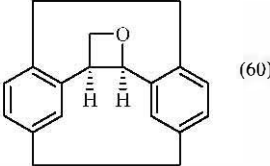
Substrate	Product (yields %)	Ref.									
		36a									
	<table border="1"> <thead> <tr> <th>react. cond.</th> <th>syn/anti</th> <th>er (syn)</th> </tr> </thead> <tbody> <tr> <td>solid state</td> <td>(100)</td> <td>27</td> </tr> <tr> <td>benzene</td> <td>(100)</td> <td>2.1</td> </tr> </tbody> </table>	react. cond.	syn/anti	er (syn)	solid state	(100)	27	benzene	(100)	2.1	
react. cond.	syn/anti	er (syn)									
solid state	(100)	27									
benzene	(100)	2.1									
		411									
	(>99)										
		411									
	(44)										
		360									
	(56)										
											
	via										
		360									
	(60)										

Table 13. Continued

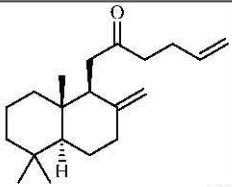
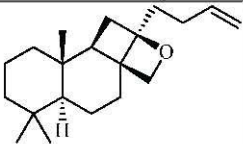
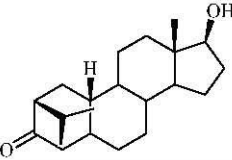
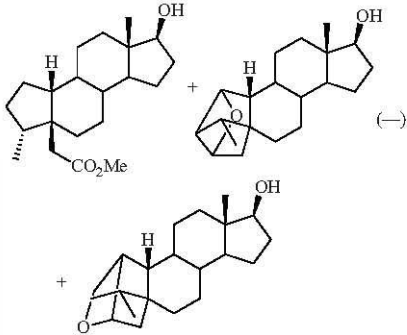
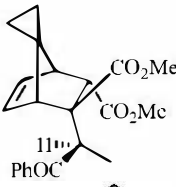
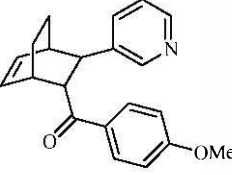
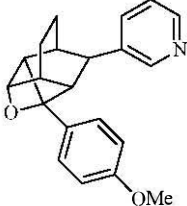
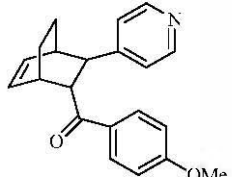
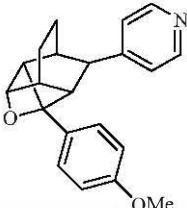
Substrate	Product (yields %)	Ref.
	 (84)	367
	 (–)	424
	No reaction	421
	 (ca. 100)	417
	 (ca. 100)	417

Table 13. *Continued*

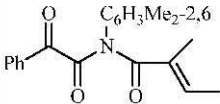
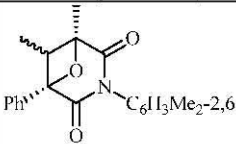
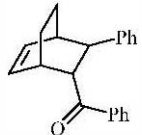
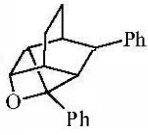
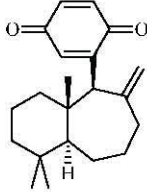
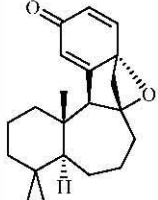
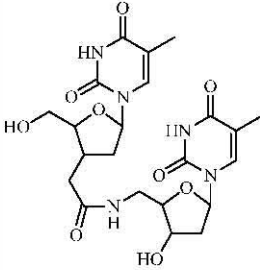
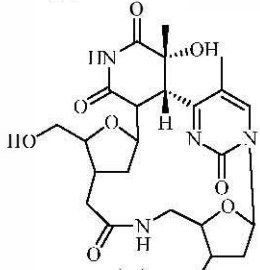
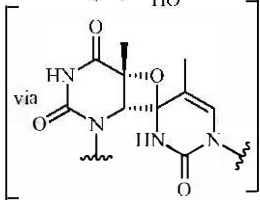
Substrate	Product (yields %)	Ref.									
		36a									
<table border="1"> <thead> <tr> <th data-bbox="482 408 572 432">react. cond.</th> <th data-bbox="572 408 684 432"><i>syn/anti</i></th> <th data-bbox="684 408 852 432">er (<i>syn</i>)</th> </tr> </thead> <tbody> <tr> <td data-bbox="482 440 572 464">solid state</td> <td data-bbox="572 440 684 464">(100)</td> <td data-bbox="684 440 852 464">20</td> </tr> <tr> <td data-bbox="482 472 572 496">benzene</td> <td data-bbox="572 472 684 496">(100)</td> <td data-bbox="684 472 852 496">2.1</td> </tr> </tbody> </table>	react. cond.	<i>syn/anti</i>	er (<i>syn</i>)	solid state	(100)	20	benzene	(100)	2.1		
react. cond.	<i>syn/anti</i>	er (<i>syn</i>)									
solid state	(100)	20									
benzene	(100)	2.1									
		417									
		425									
		375									
											

Table 13. Continued

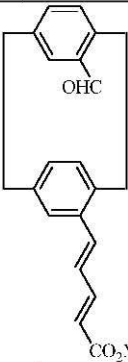
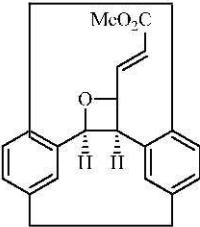
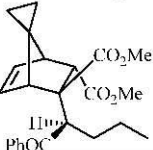
Substrate	Product (yields %)	Ref.
	 (100)	360
	No reaction	421

Table 13. Continued

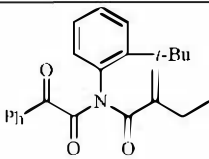
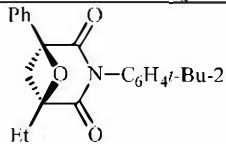
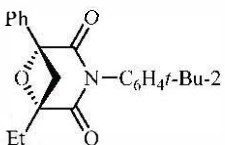
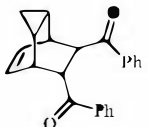
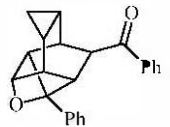
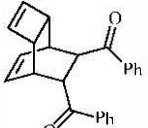
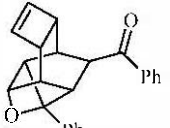
Substrate	Product (yields %)	Ref.	
 <p style="text-align: center;">I</p>	 <p style="text-align: center;">II</p>	<p>86b 86c</p>	
	 <p style="text-align: center;">III</p>		
Substrate	solvent	main product	
(<i>M</i>)- I	MeCN	(<i>R,R,M</i>)- II (81)	
(<i>P</i>)- I	MeCN	(<i>S,S,P</i>)- II	
(<i>M</i>)- I	benzene	(<i>R,R,M</i>)- II (78)	
(<i>P</i>)- I	benzene	(<i>S,S,P</i>)- II	
(<i>M</i>)- I	crystal		
(<i>P</i>)- I	crystal		
Substrate	dr	er II	er III
(<i>M</i>)- I	82:18	99.5:0.5	99.5:0.5
(<i>P</i>)- I		99:1	99:1
(<i>M</i>)- I	78:22	99.5:0.5	99.5:0.5
(<i>P</i>)- I		99:1	99:1
(<i>M</i>)- I	15:85	99:1	99:1
(<i>P</i>)- I	15:85	99:1	99:1
	 <p>(75)</p>	417	
	 <p>(34)</p>	417	

Table 13. Continued

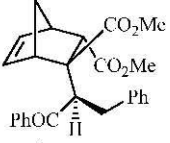
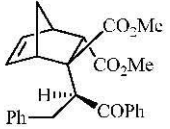
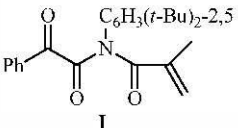
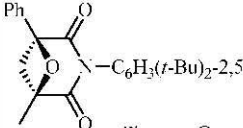
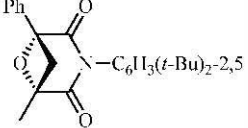
Substrate	Product (yields %)	Ref.																				
	No reaction	421																				
	No reaction	421																				
	 	86b 86c																				
	<table border="1"> <thead> <tr> <th>Substrate</th> <th>solvent</th> <th>main product</th> </tr> </thead> <tbody> <tr> <td>(-)-I</td> <td>MeCN</td> <td>(<i>R,R,M</i>)-II (78)</td> </tr> <tr> <td>(+)-I</td> <td>MeCN</td> <td>(<i>S,S,P</i>)-II</td> </tr> <tr> <td>(-)-I</td> <td>benzene</td> <td>(<i>R,R,M</i>)-II (90)</td> </tr> <tr> <td>(+)-I</td> <td>benzene</td> <td>(<i>S,S,P</i>)-II</td> </tr> </tbody> </table>	Substrate	solvent	main product	(-)- I	MeCN	(<i>R,R,M</i>)- II (78)	(+)- I	MeCN	(<i>S,S,P</i>)- II	(-)- I	benzene	(<i>R,R,M</i>)- II (90)	(+)- I	benzene	(<i>S,S,P</i>)- II						
Substrate	solvent	main product																				
(-)- I	MeCN	(<i>R,R,M</i>)- II (78)																				
(+)- I	MeCN	(<i>S,S,P</i>)- II																				
(-)- I	benzene	(<i>R,R,M</i>)- II (90)																				
(+)- I	benzene	(<i>S,S,P</i>)- II																				
	<table border="1"> <thead> <tr> <th>Substrate</th> <th>dr</th> <th>er II</th> <th>er III</th> </tr> </thead> <tbody> <tr> <td>(-)-I</td> <td>71:29</td> <td>99:1</td> <td>99:1</td> </tr> <tr> <td>(-)-I</td> <td></td> <td>99:1</td> <td>99:1</td> </tr> <tr> <td>(-)-I</td> <td>55:45</td> <td>98.5:1.5</td> <td>98.5:1.5</td> </tr> <tr> <td>(-)-I</td> <td></td> <td>98.5:1.5</td> <td>98.5:1.5</td> </tr> </tbody> </table>	Substrate	dr	er II	er III	(-)- I	71:29	99:1	99:1	(-)- I		99:1	99:1	(-)- I	55:45	98.5:1.5	98.5:1.5	(-)- I		98.5:1.5	98.5:1.5	
Substrate	dr	er II	er III																			
(-)- I	71:29	99:1	99:1																			
(-)- I		99:1	99:1																			
(-)- I	55:45	98.5:1.5	98.5:1.5																			
(-)- I		98.5:1.5	98.5:1.5																			

Table 13. Continued

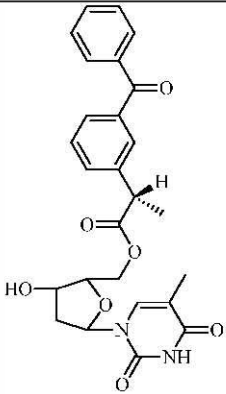
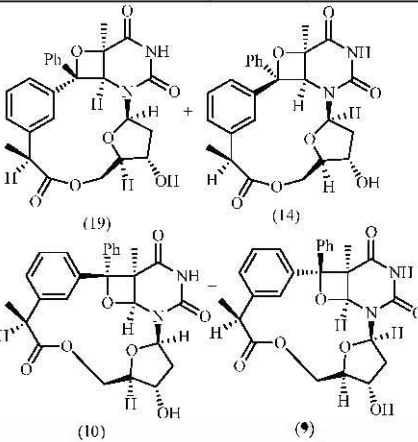
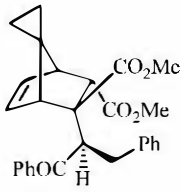
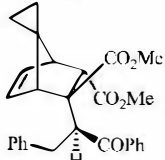
Substrate	Product (yields %)	Ref.
	 <p>(19) (14)</p> <p>(10) (9)</p>	374
	No reaction	421
	No reaction	421

Table 13. Continued

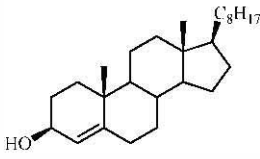
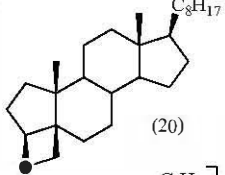
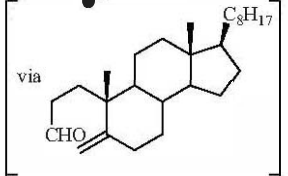
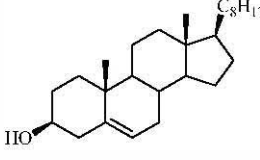
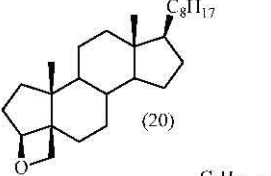
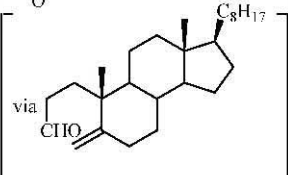
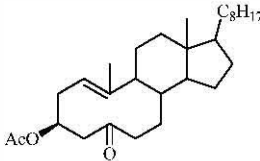
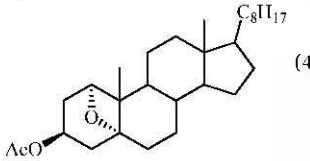
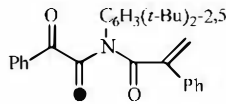
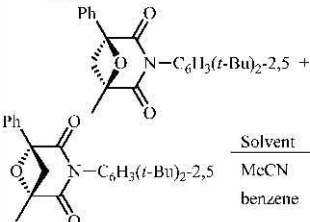
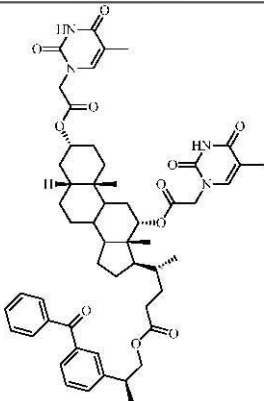
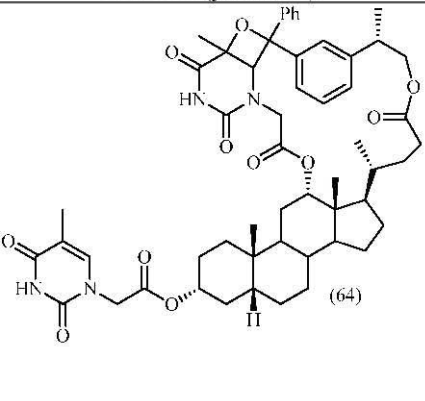
Substrate	Product (yields %)	Ref.						
	 (20) [via ]	426						
	 (20) [via ]	426						
	 (42)	427						
	 $N-C_6H_3(t-Bu)_2-2,5$	86b 86c						
	<table border="1"> <thead> <tr> <th>Solvent</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>MeCN (91)</td> <td>95:5</td> </tr> <tr> <td>benzene (90)</td> <td>89:11</td> </tr> </tbody> </table>	Solvent	dr	MeCN (91)	95:5	benzene (90)	89:11	
Solvent	dr							
MeCN (91)	95:5							
benzene (90)	89:11							

Table 13. Continued

Substrate	Product (yields %)	Ref.
	 (64)	428

Limitations Attributable to the Structure of the Unsaturated Compounds

Alkenes that react with quinone derivatives usually give the reaction product via an electron transfer mechanism. In this case, the ionization potential of the alkene is a critical parameter to allow the electron transfer to occur [115, 119, 123, 138, 155]. For example, quinone does not react with ethene (ionization energy 10.51 eV), although it reacts with *trans*-2-butene (ionization energy 9.10 eV). In the case of penta-atomic heterocyclic compounds, the aromatic character of the alkene can represent a serious limitation to the reactivity of these substrates.

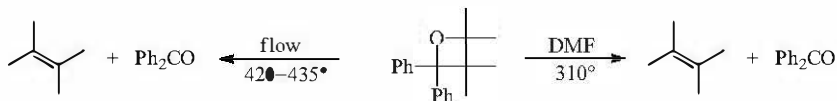
CHAPTER FOUR

APPLICATION TO SYNTHESIS

Cycloreversion

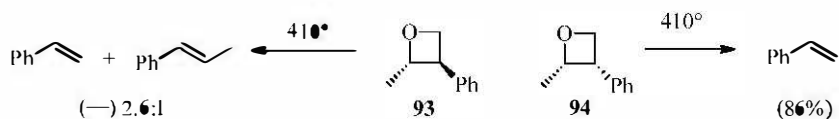
The oxetane ring can be easily opened, allowing for the synthesis of important scaffolds and the preparation of bioactive or naturally occurring compounds. Pyrolysis experiments are completely in agreement with the formation of a biradical intermediate during the fragmentation of the oxetane [429]. Pyrolysis is usually performed under nitrogen at 430–450°.

Some oxetanes are pyrolyzed in 10–20% solution or in a packed flow system (contact time, 10–15 sec). In diphenyl ether and DMF as well as in flow, high regioselectivity is observed (Scheme 133) [430]. The regioselectivity appears to be predictable on the basis of formation of the more stable biradical.



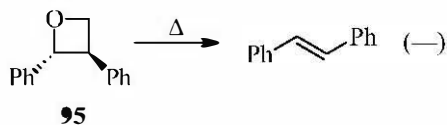
Scheme 133

The flow pyrolysis of the oxetane **93** at 410–470° (Scheme 134) affords styrene and (*E*)-phenylpropene in a 2.6:1 ratio. The resulting phenylpropene is obtained with 63% (*Z*) stereochemistry. The oxetane **94** gives mainly styrene (86%) [431].

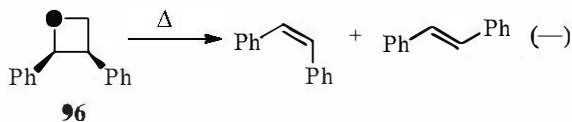


Scheme 134

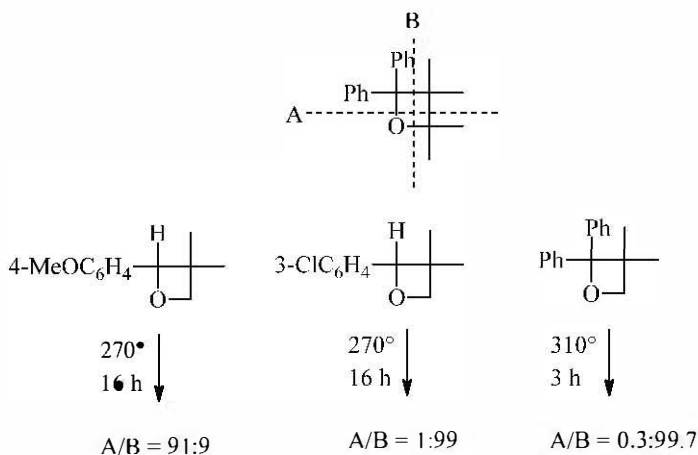
Thermolysis over 200° using pure oxetanes gives different results. Compound **95** gives only (*E*)-stilbene, while **96** does not show stereoselectivity at 280° (Schemes 135 and 136) [432]. However, the (*E*)/(*Z*) ratio shifts from 8:1 at 242° to 1:9 at 290° .



Scheme 135



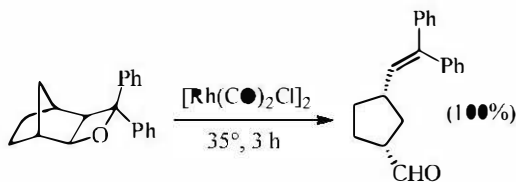
Scheme 136



Scheme 137

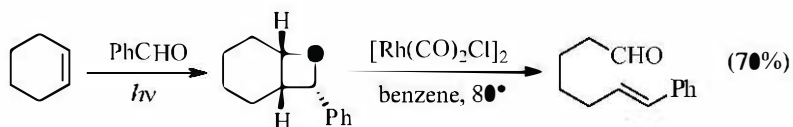
Thermolysis of oxetanes in TMEDA at 270–310° provides data on the regioselectivity of the reaction (Scheme 137) [129]. An electron donating group on an aromatic substituent on the oxetane ring favors bond A cleavage of the oxetane ring. On the other hand, both the presence of an electron withdrawing group on the aromatic substituent and the presence of two aromatic substituents at C2 of the oxetane favors B cleavage of the ring.

Some other cycloreversions of oxetanes obtained via Paternò–Büchi reactions are described [109a, 158, 379, 381, 404, 433, 434, 435]. Prolonged irradiation of the oxetane obtained in the reaction between 2,3-dihydrofuran and benzaldehyde or 4-cyanobenzaldehyde gives the corresponding metathesis product [436]. Rhodium(I) can also catalyze the same ring opening of an oxetane (Scheme 138) [437, 438].



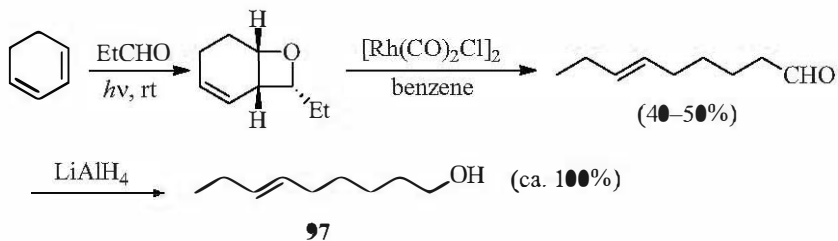
Scheme 138

The photolysis of benzaldehyde and cyclohexene affords the corresponding oxetane in 35% yield as an 8:1 mixture of stereoisomers, where the main isomer is *endo* (Scheme 139) [158]. Treatment of the oxetane mixture with TsOH in benzene at 25° or at 80° in the presence of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ yields the corresponding product of metathesis in 94% and 70% yields, respectively.

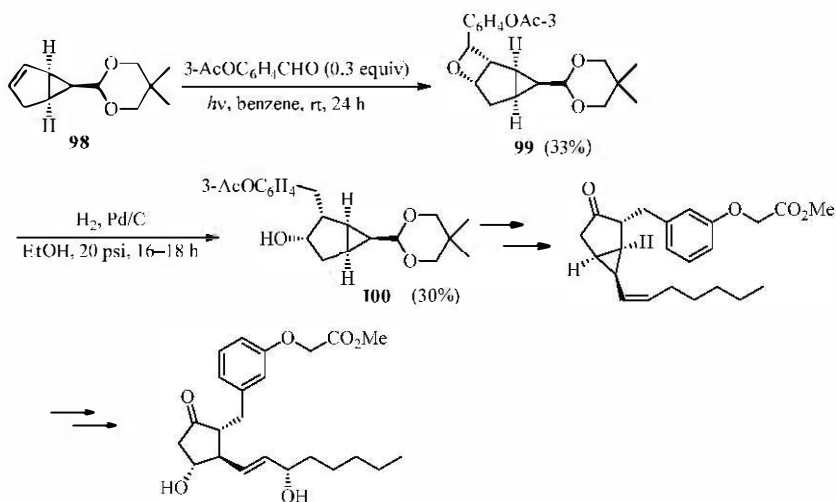


Scheme 139

This Rh-promoted metathesis reaction is used to synthesize the sex pheromone **97** of the Mediterranean fruit fly from 1,3-cyclohexadiene and propanal in 40–50% overall yields (Scheme 140).



Scheme 140

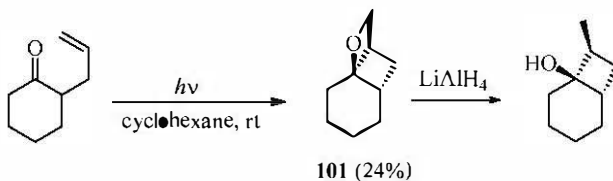


Scheme 141

Cleavage of C-O Bond to Give Alcohols

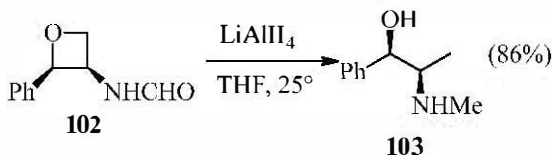
Alkene **98** reacts with benzaldehyde in a Paternò-Büchi reaction to give the corresponding oxetane [218]. The reaction of the corresponding oxetane with sodium in *n*-BuLi or with hydrogen and Pd/C yields the alcohol. This approach is used in the synthesis of a modified prostaglandin derivative (Scheme 141). In this case, a Paternò-Büchi reaction gives the oxetane **99** and the oxetane ring is subsequently opened by treatment with hydrogen on Pd/C to give the alcohol **100**.

The oxetane **101** reacts with LiAlH₄ to give the corresponding alcohol (Scheme 142) [292, 370a].



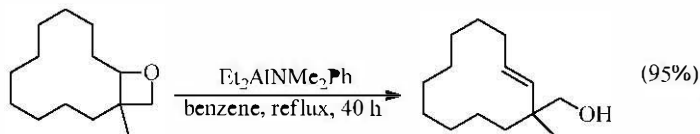
Scheme 142

Treatment of oxetane **102** with LiAlH_4 gives pseudoephedrine (**103**) (Scheme 143) [439].



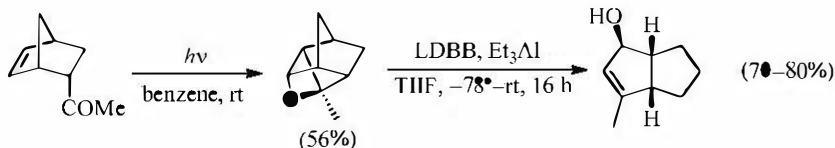
Scheme 143

Some oxetane derivatives have been treated with diethylaluminum *N*-methylanilide to obtain the corresponding homoallylic alcohol (Scheme 144) [440].



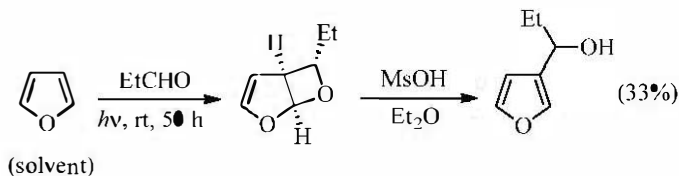
Scheme 144

The intramolecular Paternò–Büchi cyclization product of norbornene derivatives has been treated with lithium di-*tert*-butylbiphenylide (LDBB) to generate diquinanes and triquinanes (Scheme 145) [441]. LDBB selectively cleaves the C–O bond between the oxygen and the more substituted carbon.



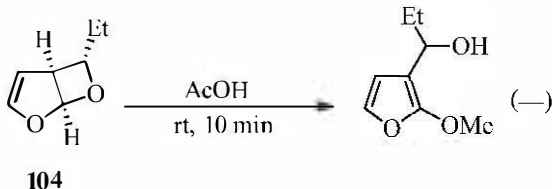
Scheme 145

Irradiation of propionaldehyde in furan as solvent gives the corresponding cycloaddition product. Treatment of this adduct with methanesulfonic acid affords the 3-furylmethanol derivative in 33% yield (Scheme 146) [310].



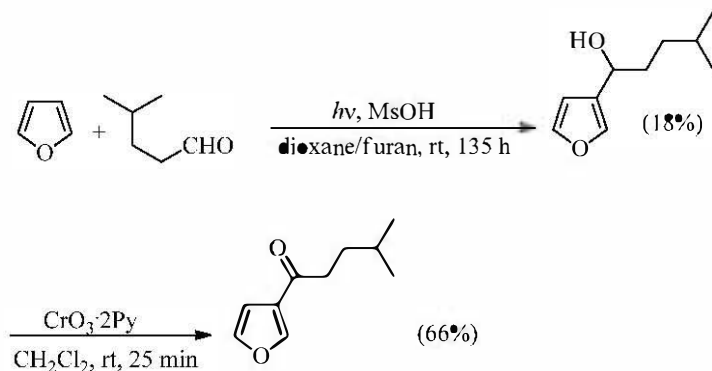
Scheme 146

The acid-catalyzed hydrolysis of cycloadduct **104** in methanol allows access to the corresponding ring-opened product (Scheme 147). The same product is obtained when the cycloadduct is treated with acetic acid [310]. Treatment of the Paternò–Büchi adducts, obtained through the photochemical reaction of furan with some aldehydes, with TsOH gives the corresponding 3-furylmethanol derivatives in 58–73% yields [73f].



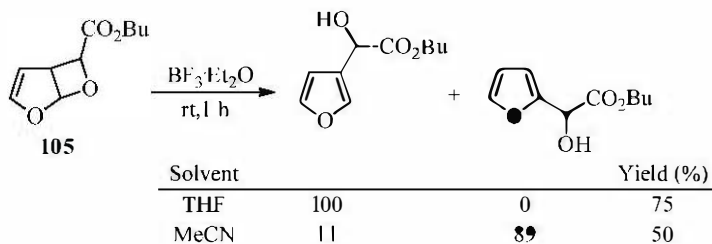
Scheme 147

The reaction described above can be applied to the synthesis of perillaketone. Furan is irradiated in the presence of 4-methylpentanal and methanesulfonic acid to give the corresponding 3-furylmethanol derivative in 18% yield. Oxidation with Collins reagent affords perillaketone in 66% yield (Scheme 148) [310].



Scheme 148

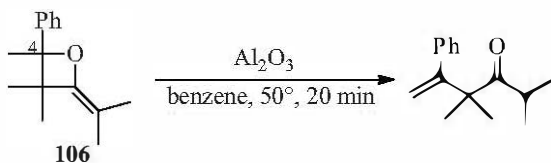
Hexetane **105** is treated with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to give the corresponding 3- and 2-furylmethanol derivatives depending on the solvent used (Scheme 149) [442].



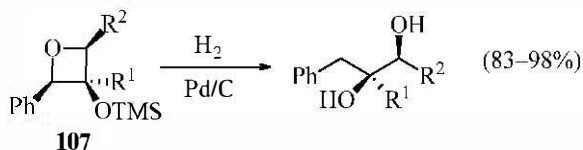
Scheme 149

Other Ring Opening Reactions

Hexetane **106**, containing a methyl group at C4 (the presence of a methyl group is essential to allow the reaction to occur), yields the ring-opened ketone product on treatment with alumina at 50°C (Scheme 150) [443].



Scheme 150

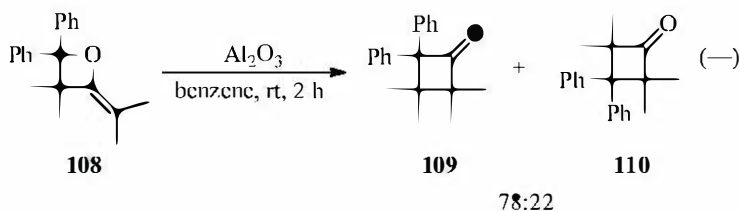


Scheme 151

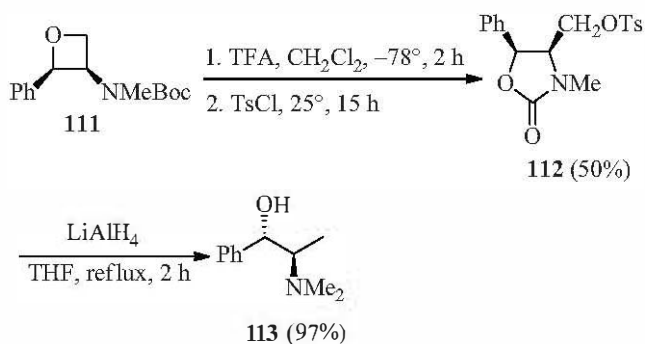
Oxetanes such as **107** can be converted into the corresponding diols by hydrogenolysis under Pd catalysis (Scheme 151). Acid-sensitive substrates can be hydrogenated using $\text{Pd}(\text{OH})_2$ [444].

Rearrangements of Oxetanes

Treatment of the oxetane **108** with alumina at room temperature gives cyclic ketones **109** and **110** in a 78:22 ratio (Scheme 152) [443].



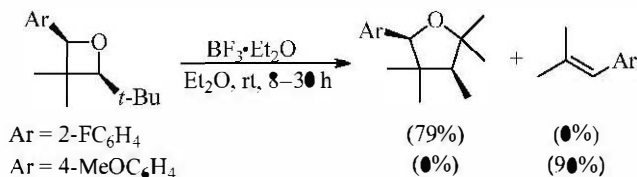
Scheme 152



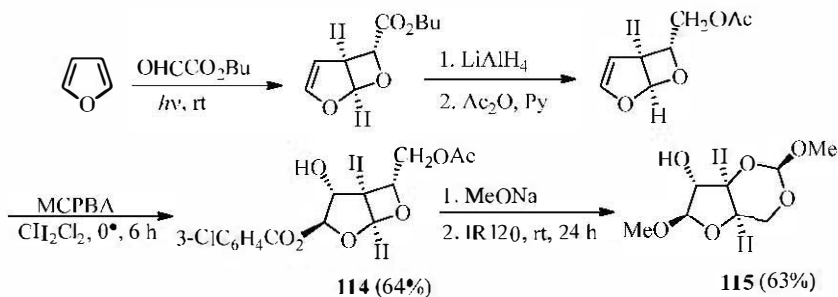
Scheme 153

Treatment of the protected aminooxetane **111** with TFA produces the oxazolidinone **112**. The reaction of **112** with LiAlH_4 affords the corresponding amino alcohol **113** (Scheme 153) [439].

Ring opening of 2-alkoxyoxetanes in water gives the corresponding 3-hydroxyaldehyde derivatives [445]. Oxetane derivatives also react with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to give a ring expansion product or a ring metathesis product (Scheme 154) [209]. The presence of electron-donating groups on the aromatic ring favors the formation of the ring metathesis products, while in the presence of electron-withdrawing groups, the ring expansion product is favored.

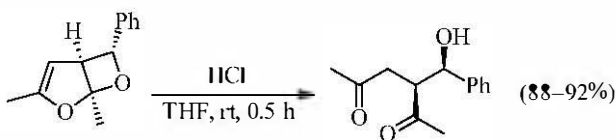
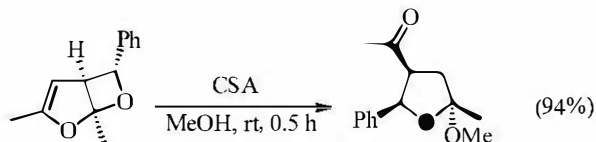


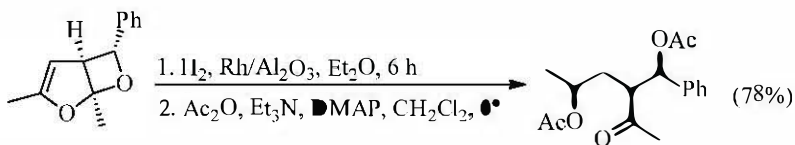
Scheme 154

**Scheme 155**

Furan reacts with butyl glyoxylate to give the corresponding oxetane which can be reduced and acetylated (Scheme 155) [446]. The subsequent reaction with MCPBA affords the corresponding hydroxy ester **114**. Treatment of this carboxylate with sodium methoxide followed by in situ acidification yields compound **115**.

The adduct obtained in the reaction between furan and a carbonyl compound has also been subjected to several modifications. Some of these are shown in Schemes 156–158 [447].

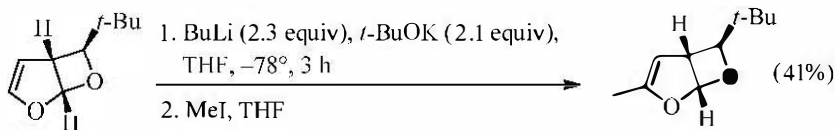
**Scheme 156****Scheme 157**



Scheme 158

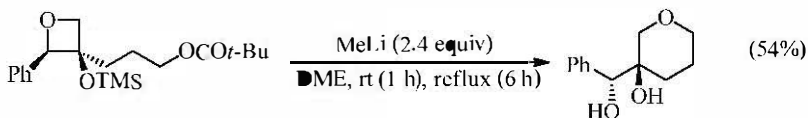
Miscellaneous Reactions

The use of unsymmetrically substituted furan derivatives in the synthesis of kadsurenone-ginkgolide hybrid is reported [75]. Thus, the cycloadduct obtained from the reaction between furan and an aldehyde is treated with an excess of Schlosser's base ($BuLi/t-BuOK$). This reaction gives the corresponding anion, which can react further with carbonyl compounds or alkyl halides (Scheme 159) [448].

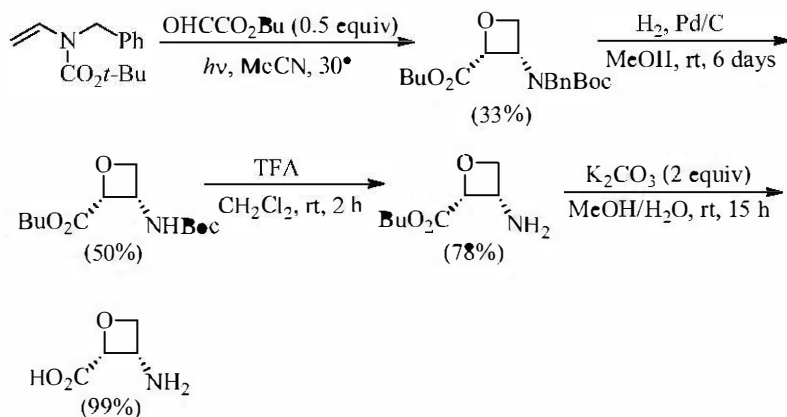


Scheme 159

Upon removal of the pivalate protecting group in the side chain of the oxetane, an intramolecular nucleophilic attack on the oxetane ring affords the corresponding pyran products (Scheme 160) [60].



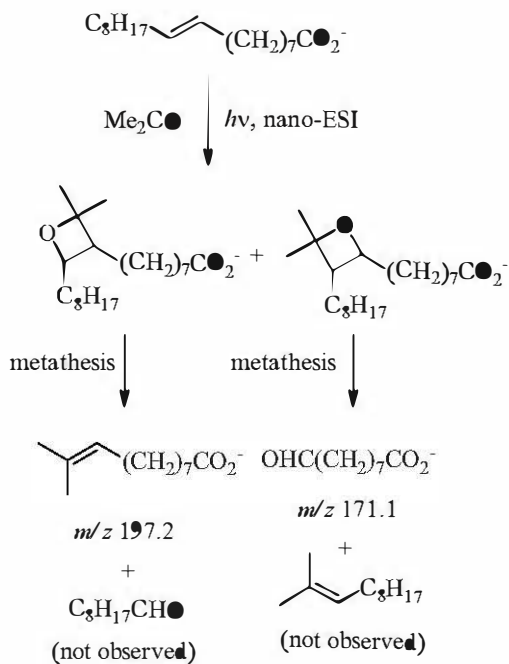
Scheme 160



Scheme 161

The reaction of α -formyl esters with enamine derivatives has been used in the synthesis of (\pm)-oxetin (Scheme 161) [297].

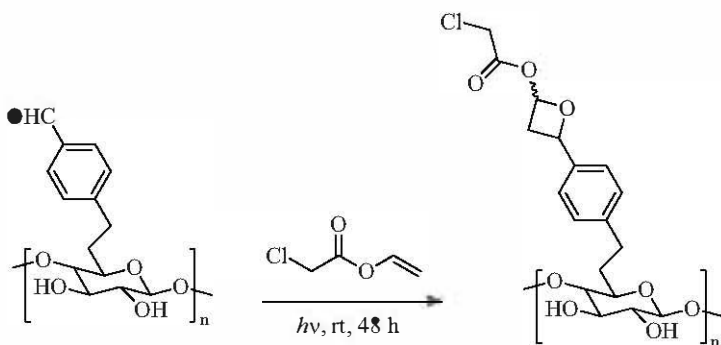
The Paternò-Büchi reaction followed by a thermal metathesis reaction represent key steps in an analytical procedure which is able to determine the composition of unsaturated lipid mixtures by mass spectrometry (Scheme 162) [449,450].



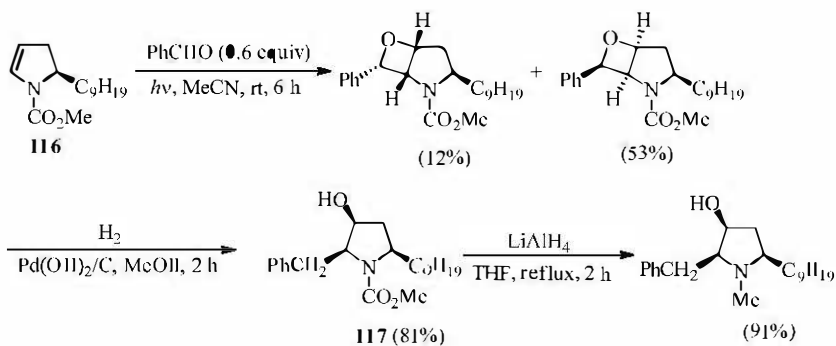
Scheme 162

An oxetane intermediate seems to be involved in a photodeprotection reaction of phosphates and acids protected with thiocromone *S,S*-dioxide moiety [451].

The Paternò-Büchi reaction has been used also to obtain grafting of modified cellulose. A cellulose structure bearing aromatic aldehydic groups reacts with alkenes (simple alkenes or polymers) to give modified celluloses (Scheme 163) [452].



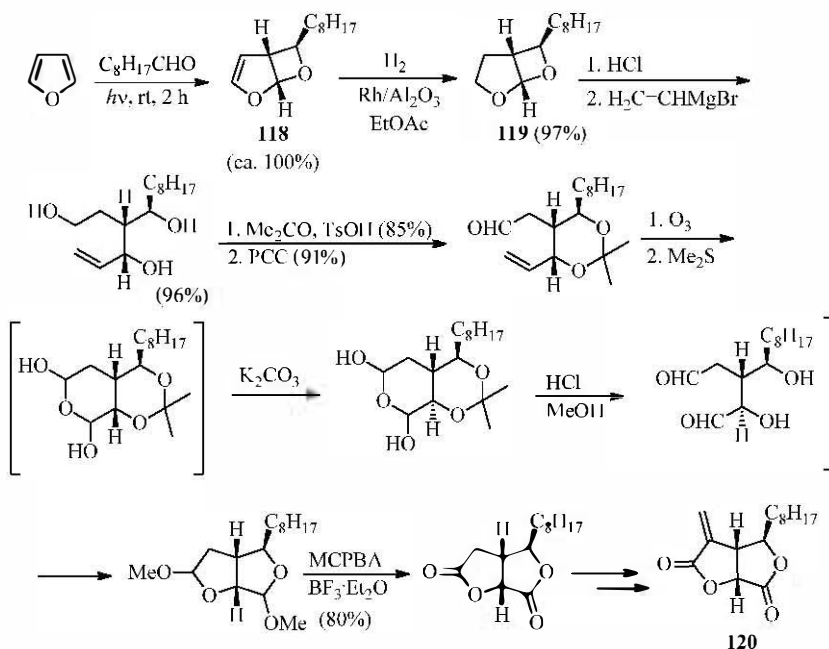
Scheme 163



Scheme 164

Synthesis of Preussin

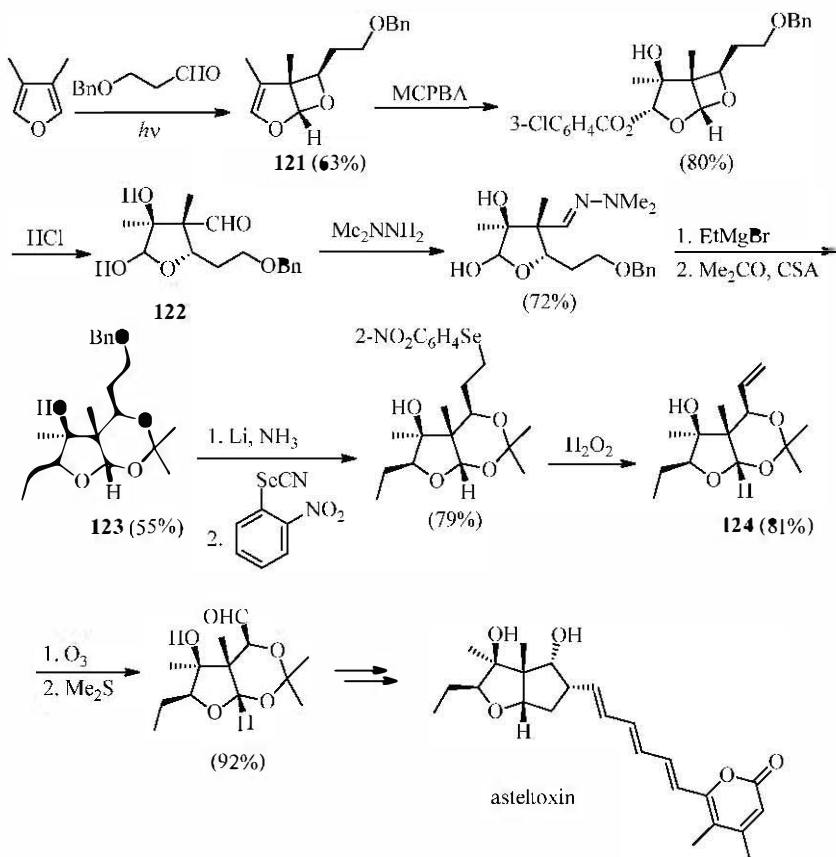
The reactivity of the enamine derivatives such as **116** can be used in the synthesis of (+)-preussin, an antifungal alkaloid (Scheme 164). Thus, the enantiomeric pure enamine derivative **116** undergoes a Paternò–Büchi reaction with benzaldehyde to give a 4:1 mixture of stereoisomeric oxetane adducts. The major stereoisomer is used in the synthesis by a ring opening reaction of the oxetane mixture with hydrogen on Pd(**●**H)₂/C to give **117** [296, 298].



Scheme 165

Synthesis of (±)-Avenaciolide

A formal synthesis of (±)-avenaciolide (**120**), an antifungal metabolite, is reported (Scheme 165). In this case, the oxetane **118** (obtained in multigram quantities in high yields and with complete stereochemical control) is treated with hydrogen to give the reduced compound. Avenaciolide contains a $C=O$ group inserted in the oxetane ring. This functionality can be incorporated into the substrate obtained after the reduction of the Paternò–Büchi adduct. Thus, a hydrolysis of **119** is followed by reaction of the resulting aldehyde with vinyl magnesium bromide. In this manner, two carbon atoms were added to the skeleton. One carbon atom is then lost during the following ozonolysis step as shown in Scheme 165. The key steps in this synthetic procedure correspond to a one-pot reaction with ozone followed by a base-catalyzed epimerisation with potassium carbonate and then cyclization in acidic medium [317].

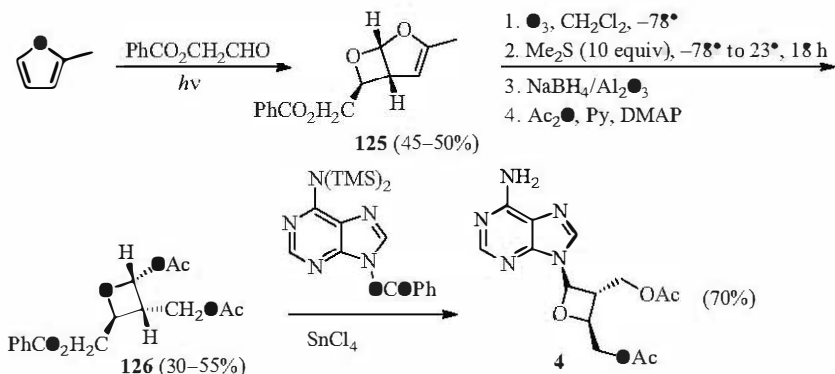


Scheme 166

Synthesis of (±)-Asteltoxin

In a synthesis of (±)-asteltoxin, the synthetic sequence used includes a photochemical coupling of 3,4-dimethylfuran with a functionalized aldehyde to give the corresponding oxetane adduct **121** in 63% yield. The subsequent reaction of **121** with MCPBA produces a protected *trans* diol that is converted into **122** through acid hydrolysis. The aldehyde thus obtained is then transformed into the corresponding hydrazone, and this substrate is then treated

with EtMgBr . This reaction with the latent α -hydroxyaldehyde proceeds with complete stereochemical control by chelation of the Grignard reagent with the hydroxyl group. The resulting product was protected as the acetonide to give **123** in 55% yield. A subsequent conversion of the benzyl ether into a seleno derivative and the elimination of the selenoxide provides **124** in 81% yield. Compound **124** is treated with ozone to give the corresponding aldehyde, which is eventually converted into asteltoxin (Scheme 166) [331, 453].



Scheme 167

Synthesis of (\pm)-oxetanocin A

Oxetanocin (**4**) is a nucleoside isolated from *Bacillus megaterium* NK 84-218 that exhibits anti-HIV activity. Oxetanocin is obtained using a Paternò-Büchi reaction between 2-methylfuran and benzoyloxyacetaldehyde [454]. The corresponding adduct **125** is treated with ozone, and the resulting product is reduced with NaBH_4 . The alcohols obtained are acetylated. Product **126** is then treated with *N*-benzoyl-disilyladenine and SnCl_4 to give **4** (Scheme 167). Another approach to the synthesis of the same compound using a Paternò-Büchi reaction is also reported [316].

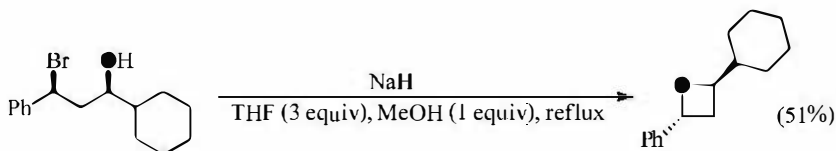
CHAPTER FIVE

COMPARISON WITH OTHER METHODS

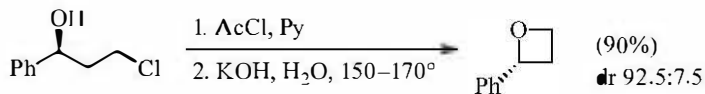
Ring Closure through Aliphatic Nucleophilic Substitution

A simple way to obtain a variety of oxetanes is by a ring closure reaction through an intramolecular nucleophilic substitution (Williamson etherification). The strongly basic reaction conditions needed to obtain a reactive nucleophile are the most important limitation of this procedure. Considering the fact that the closure proceeds by a S_N2 mechanism, the carbon on which the displacement reaction occurs can only be primary or secondary. The sequence of reactions shows high stereoselectivity.

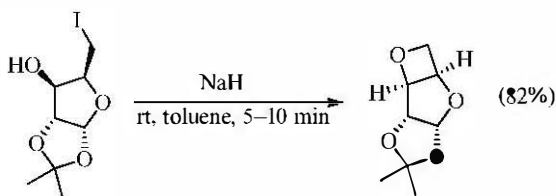
This reaction sequence is performed on 3-halogeno alcohols or acetates and proceeds with high stereoselectivity (Schemes 168 [455, 456], 169 [457], and 170 [458-462]).



Scheme 168

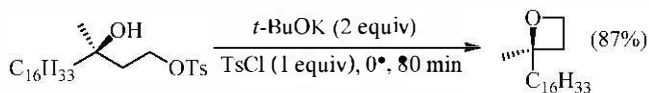


Scheme 169

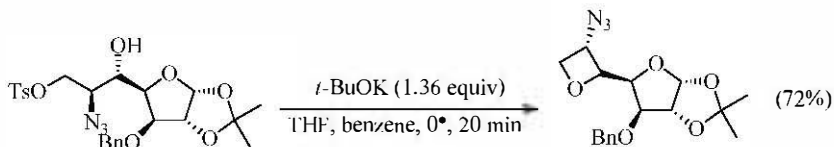


Scheme 170

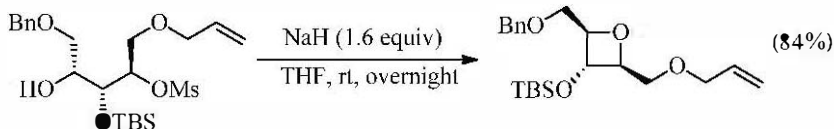
This approach is used in the construction of the oxetane ring in a synthesis of taxol [463-465]. A mono-tosylate or mesylate derivative of 1,3-diols has also been used as a substrate for the nucleophilic substitution reactions (Schemes 171 [466], 172 [467], and 173 [468-471]).



Scheme 171

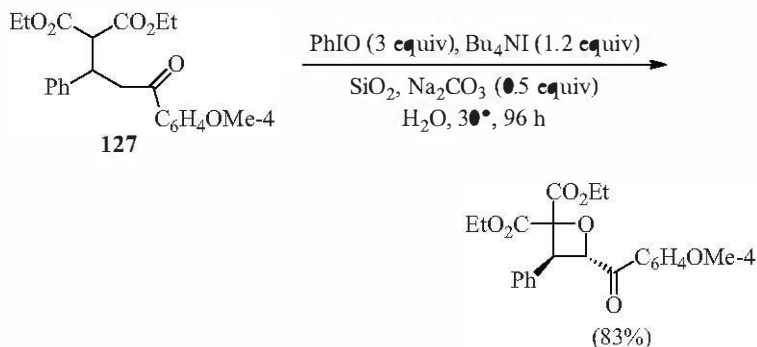


Scheme 172



Scheme 173

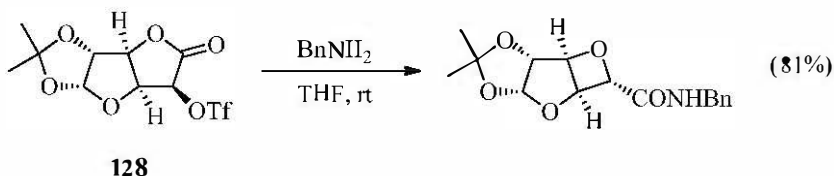
The malonate derivative **127** undergoes reaction with iodosobenzene in water to give a hydroxy malonate derivative. The hydroxy group, activated by reaction with another equivalent of iodosobenzene, reacts with an enolate to give the corresponding oxetane (Scheme 174). The diastereoselectivity of the reaction is confirmed by X-ray diffraction analysis [472].



Scheme 174

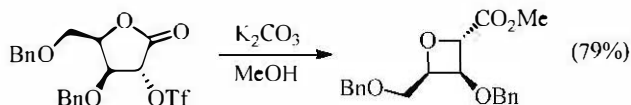
Ring Contraction

α -Hydroxy- γ -lactones derived from sugar scaffolds can be used in ring contraction reactions to afford oxetanes. In one example, the alkoxide anion generated by nucleophilic opening by the amine on lactone **128** undergoes an intramolecular S_N2 reaction with the triflate, generating the resulting oxetane (Scheme 175) [473-475].

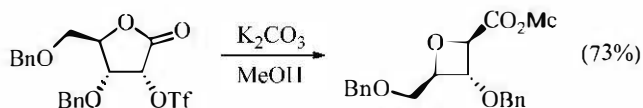


Scheme 175

It is noteworthy that similar applications of this reaction on pentafuranose derivatives give, in some cases, products showing the expected inversion of configuration, while in other cases, retention of configuration is observed (Schemes 176 and 177) [476].



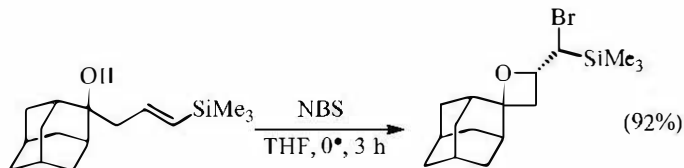
Scheme 176



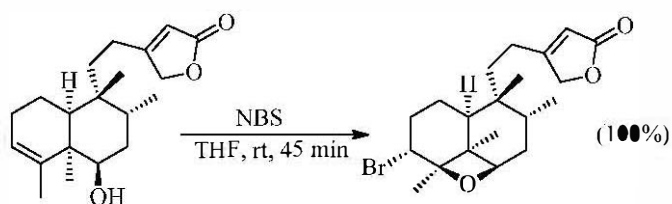
Scheme 177

Ring Closure through Electrophilic Additions

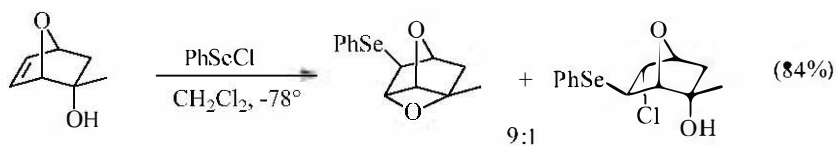
This approach towards oxetanes requires the presence of oxidants and thus compatibility of the substrates with an oxidizing environment is essential. Vinylsilane derivatives undergo an *exo* cyclization reaction in the presence of NBS (Scheme 178) [477]. The same type of attack can also occur by treating a β -hydroxyalkene with NBS, iodine, or PhSeCl (Schemes 179 [478] and 180 [479-481]).



Scheme 178



Scheme 179



Scheme 180

Similar results can be obtained using bis(*sym*-collidine)halogen derivatives [482-485].

CHAPTER SIX

EXPERIMENTAL CONDITIONS

Source of Light

Aliphatic carbonyl compounds require irradiation at *ca.* 250 nm to reach an excited state. The use of quartz permits excitation of the alkene to occur, but often this excitation of the alkene causes secondary, undesired reactions. A Vycor filter allows UV filtration of the radiation with a cutoff near 250 nm. Alternatively, an LED source with an emission at 254 nm has been used [375]. Most of the Paternò-Büchi reactions have been performed using aromatic carbonyl compounds. In this case, Pyrex can be used as the filter (cutoff 290 nm). In the reaction of aromatic thioketones, a light source at 589 nm (a Na lamp) is used [106f, 205]. In some cases, uv lamps with an output at 350 nm are used as light source for the reaction [106f, 417, 423]. To avoid photochemical decomposition of the oxetane, an optical filter with a cutoff at 320 nm has been used [282]. In the reactions of quinone derivatives with aromatic alkenes and aromatic enol esters, a glass GWV (Wertheim) filter with a cutoff at 370 nm is used [288].

In a study on the photochemical reaction of isoquinoline-1,3,4-trione with heteroaromatic, substituted alkynes, a light source with an emission wavelength higher than 400 nm must be used. The light of a medium pressure mercury lamp can be filtered by using a solution of sodium nitrite [227]. In a study on the reactivity of 9,10-phenanthrenequinone, can be obtained by using a Toshiba V-Y42 filter [193].

A light source of 420 nm is easily created by using borosilicate glass [371]. In some cases, the choice of the irradiation wavelength represents a way to select direct irradiation or else to induce a reaction to occur by charge transfer irradiation. In such cases, the wavelength can be controlled by using optical filters [79b].

Caution: do not expose the eyes or skin to UV irradiation.

Solvents

The most common solvents used in the Paternò-Büchi reaction are acetonitrile, benzene (and/or toluene), and hydrocarbons (pentane, *n*-hexane, cyclohexane). When the carbonyl compound is acetone, it is usually used as the solvent for the reaction. In many cases, when the alkene is inexpensive and it is a liquid, the photoreaction is performed without a solvent in a large excess of the alkene. Other solvents sometimes utilized are alcohols (MeOH, EtOH), chlorinated solvents (CH₂Cl₂, CHCl₃, CCl₄), and ethers (Et₂O, THF, dioxane).

In most cases, the choice of the solvent is a critical factor (the reaction may occur efficiently only in a specific solvent), but it is not possible to give a set of general rules for selecting a solvent. When an electron transfer mechanism needs to be induced, the solvent must be polar, and, in such cases acetonitrile is amongst the best to use. In these cases, the solvent favors an electron transfer process while minimizing the Weller equation, which determines the ΔG of electron transfer.

Tables

The tables cover the literature until the end of 2016 and are organized following the same divisions employed in the Scope and Limitations section. Within each table, the unsaturated compounds appear in order of increasing carbon count. Groups not included in the carbon count are α -substituents of esters, *N*-substituents of amides, *P*-substituents of alkenylphosphonates, *S*-substituents in alkenylsulfonyl compounds, *B*-substituents of borylalkenes, and protecting groups. For every compound the increasing carbon atoms of the "carbonyl" compound reacting with it are considered. Entries of the same structural class (usually phenyl) appear in order of increasing number of substituents and then by the position of those substituents (2 > 3 > 4). If the aryl substitution pattern is identical, the entries are arranged by the nature of the aryl substituent(s), with carbon-substituted (by increasing carbon count) > heteroatom-substituted (by increasing atomic number).

Unless noted otherwise, the reactions have been performed at room temperature.

BIBLIOGRAPHY

- [1] Kumarasamy, E.; Raghunathan, R.; Kandappa, S. K.; Sreenithya, A.; Jockusch, S.; Sunoj, R. B.; Sivaguru, J. Transposed Paternò-Büchi reaction. *J. Am. Chem. Soc.* **2017**, *139*, 655-662.
- [2] a) Holmes, F. A.; Waters, R. J.; Theriault, R. I.; Forman, A. D.; Newton, L. K.; Raber, M. N.; Buzdar, A. U.; Frye, D. K.; Hortobagyi, G. N. Phase II Trial of Taxol, an Active Drug in the Treatment of Metastatic Breast Cancer. *J. Natl. Cancer Inst. U. S. A.* **1991**, *83*, 1797-1805; b) McGuire, W. P.; Rowinsky, E. K.; Rosenhein, N. B.; Grumbine, F. C.; Ettinger, D. S.; Armstrong, D. K.; Donehower, R. C. Taxol: A Unique Antineoplastic Agent with Significant Activity in Advanced Ovarian Epithelial Neoplasms *Ann. Intern. Med.* **1989**, *111*, 273-279; c) Einzig, A. I.; Wiemik, P. H.; Sasloff, J.; Garl, S.; Runowicz, C.; Hanlan, K. A.; Goldberg, G. Phase II study of taxol in patients with advanced ovarian cancer. *Proc. Am. Assoc. Cancer Res.* **1990**, *31*, 187; d) Pazdur, R.; Ho, D. H.; Lassere, Y.; Bready, B.; Kvakoff, I. H.; Raber, M. N. *Proc. Am. Soc. Clin. Oncol.* **1992**, *11*, 111; e) Caldas, C.; McGuire, W. P. Paclitaxel (Taxol) therapy in ovarian carcinoma. *Semin. Oncol.* **1993**, *20*, 50-55; f) Einzig, A. I.; Hochster, H.; Wiemik, P. H.; Trump, D. L.; Dutcher, J. P.; Garowski, E.; Sasloff, J.; Smith, T. A phase II study of taxol in patients with malignant melanoma. *Invest. New Drugs* **1991**, *9*, 59-64; g) Legha, S. S.; Ring, S.; Papadopoulos, N.; Raber, M. N.; Benjamin, R. A phase II trial of taxol in metastatic melanoma. *Cancer* **1990**, *65*, 2478-2481; h) Chang, A.; Kim, K.; Glick, J.; Anderson, T.; Karp, D.; Johnson, D. Phase II Study of Taxol, Merbarone, and Piroxantrone in Stage IV Non-Small-Cell Lung Cancer: The Eastern Cooperative Oncology Group Results. *J. Natl. Cancer Inst.* **1993**, *85*, 388-394; k) Murphy, W. K.; Winn, R. J.; Fossella, F. V.; Shin, D. M.; Hynes, H. E.; Gross, H. M.; Davila, E.; Leimert, J. T.; Dhinga, H. M.; Raber, M. N.; Krakoff, I. H.; Hong, W. K. *Proc. Am. Soc. Clin. Oncol.* **1993**, *85*, 384; i) Ettinger, D. S. Overview of paclitaxel (Taxol) in advanced lung cancer. *Semin. Oncol.* **1993**, *20*, 46-49; j) Forastiere, A. A. Use

- of paclitaxel (Taxol) in squamous cell carcinoma of the head and neck. *Semin. Oncol.* **1993**, *20*, 56-60.
- [3] Wani, M. C.; Taylor, H. L.; Wall, M. E.; Coggen, P.; McPhail, A. T. Plant antitumor agents. VI. Isolation and structure of taxol, a novel antileukemic and antitumor agent from *Taxus brevifolia*. *J. Am. Chem. Soc.* **1971**, *93*, 2325-2327.
- [4] Huang, J. M.; Yokoyama, R.; Yang, C. S.; Fukuyama, Y. Merrilactone A, a novel neurotrophic sesquiterpene dilactone from *Illicium merrillianum*. *Tetrahedron Lett.* **2000**, *41*, 6111-6114.
- [5] Shimada, N.; Hasegawa, S.; Harada, T.; Tomisawa, T.; Fujii, A.; Takita, T. Oxetanocin, a novel nucleoside from bacteria. *J. Antibiot.* **1986**, *39*, 1623-625.
- [6] Hoshino, H.; Shimizu, N.; Shimada, N.; Takita, T.; Takeuki, T. Inhibition of infectivity of human immunodeficiency virus by oxetanocin. *J. Antibiot.* **1987**, *40*, 1077-1078.
- [7] Li, C.; Lee, D.; Graf, T. N.; Phifer, S. S.; Nakanishi, Y.; Burgess, J. P.; Riswan, S.; Setyowati, F. M.; Saribi, A. M.; Soejarto, D. D.; Farnsworth, N. R.; Falkinham III, J. O.; Kroll, D. J.; Kinghorn, A. D.; Wani, M. C.; Oberlies, N. H. A Hexacyclic ent-Trachylobane Diterpenoid Possessing an Oxetane Ring from *Mitrephora glabra*. *Org. Lett.* **2005**, *7*, 5709-5712.
- [8] Han, Q. B.; Zhang, J. X.; Lu, Y.; Wu, Y. S.; Zheng, Q. T.; Sun, H. D. A novel cytotoxic oxetane ent-kauranoid from *Isodon japonicus*. *Planta Med.* **2004**, *70*, 581-584.
- [9] a) Omura, S.; Murata, M.; Imamura, N.; Iwai, Y.; Tanaka, H.; Furusaki, A.; Matsumoto, T. Oxetin, a new antimetabolite from an actinomycete. *J. Antibiot.* **1984**, *37*, 1324-1332; b) Kawahata, Y.; Takatsuto, S.; Ikekawa, N.; Murata, M.; Omura, S. Synthesis of a New Amino Acid-Antibiotic, Oxetin and Its Three Stereoisomers. *Chem. Pharm. Bull.* **1986**, *34*, 3102-3110; c) Hoshino, H.; Shimizu, N.; Shimada, N.; Takita, T.; Takeuki, T. Inhibition of infectivity of human

- immunodeficiency virus by oxetanocin. *J. Antibiot.* **1987**, *40*, 1077-1078.
- [10] Pullaiah, K. C.; Surapaneni, R. K.; Rao, C. B.; Albizati, K. F.; Sullivan, B. W.; Faulkner, D. J.; He, C. H.; Clardy, J. Dictyoxetane, a novel diterpene from the brown alga *Dictyota dichotoma* from the Indian Ocean. *J. Org. Chem.* **1985**, *50*, 3665-3666.
- [11] Loh, L.; Carlson, R. W.; York, W. S.; Stacey, G. Bradyoxetin, a unique chemical signal involved in symbiotic gene regulation. *Proc. Natl. Acad. Sci.* **2002**, *99*, 14446-14451.
- [12] a) Irie, T.; Izawa, M.; Kurosawa, E. Laureatin, a constituent from *laurencia nipponica* Yamada. *Tetrahedron Lett.* **1968**, 2091-2096; b) Irie, Y.; Izawa, M.; Kurosawa, E. Laureatin and isolaureatin, constituents of *Laurencia nipponica* Yamada. *Tetrahedron* **1970**, *26*, 851-870.
- [13] Ortega, A.; Maldonado, E. Pseudoguaianolides from *Parthenium fruticosum*. *Phytochemistry* **1986**, *25*, 699-701.
- [14] Martins, D.; Oshiro, E.; Roque, N. F.; Marks, V.; Gottlieb, H. E. A sesquiterpene dimer from *Xylopiya aromatica*. *Phytochemistry* **1998**, *48*, 677-680.
- [15] Bull, J. A.; Croft, R. A.; Davis, G. A.; Doran, R.; Morgan, K. F. Oxetanes: Recent Advances in Synthesis, Reactivity, and Medicinal Chemistry. *Chem. Rev.* **2016**, *116*, 12150-12233.
- [16] a) Hammond, G. S.; Turro, N. J. *Organic Photochemistry Science* **1963**, *142*, 1541-1553; b) Arnold, D. R. The photocycloaddition of carbonyl compounds to unsaturated systems: the synthesis of oxetanes. *Adv. Photochem.* **1968**, *6*, 301-423; c) Herndon, W. C. Substituent effects in photochemical cycloaddition reactions. *Top. Curr. Chem.* **1974**, *46*, 141-179; d) Coyle, J. D. Photochemistry of carboxylic acid derivatives. *Chem. Rev.* **1978**, *78*, 97-123; e) Morrison, H. Photochemistry of organic bichromophoric molecules. *Acc. Chem. Res.* **1979**, *12*, 383-389; f) Jones, G. Synthetic

applications of the Paternò-Büchi reaction. *Org. Photochem.* **1981**, *5*, 1-122; g) Carless, H. A. J. Photochemical synthesis of oxetanes. In *Synthetic Organic Photochemistry*, Horspool, W. M.; Ed.; Plenum: New York, **1984**: pp. 425-487; h) Schreiber, S. L. [2+2] Photocycloadditions in the synthesis of chiral molecules. *Science* **1985**, *227*, 857-863; k) Mattay, J. Charge transfer and radical ions in photochemistry *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825-845; i) Porco, J. A.; Schreiber, S. L. The Paternò-Büchi reaction. In *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I.; Paquette, L. A.; Eds; Plenum: New York, **1991**: vol. 5, pp. 151-192; j) Griesbeck, A. G. Photochemical Oxetane Formation: Intermolecular Reactions. In *Handbook of Photochemistry and Photobiology*, Horspool, W. A.; Song, P. -S.; Eds; CRC Press: Boca Raton, **1994**: pp. 522-535; l) Griesbeck, A. G. Photochemical Oxetane Formation: Stereocontrol In *Handbook of Photochemistry and Photobiology*, Horspool, W. A.; Song, P. -S.; Eds; CRC Press: Boca Raton, **1994**: pp. 550-559; m) Griesbeck, A. G.; Mauder, H.; Stadtmüller, S. Intersystem crossing in triplet 1,4-biradicals: conformational memory effects on the stereoselectivity of photocycloaddition reactions. *Acc. Chem. Res.* **1994**, *27*, 70-75; n) Rivas, C.; Vargas, F. Oxetane Formation: Addition to heterocycles. In *CRC Handbook of Organic Photochemistry and Photobiology*, Horspool, W. M.; Song, P. -S.; Eds.; CRC Press: Boca Raton, **1994**: pp. 536-549; o) Bach, T. The Paternò-Büchi reaction of 3-heteroatom-substituted alkenes as a stereoselective entry to polyfunctional cyclic and acyclic molecules. *Liebigs Ann./Recueil* **1997**, 1627-1634; p) Bach T. Stereoselective Intermolecular [2 + 2]-Photocycloaddition Reactions and Their Application in Synthesis. *Synthesis* **1998**, 683-703; q) Vargas, F.; Rivas, C. Photochemical formation of oxetanes derived from aromatic ketones and substituted thiophenes and selenophenes. *Int. J. Photoener.* **2000**, *2*, 97-101; r) Bach, T. The Paternò-Büchi reaction of *N*-acyl enamines and aldehydes - The development of a new synthetic method and its application to total synthesis and molecular recognition studies. *Synlett* **2000**, 1699-1707; s) D'Auria, M.; Emanuele, L.; Racioppi, R.; Romaniello, G. The Paternò-Büchi reaction on furan derivatives. *Curr. Org. Chem.* **2003**, *7*, 1443-1459; t) D'Auria, M. Paternò-Büchi reaction on furan: regio- and stereochemistry. In *Targets in Heterocyclic Systems, Chemistry and Properties*, Attanasi, G. A.; Spinelli, D.; Eds.; Italian Society of

Chemistry: Rome, 2003: vol. 7, pp. 157-173; *u*) Griesbeck, A. G. Spin-selectivity in photochemistry: a tool for organic synthesis. *Synlett* 2003, 451-472; *v*) Griesbeck, A. G. The link between stereoselectivity and spin selectivity in intermolecular and intramolecular photochemical reactions. *J. Photosci.* 2003, 10, 49-60; *w*) Griesbeck, A. G.; Bondock, S. Oxetane formation: stereocontrol. In *Handbook of Photochemistry and Photobiology*, Horspool, W. A.; Lenci, F.; Eds.; CRC Press: Boca Raton, 2004: 59-1 - 59-19; *x*) Griesbeck, A. G.; Bondock, S. Oxetane formation: intermolecular additions. In *Handbook of Photochemistry and Photobiology*, Horspool, W. A.; Lenci, F.; Eds.; CRC Press: Boca Raton, 2004: 60-1 - 60-21; *y*) Abe, M. Photochemical oxetane formation: addition to heterocycles. In *Handbook of Photochemistry and Photobiology*, Horspool, W. A.; Lenci, F.; Eds.; CRC Press: Boca Raton, 2004: 62-1 - 62-10; *z*) Griesbeck, A. G.; Abe, M.; Bondock, S. Selectivity control in electron spin inversion processes: regio- and stereochemistry of Paternò-Büchi photocycloadditions as a powerful tool for mapping intersystem crossing processes. *Acc. Chem. Res.* 2004, 37, 919-928; *aa*) D'Auria, M.; Emanuele, L.; Racioppi, R. Regio- and diastereoselectivity in the paternò-büchi reaction on furan derivatives. *The Spectrum* 2004, 17(1), 22-27; *ab*) D'Auria, M.; Emanuele, L.; Racioppi, R. 1,2-Cycloaddition reaction of carbonyl compounds and pentaatomic heterocyclic compounds. In *Advances in Photochemistry*, Neckers, D. C.; Jenks, W. S.; Wolff, T.; Eds.; John Wiley & Sons: Hoboken, NJ, 2005: vol. 28, pp. 81-127; *ac*) Griesbeck, A. G. Photocycloaddition of alkenes to excited carbonyls. In *Synthetic Organic Photochemistry*, Griesbeck, A.G.; Mattay, J.; Eds.; Marcel Dekker: New York, 2005, pp. 89-139; *ad*) D'Auria, M.; Emanuele, L.; Racioppi, R. Regio- and stereoselectivity in the Paternò-Büchi reaction on furan derivatives. *Int. J. Photoener.* 2006, 84645; *ae*) Abe, M. recent progress regarding regio-, site-, and stereoselective formation of oxetanes in Paternò-Büchi reactions. *J. Chin. Chem. Soc.* 2008, 55, 479-486; *af*) D'Auria, M.; Emanuele, L.; Racioppi, R. 2+2 Cycloaddition on furan derivatives. In *Photochemistry Research Progress*, Sanchez, A.; Gutierrez, S. J.; Eds.; Nova Science Publishers Inc.: Hauppauge, NY, 2008: pp. 373-438; *ag*) D'Auria, M.; Racioppi, R. Concepts of stereoselective photochemistry and a case study: the Paternò-Büchi reaction. *Curr. Org. Chem.* 2009, 13, 939-954; *ah*) Vogt, F.; Jödicke, K.; Schröder,

- J.; Bach, T. Paternò-Büchi reactions of silyl enol ethers and enamides. *Synthesis* **2009**, 4269-4273; *ak*) Abe, M. Formation of a four-membered ring: oxetanes. In *Handbook of Synthetic Photochemistry*, Albini, A.; Fagnoni, M.; Eds; Wiley: New York, **2010**, pp.217-239; *ai*) Bach, T.; Hehn, J. P. Photochemical reactions as key steps in natural product synthesis. *Angew. Chem. Int. Ed.* **2011**, *50*, 1000-1045; *aj*) D'Auria, M. Paternò-Büchi Reaction. In *CRC Handbook of Organic Photochemistry and Photobiology*, Griesbeck, A. G.; Elgemöller, M.; Ghetti, F.; Eds.; CRC Press: Boca Raton, **2012**: pp. 653-681; *al*) D'Auria, M.; Racioppi, R. Oxetane synthesis through the Paternò-Büchi reaction. *Molecules* **2013**, *18*, 11384-11428; *am*) D'Auria, M. The Paternò-Büchi reaction. In *Comprehensive Organic Synthesis*, 2nd Edition, Molander, G. A.; Knochel, P.; Eds.; Elsevier: Oxford, **2014**: vol. 5, pp. 159-199; *an*) Fréneau, M.; Hoffmann, N. The Paternò-Büchi reaction—Mechanisms and application to organic synthesis. *J. Photochem. Photobiol., C: Photochem. Rev.* **2017**, *33*, 83-108.
- [17] D'Auria, M. On a dispute between Ciamician and Paternò. *EPA Newsletter* **2013**, *84*, 106-109.
- [18] Paternò, E.; Chieffi, G. Sintesi in chimica organica per mezzo della luce. Nota II. Composti degli idrocarburi non saturi con aldeidi e chetoni. *Gazz. Chim. Ital.* **1909**, *39*(I), 341-361.
- [19] Ciamician, G.; Silber, P. Chemische Lichtwirkungen. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 1386-1391.
- [20] Kharasch, M. S.; Urry, W. H.; Kuderna, B. M. Reactions of atoms and free radicals in solution. XX. The addition of aldehydes to olefins. *J. Org. Chem.* **1949**, *14*, 248-253.
- [21] Büchi, G.; Inman, C. G.; Lipinsky, E. S. Light-catalyzed organic reactions. I. The reaction of carbonyl compounds with 2-methyl-2-butene in the presence of ultraviolet light. *J. Am. Chem. Soc.* **1954**, *76*, 4327-4331.

- [22] Srinivasan, R. Photoisomerization of 5-hexen-2-one. *J. Am. Chem. Soc.* **1960**, *82*, 775-778.
- [23] Arnold, D. R.; Hinman, R. L.; Glick, A. H. Chemical properties of a carbonyl n,π^* state. The photochemical preparation of oxetanes. *Tetrahedron Lett.* **1964**, 1425-1430.
- [24] Yang, N. C.; Nussim, M.; Jorgenson, M. J.; Murov, S. Photochemical reactions of carbonyl compounds in solution. The Paternò-Büchi reaction. *Tetrahedron Lett.* **1964**, 3657-3664.
- [25] Gersdorf, J.; Mattay, J.; Gömer, H. Photoreactions of biacetyl, benzophenone, and benzil with electron-rich alkenes. *J. Am. Chem. Soc.* **1987**, *109*, 1203-1209.
- [26] a) Turro, N. J.; Wriede, P.; Dalton, J. C. Arnold, D.; Glick, A. Molecular photochemistry. V. Photocycloaddition of alkyl ketones to electron-deficient double bonds. *J. Am. Chem. Soc.* **1967**, *89*, 3950-3952; b) Dalton, J. C.; Wriede, P. A.; Turro, N. J. Photocycloaddition of acetone to 1,2-dicyanoethylene. *J. Am. Chem. Soc.* **1970**, *92*, 1318-1326.
- [27] Barltrop, J. A.; Carless, H. A. J. Photocycloaddition of alkyl ketones to α,β -unsaturated nitriles. *Tetrahedron Lett.* **1968**, 3901-3903.
- [28] Yang, N. C.; Loeschen, R.; Mitchell, D. On the mechanism of the Paternò-Büchi reaction. *J. Am. Chem. Soc.* **1967**, *89*, 5465-5466.
- [29] Turro, N. J.; Wriede, P. A. The photocycloaddition of acetone to 1-methoxy-1-buten. A comparison of singlet and triplet mechanism and singlet and triplet biradical intermediates. *J. Am. Chem. Soc.* **1970**, *92*, 320-329.
- [30] Schore, N. E.; Turro, N. J. Mechanism of the interaction of n,π^* excited alkanones with electron-rich ethylenes. *J. Am. Chem. Soc.* **1975**, *97*, 2482-2488.

- [31] a) Toki, S.; Sakurai, H. Kinetic studies of the photoreaction of benzophenone with furan. *Bull. Chem. Soc. Jpn* **1967**, *40*, 2885-2889; b) Yang, N. C.; Cohen, J. I.; Shanl, A. On the mechanism of energy transfer from n,π^* triplet state of carbonyl compounds to simple olefins. *J. Am. Chem. Soc.* **1968**, *90*, 3264-3266; c) Saltiel, J.; Neuberger, K. R.; Wrighton, M. Nature of the intermediates in the sensitized *cis-trans* photoisomerization of alkenes. *J. Am. Chem. Soc.* **1969**, *91*, 3658-3659; d) Kochevar, I. H.; Wagner, P. J. Triplet ketone-olefin interaction: energy transfer, charge transfer, or radical addition? *J. Am. Chem. Soc.* **1970**, *92*, 5742-5743; e) Caldwell, R. A.; James, S. P. Secondary isotope effects as photochemical mechanistic criteria. Photosensitized *cis-trans* olefin isomerization not involving the olefin triplet state. *J. Am. Chem. Soc.* **1969**, *91*, 5184-5186; f) Yang, N. C.; Hui, M. H.; Bellard, S. A. On the quenching of photochemical reactions and of fluorescence of alkanones by 1,3-cyclohexadiene and *cis*-1,3-pentadiene. *J. Am. Chem. Soc.* **1971**, *93*, 4056-4058; g) Wagner, P. J.; Kochevar, I. How efficient is diffusion-controlled triplet energy transfer? *J. Am. Chem. Soc.* **1968**, *90*, 2232-2238; h) Yang, N. C.; Eisenhardt, W. On the mechanism of Paterno-Büchi reaction of alkanals. *J. Am. Chem. Soc.* **1971**, *93*, 1277-1279; k) Hautala, R. R.; Turro, H. J. Mechanism for the quenching of alkanone singlets by conjugated dienes. *J. Am. Chem. Soc.* **1971**, *93*, 5595-5597; i) Gupta, A.; Hammond, G. S. Mechanisms of photochemical reactions in solutions. LXXVII. Energy wastage and exciplex formation in the quenching of a ketone triplet by sterically hindered alkenes. *J. Am. Chem. Soc.* **1976**, *98*, 1218-1223; j) Yang, N. C.; Hui, M. H.; Shold, D. M.; Turro, N. J.; Hautala, R. R.; Dawes, K.; Dalton, J. C. Quenching of the $^1n,\pi^*$ of alkanones by unsaturated compounds. *J. Am. Chem. Soc.* **1977**, *99*, 3023-3033.
- [32] Turro, N. J.; Farrington, G. L. Quenching of the fluorescence of 2-norbomanone and derivatives by electron-rich and electron-poor ethylenes. *J. Am. Chem. Soc.* **1980**, *102*, 6051-6055.
- [33] a) Goetz, M.; Frisch, I. Photocycloaddition of quinones with quadricyclane and norbornadiene. A mechanistic study. *J. Am. Chem. Soc.* **1995**, *117*, 10486-10502; b) Goetz, M.; Frisch, I. Activation energy of a biradical rearrangement measured by photo-CIDNP. *J. Phys. Chem. A* **2002**, *106*, 8079-8084.

- [34] Wang, X. Y.; Yan, B. Z.; Wang, T. CDNP study of photoinduced [2+2] cycloadditions (the Paternò-Büchi coupling) of arylacetylenes and quinone. *Chin. Chem. Lett.* **2003**, *14*, 270-273.
- [35] a) Hayashi, H. Direct observation of the 1,4-biradical of benzophenone with *cis*-3-methyl-2-pentene excited by the fourth harmonic of a Nd:YAG laser. *Bull. Chem. Soc. Jpn* **1980**, *53*, 2201-2204; b) Freilich, S. C.; Peters, K. S. Observation of the 1,4-biradical in the Paternò-Büchi reaction. *J. Am. Chem. Soc.* **1981**, *103*, 6255-6257.
- [36] Freilich, S. C.; Peters, K. S. Picosecond dynamics of the Paternò-Büchi reaction. *J. Am. Chem. Soc.* **1985**, *107*, 3819-3822.
- [37] Brogaard, R. Y.; Schalk, M.; Boguslaskiy, A. E.; Enright, G. D.; Hopf, H.; Raev, V.; Tarcoveanu, E.; Sølling, T.I.; Stolow, A. The Paternò-Büchi reaction: importance of triplet states in the excited-state reaction pathway. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8572-8580.
- [38] Harris, S. J.; Murdock, D.; Grubb, M. P.; Clark, I. P.; Greetham, G. M.; Towrie, M.; Ashfold, M. N. R. Tracking a Paternò-Büchi reaction in real time using transient electronic and vibrational spectroscopies. *J. Phys. Chem. A* **2014**, *118*, 10240-10245.
- [39] a) Mattay, J.; Gersdorf, J.; Leismann, H.; Steenken, S. Photoreaction of biacetyl and 1,3-dioxole derivatives: modification of the mechanism of the photoreaction of carbonyl compounds with electron-rich olefins. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 249-250; b) Mattay, J.; Gersdorf, J.; Buchkremer, K. Photoreactions of biacetyl with electron-rich olefins. An extended mechanism. *Chem. Ber.* **1987**, *120*, 307-318.
- [40] Bosch, E.; Hubig, S. M.; Kochi, J. K. Paternò-Büchi coupling of (diaryl)acetylenes and quinone via photoinduced electron transfer. *J. Am. Chem. Soc.* **1998**, *120*, 386-395.

- [41] Salem, L. Surface crossing and surface touching in photochemistry. *J. Am. Chem. Soc.* **1974**, *96*, 3486-3501.
- [42] Herndon, W. C. Substituent effects in photocycloaddition reactions. *Tetrahedron Lett.* **1971**, 125-128.
- [43] Bunce, N. J.; Ridley, J. E.; Zerner, M. C. On the excited states of *p*-quinones and an interpretation of the photocycloaddition of *p*-quinones to alkenes. *Theoret. Chim. Acta* **1977**, *45*, 283-300.
- [44] Bigot, B.; Devaquet, A.; Turro, N. J. Natural correlation diagrams. A unifying theoretical basis or analysis of n orbital initiated etone photoreactions. *J. Am. Chem. Soc.* **1981**, *103*, 6-12.
- [45] Minaev, B. F.; Ågren, H. Spin-orbit coupling in oxygen containing diradicals. *J. Mol. Struct. (Theochem)* **1998**, *434*, 193-206.
- [46] a) Kutateladze, A. G. Conformational analysis of singlet-triplet state mixing in Paternò-Büchi diradicals. *J. Am. Chem. Soc.* **2001**, *123*, 9279-9282; b) Kutateladze, A.; McHale, W. A. Toward parametrization of spin-orbit coupling in triplet organic diradicals separated by a partially conjugated spacer. *Arkivoc* **2005**, *4*, 88-101.
- [47] Pintér, B.; De Proft, F.; Veszprémi, T.; Geerlings, P. Regioselectivity in the [2+2] cyclo-addition reaction of triplet carbonyl compounds to substituted alkenes (Paterno-Büchi reaction): a spin-polarized conceptual DFT approach. *J. Chem. Sci.* **2005**, *117*, 561-571.
- [48] Noorizadeh, S. Minimum electrophilicity principle in photocycloaddition formation of oxetanes. *J. Phys. Org. Chem.* **2007**, *20*, 514-524.
- [49] Palmer, I. J.; Ragazos, I. N.; Bernardi, F.; Olivucci, M.; Robb, M. A. An MC-SCF study of the (photochemical) Paterno-Büchi reaction. *J. Am. Chem. Soc.* **1994**, *116*, 2121-2132.
- [50] Maeda, S.; Taketsugu, T.; Morokuma, K. Exploring pathways of photoaddition reactions by artificial force induced reaction method: a

- case study on the Paternò-Büchi reaction. *Z. Phys. Chem.* **2013**, *227*, 1421-1433.
- [51] Noorizadeh, S.; Shajirati, M. Atomic zero steric potential and the regioselectivity of reactions. *J. Phys. Chem. A* **2015**, *119*, 6468-6474.
- [52] Zhang, Y.; Xue, J.; Gao, Y.; Fun, H. -K., Xu, J. -H. Photoinduced [2+2] cycloaddition (the Paternò-Büchi reaction) of 1-acetylisatin with enol ethers-regioselectivity, diastereoselectivity and acid catalysed transformations of the spirooxane products. *J. Chem. Soc., Perkin Trans. 1* **2002**, 345-353.
- [53] D'Auria, M.; Emanuele, L.; Racioppi, R. Regio- and stereoselectivity in the Paternò-Büchi reaction of furan derivatives. *J. Photochem. Photobiol., A: Chem.* **2004**, *163*, 103-111.
- [54] Kong, F. -F.; Zhai, B. -C.; Song, Q. -H. Substituent effects on the regioselectivity of the Paternò-Büchi reaction of 5- or/and 6-methyl substituted uracils with 4,4'-disubstituted benzophenones. *Photochem. Photobiol. Sci.* **2008**, *7*, 1332-1336.
- [55] Epiotis, N. ●. Electrocyclic reactions. IV. The importance of donor-acceptor interactions in photocycloadditions involving the carbonyl group. *J. Am. Chem. Soc.* **1972**, *94*, 1946-1950.
- [56] a) Bach, T.; Kather, K. The β -silicon effect as a control element for the regioselective ring opening of oxetanes. *Tetrahedron* **1994**, *50*, 12319-12328; b) Bach, T. 3-Trimethylsilyloxy-oxetanes via a highly selective Paternò-Büchi reaction. *Tetrahedron Lett.* **1991**, *32*, 7037-7038.
- [57] Bach, T. Silyl enol ethers in Paternò-Büchi reactions. Functional group tolerance and the effect of β -alkyl substitution. *Liebigs Ann.* **1995**, 855-865.
- [58] Bach, T.; Jödicke, K.; Kather, K.; Hecht, J. Facial diastereoselectivity in the Paternò-Büchi reaction of chiral silyl enol ethers. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2271-2273.

- [59] a) Bach, T.; Jödicke, K.; Kather, K.; Fröhlich, R. 1,3-allylic strain as a control element in the Paternò-Büchi reaction of chiral silyl enol ethers: synthesis of diastereomerically pure oxetanes containing our contiguous stereogenic centers. *J. Am. Chem. Soc.* **1997**, *119*, 2437-2445; b) Bach, T.; Jödicke, K.; Wibbeling, B. Reversal of the facial diastereoselectivity in the Paternò-Büchi reaction of silyl enol ethers carrying a chiral substituent in α -position. *Tetrahedron* **1996**, *52*, 10861-10878
- [60] Bach, T.; Kather, K.; Krämer, O. Synthesis of five-, six-, and seven-membered heterocycles by intramolecular ring opening reactions of 3-oxetanol derivatives. *J. Org. Chem.* **1998**, *63*, 1910-1918.
- [61] D'Auria, M.; Racioppi, R. A DFT study of 1,4-biradical intermediates involved in stereoselective Paternò-Büchi reactions. *Eur. J. Org. Chem.* **2010**, 3831-3836.
- [62] Abe, M.; Fujimoto, K.; Nojima, M. Notable sulfur atom effects on the regio- and stereoselective formation of oxetanes in Paternò-Büchi photocycloaddition of aromatic aldehydes with silyl O,S-ketene acetals. *J. Am. Chem. Soc.* **2000**, *122*, 4005-4010.
- [63] Abe, M.; Tachibana, K.; Fujimoto, K.; Nojima, M. Regioselective formation of 3-selenyl-3-siloxyoxetanes in the Paternò-Büchi reaction of silyl Se-ketene acetals (Se-SKA). *Synthesis* **2001**, 1243-1247.
- [64] Bach, T.; Schröder, J. Photocycloaddition of N-acyl enamines to aldehydes and its application to the synthesis of diastereomerically pure 1,2-amino alcohols. *J. Org. Chem.* **1999**, *64*, 1265-1273.
- [65] a) Bach, T. N-Acyl enamines in the Paternò-Büchi reaction: stereoselective preparation of 1,2-amino alcohols by C-C bond formation. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 884-886; b) Bach, T.; Bergmann, H.; Brummerhop, H.; Lewis, W.; Harms, K. The [2+2]-photocycloaddition of aromatic aldehydes and ketones to 3,4-dihydro-2-pyridones: regioselectivity, diastereoselectivity, and reductive ring opening of the product oxetanes. *Chem. Eur. J.* **2001**, *7*, 4512-4521.

- [66] Bach, T.; Schröder, J. The Paternò-Büchi reaction of α -alkyl-substituted enecarbamates and benzaldehyde. *Synthesis* **2001**, 1117-1124.
- [67] Bach, T.; Schröder, J.; Brandl, T.; Hecht, J.; Harms, K. Facial diastereoselectivity in the photocycloaddition of chiral *N*-acyl enamines to benzaldehyde. *Tetrahedron* **1998**, *54*, 4507-4520.
- [68] a) Griesbeck, A. G.; Stadtmüller, S. Photocycloaddition of benzaldehyde to cyclic olefins: electronic control of endo stereoselectivity. *J. Am. Chem. Soc.* **1990**, *112*, 1281-1283; b) Griesbeck, A. G.; Stadtmüller, S. Regio- und stereoselektive Photocycloadditionen aromatischer Aldehyde an Furan und 2,3-Dihydrofuran. *Chem. Ber.* **1990**, *123*, 357-362; c) Griesbeck, A. G.; Stadtmüller, S. Electronic control of stereoselectivity in photocycloaddition reactions. 4. Effects of methyl substituents at the donor olefin. *J. Am. Chem. Soc.* **1991**, *113*, 6923-6928; d) Griesbeck, A. G.; Buhr, S.; Fiege, M.; Schmickler, H.; Lex, J. Stereoselectivity of triplet photocycloadditions: diene-carbonyl reactions and solvent effects. *J. Org. Chem.* **1998**, *63*, 3847-3854; e) Griesbeck, A. G.; Fiege, M.; Bondock, S.; Gudipati, M. S. Spin-directed stereoselectivity of carbonyl-alkene photocycloadditions. *Org. Lett.* **2000**, *2*, 3623-3625; f) Griesbeck, A. G.; Maptue, N.; Bondock, S.; Elgemöller, M. The excimer radiation system: a powerful tool for preparative organic photochemistry. A technical note. *Photochem. Photobiol. Sci.* **2003**, *2*, 450-451; g) D'Auria, M.; Pellegrino, F.; Viggiani, L. The diastereoselectivity of the Paternò-Büchi reaction between 2,3-dihydrofuran and aromatic carbonyl compounds in organized medium. *J. Photochem. Photobiol. A: Chem.* **2016**, *326*, 69-75.
- [69] Carless, H. A. J.; Haywood, D. J. Photochemical syntheses of 2,6-dioxabicyclo[3.2.0]heptanes. *J. Chem. Soc., Chem. Commun.* **1980**, 1067-1068.
- [70] Griesbeck, A. G.; Bondock, S.; Gudipati, M. S. Temperature and viscosity dependence of the spin-directed stereoselectivity of the carbonyl-alkene photocycloaddition. *Angew. Chem. Int. Ed.* **2001**, *40*, 4684-4687.

- [71] D'Auria, M.; Emanuele, L.; Racioppi, R. Regio- and stereoselectivity in the Paternò-Büchi reaction between 2,3-dihydrofuran and furan with benzaldehyde. *Lett. Org. Chem.* **2006**, *3*, 244-246.
- [72] Griesbeck, A. G.; Mauder, H.; Peters, K.; Peters, E. -M.; von Schnering, H. G. Photocycloadditionen mit α - und β -Naphthaldehyd: Vollständige Umkehr der Diastereoselektivität als Konsequenz unterschiedlich konfigurierter elektronischer Zustände. *Chem. Ber.* **1991**, *124*, 407-410.
- [73] a) Toki, S.; Shima, K.; Sakurai, H. Organic photochemical reactions. I. The synthesis of substituted oxetanes by the photoaddition of aldehydes to furans. *Bull. Chem. Soc. Jpn* **1965**, *38*, 760-762; b) Shima, K.; Sakurai, H. Organic photochemical reactions. IV. Photoaddition reactions of various carbonyl compounds to furan. *Bull. Chem. Soc. Jpn* **1966**, *39*, 1806-1808; c) Rivas, C.; Payo, E. Synthesis of oxetanes by photoaddition of benzophenone to furans. *J. Org. Chem.* **1967**, *32*, 2918-2920; d) Toki, S.; Sakurai, H. On the structure of the 2:1 adduct of benzophenone and furan. *Tetrahedron Lett.* **1967**, 4119-4122; e) Nakano, T.; Rivas, C.; Perez, C. Configuration and stereochemistry of photoproducts by application of the nuclear Overhauser effect. Adducts of benzophenone with methyl-substituted furans and 2,5-dimethylthiophene and of methyl-substituted maleic anhydride with thiophene and its methyl derivatives, and benzo[b]thiophene. *J. Chem. Soc. Perkin Trans. 1* **1973**, 2322-2327; f) Zamojski, A.; Koźluk, T. Synthesis of 3-substituted furans. *J. Org. Chem.* **1977**, *42*, 1089-1090; g) Rivas, C.; Bolivar, R. A.; Cucarella, M. Photoaddition of carbonyl compounds to five-membered ring heterocycles. *J. Heterocycl. Chem.* **1982**, *19*, 529-535.
- [74] Whipple, E. B.; Evanega, G. R. The assignment of configuration to the photoaddition products of unsymmetrical carbonyls to furan using pseudocontact shifts. *Tetrahedron* **1968**, *24*, 1299-1310.
- [75] Schreiber, S. L.; Desmaele, D.; Porco, J. A. Jr. On the use of unsymmetrically substituted furans in the furan-carbonyl photocycloaddition reaction: synthesis of a kadsurenone-ginkgide hybrid. *Tetrahedron Lett.* **1988**, *29*, 6689-6692.

- [76] Abe, M.; Torii, E.; Nojima, M. Paternò-Büchi photocyclization of 2-siloxyfurans and carbonyl compounds. Notable substituent and carbonyl (aldehyde vs ketone and singlet- vs triplet-excited state) effects on the regioselectivity (double-bond selection) in the formation of bicyclic *exo*-oxetanes. *J. Org. Chem.* **2000**, *65*, 3426-3431.
- [77] Carless, H. A. J.; Halfhide, A. F. E. Highly regioselective [2+2] photocycloaddition of aromatic aldehydes to acetylfurans. *J. Chem. Soc. Perkin Trans. 1* **1992**, **1081-1082**.
- [78] a) Kock, H.; Runsink, J.; Scharf, H. -D. Investigation of chiral induction in photochemical oxetane formation. *Tetrahedron Lett.* **1983**, *24*, 3217-3220; b) Kock, H.; Scharf, H. -D.; Runsink, J.; Leismann, H. Regio- und Diastereoselektivität bei der Oxetanbildung chiraler Phenylglyoxylate mit elektronenreichen Olefinen. *Chem. Ber.* **1985**, *118*, 1485-1503; c) Gotthardt, H.; Lenz, W. Unusually high asymmetric induction in the photochemical formation of oxetanes. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 868.
- [79] a) Matsumura, K.; Mori, T.; Inoue, Y. Wavelength control of diastereodifferentiating Paternò-Büchi reaction of chiral cyanobenzoates with diphenylethene through direct versus charge-transfer excitation. *J. Am. Chem. Soc.* **2009**, *131*, 17076-17077; b) Matsumura, K.; Mori, T.; Inoue, Y. Solvent and temperature effects on diastereodifferentiating Paternò-Büchi reaction of chiral alkyl cyanobenzoates with diphenylethene upon direct versus charge-transfer excitation. *J. Org. Chem.* **2010**, *75*, 5461-5469; c) Nagasaki, K.; Inoue, Y.; Mori, T. Entropy-driven diastereoselectivity improvement in the Paternò-Büchi reaction of 1-naphthyl aryl ethenes with a chiral cyanobenzoate through remote alkylation. *Angew. Chem. Int. Ed.* **2018**, *57*, 4880-4885.
- [80] Nehrings, A.; Scharf, H. -D.; Runsink, J. Photochemical synthesis of an L-erythrose building block and its use in the preparation of methyl 2,3,6-isopropylidene- β -L-apio-L-furanoside. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 877-878.

- [81] Thopate, S. R.; Kulkarni, M. G.; Puranik, V. G. The Paternò-Büchi reaction of L-ascorbic acid. *Angew. Chem. Int. Ed.* **1998**, *37*, 1110-1112.
- [82] Bach, T.; Bergmann, H.; Harms, K. High facial diastereoselectivity in the photocycloaddition of a chiral aromatic aldehyde and an enamide induced by intermolecular hydrogen bond. *J. Am. Chem. Soc.* **1999**, *121*, 10650-10651.
- [83] a) Jarosz, S.; Zamojski, A. Asymmetric photocycloaddition between furan and chiral alkyl glyoxytes. *Tetrahedron* **1982**, *38*, 1447-1451; b) Pelzer, R.; Scharf, H. -D.; Buschmann, H.; Runsink, J. Derivate der (+)-Menthyl-glyoxylate in der Paternò-Büchi-Reaktion. Einfluß von Substituenten im Glyoxylsäurerest auf die Diastereoselektivität. *Chem. Ber.* **1989**, *122*, 1187-1192.
- [84] D'Auria, M.; Emanuele, L.; Racioppi, R. On the Paternò-Büchi reaction of chiral phenylglyoxylate esters with furan derivatives. *Photochem. Photobiol. Sci.* **2003**, *2*, 904-913.
- [85] Pelzer, R.; Jütten, P.; Scharf, H. -D. Isolektivität bei der asymmetrischen Paterno-Büchi-Reaktion unter Verwendung von Kohlenhydraten als chirale Auxiliare. *Chem. Ber.* **1989**, *122*, 487-491.
- [86] a) Sakamoto, M.; Takahashi, M.; Fujita, T.; Watanabe, S.; Nishio, T.; Iida, I.; Aoyama, H. Solid state photochemical reaction of *N*- α , β -unsaturated carbonyl)benzoylformamides. *J. Org. Chem.* **1997**, *62*, 6298-6308; b) Raghunathan, R.; Kumarasamy, E.; Ugrinov, A.; Sivaguru, J. Intramolecular Paternò-Büchi reaction of atropisomeric α -oxoamides in solution and in the solid-state. *Chem. Commun.* **2013**, *49*, 8713-8715; c) Kumarasamy, E.; Ayitou, A. J. -L.; Vallavoju, N.; Raghunathan, R.; Iyer, A.; Clay, A.; Kandappa, S. K.; Sivaguru, J. Tale of twisted molecules. Atropselective photoreactions: turning light induced asymmetric transformations through non-biaryl atropisomers. *Acc. Chem. Res.* **2016**, *49*, 2713-2724.

- [87] Kang, T.; Scheffer, J. R. An unexpected Paternò-Büchi reaction in the crystalline state. *Org. Lett.* **2001**, *3*, 3361-3364.
- [88] D'Auria, M.; Emanuele, L.; Racioppi, R. Stereoselectivity in the reaction of chiral phenylglyoxylate esters with furan within zeolites and cyclodextrin. *Lett. Org. Chem.* **2008**, *5*, 249-256.
- [89] a) Adam, W.; Peters, K.; Peters, E. M.; Stegmann, V. R. Hydroxy-directed regio- and diastereoselective [2+2] photocycloaddition (Paternò-Büchi reaction) of benzophenone to chiral allylic alcohols. *J. Am. Chem. Soc.* **2000**, *122*, 2958-2959; b) Adam, W.; Stegmann, V. R. Unusual temperature dependence in the *cis/trans*-oxetane formation discloses competitive syn versus anti attack for the Paternò-Büchi reaction of triplet-excited ketones with *cis*- and *trans*-cyclooctenes. Conformational control of diastereoselectivity in the cyclization and cleavage of preoxetane diradicals. *J. Am. Chem. Soc.* **2002**, *124*, 3600-3607.
- [90] Bach, T.; Schröder, J.; Harms, K. Diastereoselective photocycloaddition of an axial chiral enamide. *Tetrahedron Lett.* **1999**, *40*, 9003-9004.
- [91] Abe, M.; Terazawa, M.; Nozaki, K.; Masuyama, A.; Hayashi, T. Notable temperature effect on the stereoselectivity in the photochemical [2+2] cycloaddition reaction (Paternò-Büchi reaction) of 2,3-dihydrofuran-3-ol derivatives with benzophenone *Tetrahedron Lett.* **2006**, *47*, 2527-2530.
- [92] Adam, W.; Stegmann, V. R. Hydroxy-group directivity in the regioselective and diastereoselective [2+2] photocycloaddition (Paternò-Büchi reaction) of aromatic carbonyl compounds to chiral and achiral allylic substrates; the preparation of oxetanes with up to three stereogenic centers as synthetic building blocks. *Synthesis* **2001**, 1203-1214.
- [93] Griesbeck, A. G.; Bondock, S. Paternò-Büchi reactions of allylic alcohols and acetates with aldehydes: hydrogen-bond interaction in

- the excited singlet and triplet states? *J. Am. Chem. Soc.* **2001**, *123*, 6191-6192.
- [94] D'Auria, M.; Racioppi, R.; Romaniello, G. The Paternò-Büchi Reaction on 2-furylmethanols. *Eur. J. Org. Chem.* **2000**, 3265-3272.
- [95] D'Auria, M.; Racioppi, R. Paternò-Büchi reaction on 5-methyl-2-furylmethanol derivatives. *Arkivoc* **2000**, *1*, 133-140.
- [96] Hisamoto, K.; Hiraga, Y.; Abe, M. Hydroxy-group effect on the regioselectivity in a photochemical oxetane formation reaction (the Paternò-Büchi reaction) of geraniol derivatives. *Photochem. Photobiol. Sci.* **2011**, *10*, 1469-1473.
- [97] D'Auria, M.; Emanuele, L.; Poggi, G.; Racioppi, R.; Romaniello, G. On the stereoselectivity of the Paternò-Büchi reaction between carbonyl compounds and 2-furylmethanol derivatives. The case of aliphatic aldehydes and ketones. *Tetrahedron* **2002**, *58*, 5045-5051.
- [98] D'Auria, M.; Emanuele, L.; Racioppi, R. The stereoselectivity of the Paternò-Büchi reaction between tertiary 2-furylmethanol derivatives and aromatic carbonyl compounds. On the nature of the hydroxy directing effect. *Photochem. Photobiol. Sci.* **2004**, *3*, 927-932.
- [99] a) Yabuno, Y.; Hiraga, Y.; Abe, M. Site- and stereoselectivity in the photochemical oxetane formation reaction (Paternò-Büchi reaction) of tetrahydrobenzofuranols with benzophenone: hydroxy-directed diastereoselectivity. *Chem. Lett.* **2008**, *37*, 822-823; b) Yabuno, Y.; Hiraga, Y.; Takagi, R.; Abe, M. Concentration and temperature dependency of regio- and stereoselectivity in a photochemical [2+2] cycloaddition reaction (the Paternò-Büchi reaction): origin of the hydroxy-group directivity. *J. Am. Chem. Soc.* **2011**, *133*, 2592-2604.
- [100] D'Auria, M.; Emanuele, L.; Racioppi, R. Stereoselectivity in the Paternò-Büchi reaction on chiral allylic alcohol, for a discussion of the hydroxy directing effect. *Lett. Org. Chem.* **2005**, *2*, 132-135.

- [101] D'Auria, M.; Emanuele, L.; Racioppi, R.; Valente, A. Paternò-Büchi reaction between aromatic carbonyl compounds and 1-(3-furyl)alkanols. *Photochem. Photobiol. Sci.* **2008**, *7*, 98-103.
- [102] a) Buschmann, H.; Scharf, H. -D.; Hoffmann, N.; Plath, M. W.; Runsink, J. Chiral induction in photochemical reactions. 10. The principle of isoinversion: a model of stereoselection developed from the diastereoselectivity of the Paternò-Büchi reaction *J. Am. Chem. Soc.* **1989**, *111*, 5367-5373; b) Buschmann, H.; Scharf, H. -D.; Hoffmann, N.; Esser, P. The isoinversion principle - A general model of chemical selectivity *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 477-515.
- [103] Adam, W.; Stegmann, V. R.; Weinkötz, S. Unusual temperature-dependent diastereoselectivity in the [2+2] photocycloaddition (Paternò-Büchi reaction) of benzophenone to *cis*- and *trans*-cyclooctene through conformational control. *J. Am. Chem. Soc.* **2001**, *123*, 2452-2453.
- [104] a) Barlow, M. G.; Coles, B.; Haszeldine, R. N. Heterocyclic polyfluoro-compounds. Part 31. Photochemical oxetan formation from fluoroketones and perfluoroaldehydes and 1,2-difluoroethylene. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2258-2267; b) Barlow, M. G.; Coles, B.; Haszeldine, R. N. Heterocyclic polyfluoro-compounds. Part 33. Competing 1,2- and 1,4-photochemical addition of hexafluorobiacetyl to 1,2-difluoroethylene. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2523-2526; c) Bissell, E. R.; Fields, D. B. Addition of acetaldehyde to fluoroethylene. *J. Org. Chem.* **1964**, *29*, 249-252; d) Harris, J. F.; Coffman, D. D. Synthesis of polyfluoroöxetanes by photoinitiated addition of fluorocarbonyl compounds to fluoroölefins. *J. Am. Chem. Soc.* **1962**, *84*, 1553-1561; e) Farid, S.; Hess, D. Photoreaktionen von *o*-Chinonen mit Ölefinen: Addition von Phenanthrenchinon-(9.10) an Chlorolefine und Phenanthrenderivative. *Chem. Ber.* **1969**, *102*, 3747-3764.
- [105] a) Barltrop, J. A.; Carless, H. A. J. Photocycloaddition of alkyl ketones to α,β -unsaturated nitriles. *Tetrahedron Lett.* **1968**, 3901-3903; b) Barltrop, J. A.; Carless, H. A. J. Organic photochemistry.

- XIII. Photocycloaddition of aliphatic ketones to α,β -unsaturated nitriles. *J. Am. Chem. Soc.* **1972**, *94*, 1951-1959; c) Turro, N. J.; Lee, C.; Schore, N.; Barltrop, J.; Carless, H. A. J. Structure-reactivity correlations for the quenching of acetone fluorescence by enol ethers and by conjugated unsaturated nitriles. *J. Am. Chem. Soc.* **1971**, *93*, 3079-3080; d) Ryang, H. -S.; Shima, K.; Sakurai, H. Photoaddition reaction of biacetyl. *J. Org. Chem.* **1973**, *38*, 2860-2865; e) Chung, W. -S.; Liu, Y. -D.; Wang, N. -J. Face selectivity in the Paterno-Büchi reactions of methacrylonitrile to 5-substituted adamantan-2-ones. *J. Chem. Soc. Perkin Trans. 1* **1995**, 581-586; f) Beereboom, J. J.; von Wittenau, M. S. The photochemical conversion of fumaronitrile and acetone to oxetanes. *J. Org. Chem.* **1965**, *30*, 1231-1234; g) Turro, N. J.; Wriede, P. A.; Dalton, J. C. Molecular photochemistry. VIII. Evidence for a singlet-state complex on the photocycloaddition of acetone to *trans*-1,2-dicyanoethylene. *J. Am. Chem. Soc.* **1968**, *90*, 3274-3275; h) Funke, C. W.; Cerfontain, H. Photochemical oxetan formation: the Paterno-Büchi reaction of aliphatic aldehydes and ketones with alkenes and dienes. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1902-1908; k) Turro, N. J.; Wriede, P. A. Photocycloaddition of some alkyl ketones to 1,2-dicyanoethylene, maleic anhydride, and 1-methoxy-1-butene. *J. Org. Chem.* **1969**, *34*, 3562-3265.
- [106] a) Friedrich, L. E.; Schuster, G. B. Photochemical preparation of a stable oxetane. *J. Am. Chem. Soc.* **1969**, *91*, 7204-7205; b) Albone, E. S. The photochemistry of the system dimethyl maleate-dimethyl fumarate-acetone. A new mechanism for oxetane formation. *J. Am. Chem. Soc.* **1968**, *90*, 4663-4666; c) Gotthardt, H. Photocycloadditionen der Thione and 1,2- und 1,3-diene und an elektronenarme Olefine. *Chem. Ber.* **1972**, *105*, 2008-2024; d) Vargas, F.; Rivas, C. Photocycloaddition of acetylselenophene to double bond containing substrates. *J. Photochem. Photobiol. A: Chem.* **2001**, *138*, 1-5; e) Cookson, R. C.; Frankel, J. J.; Hudec, J. Structures of photodimers of the dimethyl-*p*-benzoquinones. *Chem. Commun.* **1965**, 16; f) Gotthardt, H.; Lenz, W. Dependence of the optical induction on the mechanism of the photochemical thietane formation. *Tetrahedron Lett.* **1979**, 2879-2880.
- [107] D'Annibale, A.; D'Auria, M.; Prati, F.; Romagnoli, C.; Stoia, S.; Racioppi, R.; Viggiani, L. Paternò-Büchi reaction versus hydrogen

abstraction in the photochemical reactivity of alkenyl boronates with benzophenone. *Tetrahedron* **2013**, *69*, 3782-3795.

- [108] Knipe, R. H.; Gordon, A. S.; Ware, W. R. Quenching of Electronically Excited Hexafluoroacetone by Perfluoropropene. *J. Chem. Phys.* **1969**, *51*, 840.
- [109] a) Srinivasan, R.; Hill, K. A. Photosensitized reactions of cyclobutene in solution. *J. Am. Chem. Soc.* **1966**, *88*, 3765-3769; b) Barltrop, J. A.; Carless, H. A. J. Photocycloaddition of alkyl ketones to conjugated dienes. *Chem. Commun.* **1970**, 1637-1638 c) Barltrop, J. A.; Carless, H. A. J. Organic Photochemistry. XIV. Photocycloaddition of alkyl ketones to conjugated dienes. *J. Am. Chem. Soc.* **1972**, *94*, 8761-8768.
- [110] a) Kwiatkowski, G. T., Selley, D. B., The photochemistry of conjugated acetylenic olefins and derivatives. *Tetrahedron Lett.* **1968**, 3471-3474; b) Jorgenson, M. J. Photoaddition of acetylenic ketones to olefins. *Tetrahedron Lett.* **1966**, 5811.
- [111] Yang, N. C.; Kimura, M.; Eisenhardt, W. Paterno-Büchi reactions of aromatic aldehydes with 2-butenes and their implication on the rate of intersystem crossing of aromatic aldehydes. *J. Am. Chem. Soc.* **1973**, *95*, 5058-5060.
- [112] Bunce, N. J.; Hadley, M. On the mechanism of oxetan formation in the photocycloaddition of *p*-benzoquinone to alkenes *Can. J. Chem.* **1975**, *53*, 3240-3246.
- [113] a) Arnold, D. R.; Birtwell, R. J.; Clarke, B. M. Jr. The Photochemical Reactivity of Some Benzoylthiophenes. II. Photocycloaddition. *Can. J. Chem.* **1974**, *52*, 1681-1687; b) Arnold, D. R.; Hadjiantoniou, C. P. The photochemical reactivity of some benzoylthiophenes. IV. The effect of an adjacent methyl group on the excited state reactivity of 3-benzoylthiophene. *Can. J. Chem.* **1978**, *56*, 1970-1984; c) Kubo, Y.; Suto, M.; Tojo, S.; Araki, T. Photochemical reaction of *N*-methylnaphthalene-1,8-dicarboximide with alkenes, dienes, and furans. Cyclobutane and oxetane formation. *J. Chem. Soc. Perkin*

- Trans. 1* **1986**, 771-779; d) Ohkura, K.; Aizawa, K.; Mukaida, R.; Akizawa, H.; Seki, K. -I. New results on the photoreactivity of 5-fluoro-1,3-dimethyluracil with methoxylated naphthalenes. *Heterocycles* **2012**, *86*, 1465-1481; e) Seki, K.-I.; Aizawa, K.; Sugaoi, T.; Kimura, M.; Ohkura, K. Synthesis of highly conjugated arylpropenyldiene-1,3-diazin-2-ones via Paterno-Büchi reaction by photoreaction of 5-fluoro-1,3-dimethyluracil with 1-methoxynaphthalenes. *Chem. Lett.* **2008**, *37*, 872-873.
- [114] a) Carless, H. A. J. Photochemical reactions of acetone with 2,3-dimethylbut-2-ene. *J. Chem. Soc., Perkin Trans. 2* **1974**, 834-842; b) Shima, K.; Kawamura, T.; Tanabe, K. Organic photochemical reactions. XXII. The photoaddition of methyl pyruvate to methyl-substituted olefins. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2347-2348; c) Shima, K.; Sawada, T.; Yoshinaga, H. Organic photochemical reactions. XXVI. Photoaddition of singlet and triplet methyl pyruvate with 2,3-dimethyl-2-butene. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 608-612; d) Ryang, H. -S.; Shima, K.; Sakurai, H. A novel photochemical reaction of biacetyl with methyl-substituted olefins via the biradical intermediate. *J. Am. Chem. Soc.* **1971**, *93*, 5270-5271; e) Turro, N. J.; Shima, K.; Chung, C. -J.; Tanielian, C.; Kanfer, S. Photoreactions of biacetyl and tetramethylethylene. Solvent and temperature effects. *Tetrahedron Lett.* **1980**, *21*, 2775-2778.
- [115] Haga, N.; Takayanagi, H.; Tokumaru, K. Photoinduced electron transfer between acenaphthylene and 1,4-benzoquinones. Formation of dimers of acenaphthylene and 1:1 adducts and effect of excitation mode on reactivity of the charge-transfer complexes. *J. Chem. Soc., Perkin Trans. 2* **2002**, 734-745.
- [116] a) Cantrell, T. S. Photochemical reactions of α,β -unsaturated acids, esters, and nitriles. *J. Org. Chem.* **1975**, *40*, 1447-1450; b) Cantrell, T. S. Reactivity of photochemically excited 3-acylthiophenes, 3-acylfurans, and the formylthiophenes and furans. *J. Org. Chem.* **1977**, *42*, 3774-3776; c) Desorby, V.; Margaretha, P. Oxetane vs. cyclobutane formation in the photocycloaddition of enones to olefins. The photoaddition of 6-fluoro-4,4-dimethyl-2-cyclohexenone to 2,3-dimethyl-2-butene. *Helv. Chim. Acta* **1975**, *58*, 2161-2163; d) Thi, V. ●.; Margaretha, P. Photoaddition reactions of 5-fluoro-4,4-dimethyl-

- 2-cyclopentenone. *Helv. Chim. Acta* **1976**, *59*, 2236-2243; e) Nelson, P. I.; Östrem, D.; Lassila, J. D.; Chapman, L. Photochemical addition of 4,4-dimethyl-2-cyclohexenone to tetramethylethylene. *J. Org. Chem.* **1969**, *34*, 811-813; f) Altmeyer, I.; Margaretha, P. Photochemistry of chlorinated 2-cycloalkenones. *Helv. Chim. Acta* **1977**, *60*, 874-881; g) Yoshida, Z.; Kimura, M.; Yoneda, S. Photochemical oxetane formation from 4-substituted 2-cyclopentenones. *Tetrahedron Lett.* **1975**, 1001-1004.
- [117] Hoye, T. R.; Richardson, W. S. A short, oxetane-based synthesis of (\pm)-sarracenin. *J. Org. Chem.* **1989**, *54*, 688-693.
- [118] Öwsley, D. C.; Bloomfield, J. J. Photochemical synthesis at low temperatures. Part. III. Ready synthesis of bicyclo[4.2.0]octan-2-ones from cyclohexenones and ethylene. *J. Chem. Soc. (C)* **1971**, 3445-3447.
- [119] Bryce-Smith, D.; Gilbert, A.; Johnson, M. G. Liquid-phase photolysis. Part X. Formation of spiro-oxetans by photoaddition of olefins to *p*-benzoquinone. *J. Chem. Soc. (C)* **1967**, 383-389.
- [120] Barltrop, J. A.; Carless, H. A. J. Photocycloaddition of alkyl ketones to conjugated dienes. *Chem. Commun.* **1970**, 1637-1638.
- [121] Dowd, P.; Gold, A.; Sachdev, K. Oxetane formation in the photochemical reaction of cyclobutanones with butadiene, cyclopentadiene, and piperylene. *J. Am. Chem. Soc.* **1970**, *92*, 5725-5726.
- [122] Barltrop, J. A.; Carless, H. A. J. Organic photochemistry. XI. The photocycloaddition of benzophenone to conjugated dienes. *J. Am. Chem. Soc.* **1971**, *93*, 4794-4801.
- [123] Bryce-Smith, D.; Gilbert, A.; Johnson, M. G. Photoadditions of diphenylacetylene. Cyclo-octa-1,3-diene and cyclo-octene to anthraquinone. *Tetrahedron Lett.* **1968**, 2863-2866.

- [124] Carless, H. A. J. Photocycloaddition of acetone to acyclic olefins. *Tetrahedron Lett.* **1973**, 3173-3174.
- [125] Hussain, S.; Agosta, W. C. Photochemical [3+2] cycloaddition of α,β -acetylenic ketones with simple olefins. *Tetrahedron* **1981**, *4*, 3301-3305.
- [126] Yoshida, Z.; Kimura, M.; Yoneda, S. Photochemical cycloaddition of 4-cyclopentene-1,3-diones with olefins. Selective oxetane formation. *Tetrahedron Lett.* **1974**, 2519-2522.
- [127] Cantrell, T. S. Photochemical reactions of 2-acylthiophenes, -furans, and -pyrroles with alkenes. *J. Org. Chem.* **1974**, *39*, 2242-2246.
- [128] Kanaoka, Y.; Yoshida, K.; Hatanaka, Y. Photoaddition of olefins to cyclic imides: intermolecular oxetane formation and ring expansion. *J. Org. Chem.* **1979**, *44*, 664-666.
- [129] Imai, T.; Nishida, S. Thermal fragmentation of 3-alkyl-2-phenyloxetanes, 3,3-dimethyl-2-aryloxetanes, and related compounds. A case study of 2-aryl-substituted oxetanes. *Can. J. Chem.* **1981**, *59*, 2503-2509.
- [130] Arnold, D. R.; Clarke B. M. Jr. The photochemical reactivity of some benzoylthiophenes. III. The effect of an adjacent methyl group on the excited state reactivity of 2-benzoylthiophene. *Can. J. Chem.* **1975**, *53*, 1-11.
- [131] Farid, S.; Scholz, K. -H. Photoreactions of *o*-quinones with olefins: competition between cyclo- and R-H-addition. *Chem. Commun.* **1968**, 412-413.
- [132] Caldwell, R. A. Isotope and substituent effects on the interaction of benzophenone with simple olefins. Apparent insufficiency of the Schenk mechanism. *J. Am. Chem. Soc.* **1970**, *92*, 1439-1441.

- [133] Ruotsalainen, H. Photochemical reactions of benzaldehyde and chloro-substituted benzaldehyde with 3-chloro-2-methyl-1-propene. *Acta Chem. Scand. B* **1978**, *32*, 417-420.
- [134] Gold, E. H.; Ginsburg, D. Low-temperature photolysis of cyclopentadiene. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 246.
- [135] Carless, H. A. J. Photocycloaddition of benzophenone to a conjugated enyne. *Tetrahedron Lett.* **1972**, 2265-2266.
- [136] Sauers, R. R.; Henderson, T. R. Photochemistry of polycyclic 5-acylnorbornenes. *J. Org. Chem.* **1974**, *39*, 1850-1853.
- [137] Carless, H. A. J.; Maitra, A. K. Photocycloaddition of acetaldehyde to (*E*)- and (*Z*)-penta-1,3-diene. *Tetrahedron Lett.* **1977**, 1411-1412.
- [138] Inoue, H.; Ezaki, A.; Tomono, H.; Hida, M. Photocycloaddition of 1-aminoanthraquinones to dienes by visible light irradiation. *J. Chem. Soc., Chem. Commun.* **1979**, 860-861.
- [139] Hara, M.; Odaira, Y.; Tsutsumi, S. Photoaddition of diethyl oxomalonate to olefins. *Tetrahedron Lett.* **1967**, 2981-2984.
- [140] Chung, W. -S.; Ho, C. -C. Photochemistry of acetone in the presence of exocyclic olefins: an unexpected competition between the photoconia and Paternò-Büchi reactions. *Chem. Commun.* **1997**, 317-318.
- [141] Cantrell, T. S. Photochemical transformations of some β -substituted enones. *Tetrahedron* **1971**, *27*, 1227-1237.
- [142] Hu, S.; Neckers, D. C. Rapid regio- and diastereoselective Paternò-Büchi reaction of alkyl phenylglyoxylates. *J. Org. Chem.* **1997**, *62*, 564-567.
- [143] Maruyama, K.; Muraoka, M.; Naruta, Y. Keto oxetanes produced from photocycloaddition of *o*-quinone and their thermolysis. Reaction of 9,10-phenanthrenequinone with internally highly strained cyclic olefins. *J. Org. Chem.* **1981**, *46*, 983-989.

- [144] Paternò, E.; Chieffi, G.; Perret, G. Sintesi in chimica organica per mezzo della luce. VIII. Esperienze varie. *Gazz. Chim. Ital.* **1914**, *44*(I), 151-164.
- [145] Shigemitsu, Y.; Odaira, Y.; Tsutsumi, S. Photocycloaddition of acetylcyanide to olefins. *Tetrahedron Lett.* **1967**, 55-59.
- [146] Ryang, H. -S.; Shima, K.; Sakurai, H. Photocycloaddition of biacetyl to various olefins. *Tetrahedron Lett.* **1970**, 1091-1094.
- [147] Cantrell, T. S. Photochemical cycloaddition of benzonitrile to alkenes. Factors controlling the site of addition. *J. Org. Chem.* **1977**, *42*, 4238-4245.
- [148] Cantrell, T. S. J. Photochemical reactions of methyl benzoate. *Chem. Soc., Chem. Commun.* **1973**, 468-469.
- [149] Patel, D. J.; Schuster, D. I. Characterization of the reactive excited state in the photochemistry of a cyclohexadienone. *J. Am. Chem. Soc.* **1967**, *89*, 184-186.
- [150] Netto-Ferreira, J. C.; Silva, M. T.; Puget, F. P. Photochemistry of cyclic vicinal tricarbonyl compounds. [2+2] Photocycloaddition of 1,2,3-indanetrione to electron rich olefins. *J. Photochem. Photobiol. A: Chem.* **1998**, *119*, 165-170.
- [151] Friedrichsen, W. Photoreaktionen des 4,6-dimethylbenzofuran-2,3-dions. *Liebigs Ann. Chem.* **1975**, 1545-1562.
- [152] Wilson, R. M.; Musser, A. K. Photocyclization involving quinone-olefin charge-transfer exciplexes. *J. Am. Chem. Soc.* **1980**, *102*, 1720-1722.
- [153] Fukuyama, T.; Kajihara, Y.; Hino, Y.; Ryu, I. Continuous microflow [2+2] photocycloaddition reactions using energy-saving compact light sources. *J. Flow Chem.* **2011**, *1*, 40-45.

- [154] Bondock, S. A concise diastereoselective photochemical synthesis of 3-hydroxyfuran-2(3*H*)-ones. *J. Heterocycl. Chem.* **2012**, *49*, 555-560.
- [155] Wang, W.; Zhang, W. -J.; Wang, L.; Quah, C. K.; Fun, H. -K.; Xu, J. -H.; Zhang, Y. Photoinduced reactions of *para*-quinones with bicyclopopylidene leading to diverse polycyclic compounds with spirocyclopropanes. *J. Org. Chem.* **2013**, *78*, 6211-6222.
- [156] Christl, M.; Braun, M. Photocycloaddition of benzvalene. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 601-603.
- [157] Kubota, T.; Shima, K.; Toki, S.; Sakurai, H. The photoaddition of propionaldehyde to cyclohexa-1,3-diene. Oxetan formation by a singlet mechanism. *Chem. Commun.* **1969**, 1462-1463.
- [158] Jones, G. II; Acquadro, M. A.; Carmody, M. A. Long-chain enals via carbonyl-olefin metathesis. An application in pheromone synthesis. *J. Chem. Soc., Chem. Commun.* **1975**, 206-207.
- [159] Shima, K.; Kubota, T.; Sakurai, H. Organic photochemical reactions. XXIV. Photocycloaddition of propal to 1,3-cyclohexadiene. *Bull. Chem. Soc. Jpn* **1976**, *49*, 2567-2571.
- [160] Shimizu, N.; Ishikawa, M.; Ishikura, K.; Nda, S. A new substrate to investigate radical cycloaddition. III. Photocycloaddition of aromatic carbonyl compounds to vinylcyclopropane and its derivatives. *J. Am. Chem. Soc.* **1974**, *96*, 6456-6462.
- [161] Saltiel, J.; Coates, R. M.; Dauben, W. G. Photochemical cycloaddition of 2,3-dimethyl-1,3-butadiene and 1,2-dimethylcyclobutene to benzophenone. *J. Am. Chem. Soc.* **1966**, *88*, 2745-2748.
- [162] Bradshaw, J. S. Ultraviolet irradiation of carbonyl compounds in cyclohexene and 1-hexene. *J. Org. Chem.* **1966**, *31*, 237-240.
- [163] Borrell, P.; Sedlar, J. Photochemical reaction between acetone and cyclohexene in the liquid phase at 313 nm. *J. Chem. Soc. (C)* **1970**, 1670-1679.

- [164] Gáplovský, A.; Donovalová, J.; Toma, Š.; Kubinec, R. Ultrasound effects on photochemical reactions, Part 1: photochemical reactions of ketones with alkenes *Ultrasonics Sonochem.* **1997**, *4*, 109-115.
- [165] Bryce-Smith, D.; Gilbert, A. Photoaddition of *p*-quinones to olefin: new syntheses of oxetans and phenols. *Proc. Chem. Soc.* **1964**, 64.
- [166] Gream, G. E.; Mular, M.; Paice, J. C. Some photochemical reactions of α -diketones with olefins. *Tetrahedron Lett.* **1970**, 3479-3482.
- [167] Barttrop, J. A.; Hesp, B. Organic photochemistry. Part III. The effect of light on some Diels-Alder systems. *J. Chem. Soc. (C)* **1965**, 5182-5188.
- [168] Barttrop, J. A.; Hesp, B. Organic photochemistry. Part V. The illumination of some quinones in the presence of conjugated dienes and other olefinic systems. *J. Chem. Soc. (C)* **1967**, 1625-1635.
- [169] Japar, S. M.; Davidson, J. A.; Abrahamson, E. W. The path of triplet excitation energy in simple carbonyl-monoolefins system in the liquid phase. *J. Phys. Chem.* **1972**, *76*, 478-487.
- [170] Cantrell, T. S.; Allen, A. C. Photochemical reactions of arenecarboxylic acid esters with electron-rich alkenes: 2+2 cycloaddition, hydrogen abstraction, and cycloreversion. *J. Org. Chem.* **1989**, *54*, 135-139.
- [171] Saba, S.; Wolff, S.; Schöder, C.; Margaretha, P.; Agosta, W. C. Studies on the photochemical reactions of α,β -acetylenic ketones with tetramethylethylene. *J. Am. Chem. Soc.* **1983**, *105*, 6902-6907.
- [172] Kaneko, Y.; Hu, S.; Neckers, D. C. Photochemical reactivities of alkyl thiophenoglyoxylates and alkyl furanglyoxylates. *J. Photochem. Photobiol. A: Chem.* **1998**, *114*, 173-179.
- [173] Cantrell, T. S. Divergent pathways in the photochemical reactions of benzonitrile. *J. Am. Chem. Soc.* **1972**, *94*, 5929-5931.

- [174] Carless, H. A. J.; Trivedi, H. S. Photocycloaddition of *ortho*-methyl substituted benzaldehydes to 2,3-dimethylbut-2-ene. *J. Chem. Soc., Chem. Commun.* **1975**, 581-582.
- [175] Cantrell, T. S. Photochemical reactions of benzoyl cyanide and benzoyl halides with alkenes. *J. Chem. Soc., Chem. Commun.* **1975**, 637-638.
- [176] Nakano, M.; Nishiyama, Y.; Tanimoto, H.; Morimoto, T.; Kakiuchi, K. Remarkable improvement of organic photoreaction efficiency in the flow microreactor by slug flow condition in water. *Org. Process Res. Dev.* **2016**, *20*, 1626-1632.
- [177] Catalani, L. H.; Rezende, D. d. B.; de Arruda Campos, I. P. Olefin photoaddition to 4-oxoisophorone. *J. Chem. Res. (S)* **2000**, 111-113.
- [178] Hanifin, J. W.; Cohen, E. Photoaddition reactions of chromone. *Tetrahedron Lett.* **1966**, 5421-5426.
- [179] Shima, K.; Takeo, S.; Yokoama, K.; Yamaguchi, H. Organic photochemical reactions. XXV. The photoaddition of 1-phenyl-1,2-propanedione to olefins. *Bull. Chem. Soc. Jpn* **1977**, *50*, 761-762.
- [180] Silva, M. T.; Braz-Filho, R.; Netto-Ferreira, J. C. Photochemistry of cyclic vicinal triarbonyl compounds. Photochemical reaction of 1,2,3-indanetrione with 2,3-dimethyl-2-butene: hydrogen abstraction and photocycloaddition, *J. Braz. Chem. Soc.* **2000**, *11*, 479-485.
- [181] Shigemitsu, Y.; Yamamoto, S.; Miyamoto, T.; Odaira, Y. A Novel photocycloaddition of *o*-dibenzoylbenzene to olefins. *Tetrahedron Lett.* **1975**, 2819-2820.
- [182] Yang, N. C.; Chiang, W. Photochemical addition of aromatic aldehydes to 1,3,5-cycloheptatriene, a $6\pi_s + 2\pi_s$ photocycloaddition. *J. Am. Chem. Soc.* **1977**, *99*, 3163-3166.
- [183] Fehnel, E. A.; Brokaw, F. C. Photocycloaddition reactions of norbornadiene and quadricyclane with *p*-benzoquinone. *J. Org. Chem.* **1980**, *45*, 578-582.

- [184] Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Parekh, C. T.; Smith, P. G. The inter- and intramolecular addition of aromatic ketone triplets to quadricyclenes. Comparison with the corresponding reactivities of norbornadiene, methylenenorbornene, methylenenorbornane and norbornene. *Tetrahedron* **1980**, *36*, 397-407.
- [185] Kubota, T.; Shima, K.; Sakurai, H. The photocycloaddition of benzophenone to norbornadiene. *Chem. Lett.* **1972**, 343-346.
- [186] Gorman, A. A.; Leyland, R. L. The reaction of benzophenone triplets with norbornadiene and quadricyclene. *Tetrahedron Lett.* **1972**, 5345-5348.
- [187] Christl, M.; Braun, M. [2+2] Photocycloaddition of homobenzvalene. *Liebigs Ann./Recueil* **1997**, 1135-1141.
- [188] Reusch, W. A stereospecific photochemical addition of acetone to norbornylene. *J. Org. Chem.* **1962**, *27*, 1882-1883.
- [189] Sauers, R. R.; Valenti, P. C.; Tavss, E. The importance of steric effects on the photocycloaddition of biacetyl to norbornenes. *Tetrahedron Lett.* **1975**, 3129-3132.
- [190] Maruyama, K.; Arakawa, S.; Otsuki, T. Photochemistry of epoxyquinones: photoinduced cycloaddition of 2,3-epoxy-1,4-naphthoquinones with olefins. *Tetrahedron Lett.* **1975**, 2433-2436.
- [191] Gorman, A. A.; Leyland, R. L.; Parekh, C. T.; Rodgers, M. A. J. The reaction of triplet benzophenone with 5-methylenenorborn-2-ene: regioselective oxetane formation. *Tetrahedron Lett.* **1976**, 1391-1394.
- [192] Scharf, D.; Korte, F. Photosensibilisierte cyclodimerisierung von Norbornen. *Tetrahedron Lett.* **1963**, 821-823.
- [193] Maruyama, K.; Iwai, T.; Naruta, Y.; Otsuki, T.; Miyagi, Y. Photoaddition reaction of 9,10-phenanthrenequinone with alicyclic

- olefins. Product distribution. *Bull. Chem. Soc. Jpn* **1978**, *51*, 2052-2058.
- [194] Maruyama, K.; Iwai, T.; Naruta, Y. Products and modes of photocycloaddition of 9,10-phenanthraquinone with cyclic olefins. *Chem. Lett.* **1975**, 1219-1222.
- [195] Hautala, R. R.; Dawes, K.; Turro, N. J. Stereoselectivity and regioselectivity of the photocycloaddition of α -methyl-2,4-hexadiene and acetone. *Tetrahedron Lett.* **1972**, 1229-1232.
- [196] Jones, G. II; Khalil, Z. H.; Phan, X. T.; Chen, T. -J.; Welankiwar, S. Divergent stereoselectivity in the photoaddition of alkanals and medium ring cycloalkenes. *Tetrahedron Lett.* **1981**, *22*, 3823-3826.
- [197] Wilson, R. M.; Gardner, E. J.; Elder, R. C.; Squire, R. H.; Florian, L. R. The laser initiated oxidative photoaddition of *p*-benzoquinone to cyclooctatetraene. *J. Am. Chem. Soc.* **1974**, *96*, 2955-2963.
- [198] Sakurai, H.; Shima, K.; Aono, I. The synthesis of oxetanes by the photochemical reaction of aliphatic aldehydes and styrene. *Bull. Chem. Soc. Jpn* **1965**, *38*, 1227.
- [199] Odaira, Y.; Shimodaira, T.; Tsutsumi, S. New oxetans from carboxylate esters: the photocycloaddition of ethyl cyanofornate to olefins. *Chem. Commun.* **1967**, 757.
- [200] Carless, H. A. J.; Maitra, A. K.; Trivedi, H. S. Photochemical cycloaddition of aldehydes to styrenes. *J. Chem. Soc., Chem. Commun.* **1979**, 984-985.
- [201] Fu, H. -P.; Zhang, M.; Shi, H. -G.; Xu, S. -H. Photoinduced [2+2] cycloaddition (the Paterno-Büchi reaction) of *N*-methyl-,4,5,6,7-tetrachlorophthalimide. *Res. Chem. Intermed.* **2004**, *30*, 383-395.
- [202] Xue, J.; Zhang, Y.; Fun, H. -K.; Xu, J. -H. Photoinduced [2+2] cycloaddition (the Paterno-Büchi reaction) of 1*H*-1-acetylinole-2,3-dione with alkenes. *J. Chem. Soc., Perkin Trans. 1* **2001**, 183-191.

- [203] Shima, K.; Sakai, Y.; Sakurai, H. Organic Photochemical Reactions. XIV. The Photocycloaddition of Acetone to Cyclooctene and 1,3-Cyclooctadiene. *Bull. Chem. Soc. Jpn* **1971**, *44*, 215-218.
- [204] Yamada, K.; Yoshioka, M.; Sugiyama, N. A photochemical cycloaddition of thiobenzophenone to conjugated dienes. *J. Org. Chem.* **1968**, *33*, 1240-1243.
- [205] Ohno, A.; Ohnishi, Y.; Tsuchihashi, G. Photocycloaddition of thiocarbonyl compounds to olefin. The reaction of thiobenzophenone with case-III olefins. *Tetrahedron Lett.* **1969**, 283-286.
- [206] Griesbeck, A. G.; Bondock, S. Spin-imposed stereoselection in the photocycloaddition of (*Z*) and (*E*)-cyclooctene to aliphatic aldehydes. *Photochem. Photobiol. Sci.* **2002**, *1*, 81-83.
- [207] Bryce-Smith, D.; Gilbert, A. 1:1- and 2:1-photoaddition of cyclooctene and cyclo-octa-1,5-diene to chloranil. *Tetrahedron Lett.* **1964**, 3471-3473.
- [208] Katsuhara, Y.; Shigemitsu, Y.; Odaira, Y. Photoaddition reactions of pyromellitic acid tetramethylester to olefins. *Bull. Chem. Soc. Jpn* **1971**, *44*, 1169.
- [209] Carless, H. A. J.; Trivedi, H. S. New ring expansion reactions of 2-*t*-butyloxetans. *J. Chem. Soc., Chem. Commun.* **1979**, 382-383.
- [210] Farid, S.; Shealer, S. E. Oxetan formation from photoexcited charge-transfer complexes of anhydrides with electron-rich olefins. *J. Chem. Soc., Chem. Commun.* **1973**, 296-297.
- [211] Krauch, C. H.; Farid, S.; Scheck, G. Photoaddition von Phenanthrenchinon-(9.10) and benzocyclische Olefine zu Keto-oxetanen als neuartige Cycloadditionreaktion der Chinone. *Chem. Ber.* **1965**, *98*, 3102-3117.
- [212] Fleming, S. A.; Gao, J. J. Stereocontrol of Paterno-Büchi photocycloaddition. *Tetrahedron Lett.* **1997**, *38*, 5407-5410.

- [213] Nozaki, H.; Ohtani, I.; Noyori, R.; Kawanisi, M. Photochemical reaction of *trans*-anethole. *Tetrahedron* **1968**, *24*, 2183-2192.
- [214] Motomoto, Y.; Yoshioka, M.; Yamada, K.; Sugiyama, N. A photochemical cycloaddition of thiobenzophenone to α -phellandrene. *J. Org. Chem.* **1967**, *32*, 3676-3679.
- [215] Edwards, J. H.; McQuillin, F. J.; Wood, M. Selectivity in the addition of organic radicals to alkene bond. *J. Chem. Soc., Chem. Commun.* **1978**, 438-439.
- [216] Nitta, M.; Kuroki, T.; Sugiyama, H. Photochemical cycloaddition of benzophenone to 7-methylenetetrahydro[3.3.0.0.2,8.0^{4,6}]octan-3-one and its alcohol derivative. *J. Chem. Soc., Chem. Commun.* **1980**, 378-380.
- [217] Carless, H. A. J.; Trivedi, H. S. Synthesis of oxetans by photocycloaddition of aromatic aldehydes to hexamethyl(Dewar benzene). *J. Chem. Soc., Chem. Commun.* **1981**, 950-951.
- [218] Morton, D. R.; Morge, R. A. Total synthesis of 3-oxa-4,5,6-trinor-3,7-inter-*m*-phenylene prostaglandins. I. Photochemical approach. *J. Org. Chem.* **1978**, *43*, 2093-2101.
- [219] Farid, S.; Hartman, S. E.; DeBoer, C. D. Reversible energy transfer and oxetane formation in the photoreactions of carbonyl compounds with benzofurans. *J. Am. Chem. Soc.* **1975**, *97*, 808-812.
- [220] Tominaga, T.; Tsutsumi, S. Photocycloaddition of carbamates to 1,1-diphenylethylene. *Tetrahedron Lett.* **1969**, 3175-3178.
- [221] Tominaga, T.; Odaira, Y.; Tsutsumi, S. The photochemical synthesis of oxetanes from diethyl oxalate. *Bull. Chem. Soc. Jpn* **1967**, *40*, 2451.
- [222] Sun, D.; Hubig, S. M.; Kochi, J. K. Oxetane from [2+2] cycloaddition of stilbenes to quinone via photoinduced electron transfer. *J. Org. Chem.* **1999**, *64*, 2250-2258.

- [223] Hubig, S. M.; Sun, D.; Kochi, J. K. Photodynamics of the Paterno-Büchi cycloaddition of stilbene to quinone. Unusual modulation of electron-transfer kinetics by solvent and added salt. *J. Chem. Soc., Perkin Trans. 2* **1999**, 781-788.
- [224] Gan, C. Y.; Gable, R. W.; Lambert, J. N. Exploration of the Paterno-Büchi reaction as a potential route to the oxetan ring of Taxol. *Aust. J. Chem.* **1999**, 52, 629-637.
- [225] Nagasaki, K.; Inoue, Y.; Mori, T. Contrasting behaviour of exciplex ensembles in the diastereodifferentiating Paternö-Büchi reaction of chiral cyanobenzoate with naphthyl- and phenylethenes on direct or charge-transfer excitation. *Aust. J. Chem.* **2015**, 68, 1693-1699.
- [226] Friedrich, L. E.; Bower, J. D. Detection of an oxetene intermediate in the photoreaction of benzaldehyde with 2-butyne. *J. Am. Chem. Soc.* **1973**, 95, 6869-6870.
- [227] Yu, H.; Li, J.; Kuo, Z.; Du, X.; Wei, Y.; Fun, H. -K.; Xu, J.; Zhang, Y. Photoinduced tandem reactions of isoquinoline-1,3,4-trione with alkynes to build aza-polycycles. *J. Org. Chem.* **2010**, 75, 2989-3001.
- [228] Farid, S.; Kothe, W.; Pfundt, G. Competitive photoadditions of acetylenes to the C=C and C=O bonds of p-quinones. *Tetrahedron Lett.* **1968**, 4147-4150.
- [229] Bradshaw, J. S.; Knudsen, R. D.; Tarish, W. W. Irradiation of benzaldehyde in 1-hexyne. *J. Org. Chem.* **1975**, 40, 529-530.
- [230] Büchi, G.; Kofron, J. T.; Koller, E.; Rosenthal, D. Light catalyzed organic reactions. V. The addition of aromatic carbonyl compounds to a disubstituted acetylene. *J. Am. Chem. Soc.* **1956**, 78, 876-877.
- [231] Miyamoto, T.; Shigemitsu, Y.; Odaira, Y. Photoaddition of carboxylate esters to diphenylacetylene. *Chem. Commun.* **1969**, 1410.

- [232] Bryce-Smith, D.; Fray, G. I.; Gilbert, A. A photoadduct of *p*-benzoquinone and diphenylacetylene. *Tetrahedron Lett.* **1964**, 2137-2139.
- [233] Pappas, S. P.; Portnoy, N. A. Substituent effects on the photoaddition of diphenylacetylene to 1,4-Naphthoquinones. *J. Org. Chem.* **1968**, *33*, 2200-2203.
- [234] Ishibe, N.; Hashimoto, K.; Yamaguchi, Y. Photoaddition of allenes to *p*-quinones. *J. Chem. Soc., Perkin Trans. 1* **1975**, 318-323.
- [235] Hogeveen, H.; Smit, P. J. Photochemical formation of a spiro-compound from benzophenone and allene. *Rec. Trav. Chem. Pays-Bas* **1966**, *85*, 1188-1190.
- [236] Arnold, D. R.; Glick, A. H. The photocycloaddition of carbonyl compounds to allenes. *Chem. Commun.* **1966**, 813-814.
- [237] Gotthardt, H.; Steinmetz, R.; Hammond, G. S. Photocyclic addition of carbonyl compounds to allenes. *Chem. Comm.* **1967**, 480-482.
- [238] Gotthardt, H.; Steinmetz, R.; Hammond, G. S. Mechanisms of photochemical reactions in solution. LIII. Cycloaddition of carbonyl compounds to allenes. *J. Org. Chem.* **1968**, *33*, 2774-2780.
- [239] Howell, A. R.; Fan, R.; Trung, A. Preparation of 2-alkylidene oxetanes: An investigation of the Paterno-Büchi reaction between aliphatic aldehydes and allenes. *Tetrahedron Lett.* **1996**, *37*, 8651-8654.
- [240] Ogino, K.; Matsumoto, T.; Kawai, T.; Kozura, S. Photochemical reaction of duroquinone with allenes and ketenimines. Photoinduced cycloaddition and molecular rearrangement. *J. Org. Chem.* **1979**, *44*, 3352-3356.
- [241] Ishibe, N.; Tanigushi, I. Photochemical addition of tetramethylallene to 1,4-quinones. *Tetrahedron* **1971**, *27*, 4883-4887.

- [242] Ogino, K.; Yamashina, S.; Matsumoto, T.; Kozuka, S. Photocycloadditions of p-quinones to ketenimines. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1552-1559.
- [243] Singer, L. A.; Bartlett, P. D. The photocycloaddition of aromatic aldehydes and ketones to dimethyl-N-(2-cyano-2-propyl)ketenimine *Tetrahedron Lett.* **1964**, 1887-1892.
- [244] Krow, G. R. Synthesis and Reactions of Ketenimines. *Angew. Chem. Int. Ed. Engl.* **1971**, 10, 435-449.
- [245] Singer, L. A.; Davis, G. A.; Knutsen, R. L. Photocycloaddition of acetone to ketenimines. Syn-anti exchange barriers in β -iminooxetanes. *J. Am. Chem. Soc.* **1972**, 94, 1188-1193.
- [246] Smith, A. B. III; Dieter, R. K. Intramolecular photochemical oxetane formation in two $\beta,\gamma\text{-}\gamma',\delta'$ -diunsaturated ketones. *Tetrahedron Lett.* **1976**, 327-330.
- [247] Singer, L. A.; Davis, G. A. The Photocycloaddition of Benzophenone to Ketenimines. *J. Am. Chem. Soc.* **1967**, 89, 598-605.
- [248] Visser, R. G.; Baaij, J. P. B.; Brouwer, A. C.; Bos, H. J. T. Photochemical (2+2) cycloaddition of aromatic thiones to ketenimines. Acid catalyzed rearrangement of 2-iminothietanes. *Tetrahedron Lett.* **1977**, 4343-4344.
- [249] Kundracev, W.; Frei, B.; Wolf, H. R.; Jeger, C. Photolysis of Homoconjugated Allene Ketones. *Heterocycles* **1982**, 17, 139-150.
- [250] Mattay, J.; Runsink, J.; Heckendorn, R.; Winkler, T. Photoreactions of benzonitrile with cyclic enol ethers. *Tetrahedron* **1987**, 43, 5781-5789.
- [251] Griesbeck, A. G.; Bondock, S.; Cygon, P. Substantial ^2H -Magnetic Isotope Effects on the Diastereoselectivity of Triplet Photocycloaddition Reactions. *J. Am. Chem. Soc.* **2003**, 125, 9016-9017.

- [252] Ogata, M.; Watanabe, H.; Kanō, H. Photochemical cycloaddition of benzophenone to furans. *Tetrahedron Lett.* **1967**, 533-537.
- [253] Polman, H.; Boleij, J. S. M.; Bos, H. J. T. Chemistry of acetylenic ethers 98: Photochemical addition of benzophenone and 4, 4'-dimethylbenzophenone to 1-methoxy-1-propyne alkylidenecycloheptatrienes. *Recl. Trav. Chem. Pays-Bas* **1972**, *91*, 1088-1094.
- [254] Bos, H. J. T.; Schinkel, H.; Wijsman, T. C. M. Photocycloadditions of aromatic thiones to allenes. *Tetrahedron Lett.* **1971**, 3905-3906.
- [255] Griesbeck, A. G.; Bondock, S.; Lex, J. Synthesis of erythro- α -Amino β -hydroxy Carboxylic Acid Esters by Diastereoselective Photocycloaddition of 5-Methoxyoxazoles with Aldehydes. *J. Org. Chem.* **2003**, *68*, 9899-9906.
- [256] Schroeter, S. H.; Orlando, C. M. Jr. Photocycloaddition of various ketones and aldehydes to vinyl ethers and ketene diethyl acetal. *J. Org. Chem.* **1969**, *34*, 1181-1187.
- [257] Shima, K.; Sakurai, H. Photocycloaddition of various ketones and aldehydes to vinyl ethers and ketene diethyl acetal. *Bull. Chem. Soc. Jpn* **1969**, *42*, 849.
- [258] Turro, N. J.; Lee, C.; Schore, N.; Barltrop, J.; Carless, H. A. J. Molecular photochemistry. XLV. Structure-reactivity correlations for the quenching of acetone fluorescence by enol ethers and by conjugated unsaturated nitriles. *J. Am. Chem. Soc.* **1971**, *93*, 3079-3080.
- [259] Gáplovský, A.; Donovalová, J.; Toma, Š.; Kubinec, R. Ultrasound effects on photochemical reactions, Part 1: photochemical reactions of ketones with alkenes. *Ultrasonics Sonochem.* **1997**, *4*, 109-115.
- [260] Araki, Y.; Nagasawa, J.; Ishido, Y. Synthetic studies of carbohydrate derivatives by photochemical reactions. Part 16. Synthesis of DL-apiose derivatives by photochemical cycloaddition of 1,3-

- dihydroxypropan-2-one derivatives with ethenediol or ethenol derivatives. *J. Chem. Soc., Perkin Trans. 1* **1981**, 12-23.
- [261] Mazzocchi, P. H.; Minamikawa, S.; Bowen, M. Photoaddition of Vinyl Ethers to N-Methylphthalimide. Competing 2+2 Processes. *Heterocycles* **1978**, *9*, 1713-1716.
- [262] Paternò, E.; Chieffi, G. Sintesi in chimica organica per mezzo della luce. Nota V. Comportamento degli acidi e degli eteri col benzofenone. *Gazz. Chim. Ital.* **1910**, *40*(II), 321-331.
- [263] Chapman, ●. L.; Koch, T. H.; Klein, F.; Nelson, P. J.; Brown, E. L. Photochemical transformations. XXV. Two triplet mechanisms in photochemical addition of 2-cyclohexenones to 1,1-dimethoxyethylene. *J. Am. Chem. Soc.* **1968**, *90*, 1657-1658.
- [264] Jones, G. II; Santhanam, M.; Chiang, S. -H. Photoaddition of biacetyl and alkenes. Reaction stereochemistry, multiplicity, and photokinetics. *J. Am. Chem. Soc.* **1980**, *102*, 6088-6095.
- [265] Weuthen, M.; Scharf, H. -D.; Runsink, J. 3-Acetyl-2,3-dihydro-2,2-dimethyloxazol; Darstellung, Eigenschaften und Einsatz als olefinischer Partner in der Paterno-Büchi-Reaktion. *Chem. Ber.* **1987**, *120*, 1023-1026.
- [266] Turro, N. J.; Wriede, P. A. Molecular photochemistry. X. Photocycloaddition of acetone to 1-methoxy-1-butene. A comparison of singlet and triplet mechanisms and biradical intermediates. *J. Am. Chem. Soc.* **1968**, *90*, 6863-6864.
- [267] Schroeter, S. H. A novel synthesis of β -lactones. *Tetrahedron Lett.* **1969**, 1591-1593.
- [268] Ralph, M.; Ng, S.; Booker-Milburn, K. I. Short Flow-Photochemistry Enabled Synthesis of the Cytotoxic Lactone (+)-Goniofufurone. *Org. Lett.* **2016**, *18*, 968-971.

- [269] Araki, Y.; Senna, K.; Matsuura, K.; Ishido, Y. Supplementary aspects in the photochemical addition of acetone to 3, 4, 6-tri-O-acetyl-D-glucal. *Carbohydr. Res.* **1978**, *60*, 389-395.
- [270] Ong, K. -S.; Whistler, R. L. Photochemical addition of acetone to D-glucal triacetate and subsequent oxetane ring cleavage. *J. Org. Chem.* **1972**, *37*, 572-574.
- [271] Matsuura, K.; Araki, Y.; Ishido, Y. Solvent effects on the photochemical addition of acetone to 3,4,6-tri-O-acetyl-D-glucal. *Carbohydr. Res.* **1973**, *29*, 459-468.
- [272] Matsuura, K.; Araki, Y.; Ishido, Y. Synthetic Studies of Carbohydrate Derivatives with Photochemical Reaction. III. Solvent Effects on the Photocycloaddition of Acetone to 3,4,6-Tri-O-acetyl-D-glucal. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3496-3498.
- [273] Schroeter, S. H. The directing effect of alkoxy-groups in the photocycloaddition of carbonyl compounds to olefins. *J. Chem. Soc. D: Chem. Commun.* **1969**, 12.
- [274] Smith, A. B. III; Sulikowski, G. A.; Sulikowski, M. M.; Fujimoto, K. Applications of an asymmetric [2 + 2]-photocycloaddition. Total synthesis of (-)-echinosporin. Construction of an advanced 11-deoxyprostaglandin intermediate. *J. Am. Chem. Soc.* **1992**, *114*, 2567-2576.
- [275] Buhr, S.; Griesbeck, A. G.; Lex, J.; Mattay, J.; Schröer, J. Stereoselectivity in the Paternò-Büchi reaction of 2,2-diisopropyl-1,3-dioxol with methyl trimethylpyruvate. *Tetrahedron Lett.* **1996**, *37*, 11951-1196.
- [276] Park, S. -K.; Lee, S. -J.; Baek, K.; Yu, C. -M. Diastereoselective Routes in the Paternò-Büchi Reaction of Cyclic Enol Ortho Ester with Aldehydes. *Bull. Korean Chem. Soc.* **1998**, *19*, 35-36.
- [277] Bos, H. J. T.; Boleij, J. Chemistry of acetylenic ethers 93. Photochemical additions of acetylenes (I) reactions of ketones with 1-

- methylthio-1-propyne. *Recl. Trav. Chem. Pays-Bas* **1969**, *88*, 465-473.
- [278] Mosterd, A.; Matser, H. J.; Bos, H. J. T. Photoaddition of non-cisoid 1,2-diketones(1) and phenylglyoxal(1) to alkylthioacetylenes(2); preparation of 3-alkylthiofurans(5) *Tetrahedron Lett.* **1974**, 4179-4180.
- [279] Bos, H. J. T.; van der Bend, H. T.; Boleij, J. S. M.; Everaars, C. J. A.; Polman, H. Chemistry of acetylenic ethers 95: Photochemical additions of acetylenes II reactions of ketones with 1-alkynyl ethers. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 65-74.
- [280] Khan, N.; Morris, T. H.; Smith, E. H.; Walsh, R. Alkenyl sulphides and ketene S,S-dithioacetals as olefin components in the Paterno-Büchi reaction: a regioselective synthesis of oxetanes. *J. Chem. Soc. Perkin Trans. 1* **1991**, 865-80.
- [281] Morris, T. H.; Smith, E. H.; Walsh, R. Oxetane synthesis: methyl vinyl sulphides as new traps of excited benzophenone in a stereoselective and regiospecific Paterno-Büchi reaction. *J. Chem. Soc., Chem. Commun.* **1987**, 964-965.
- [282] Abe, M.; Taniguchi, K.; Hayashi, T. Exo-selective formation of bicyclic oxetanes in the photocycloaddition reaction of carbonyl compounds with vinylene carbonate: the important role of intermediary triplet diradicals in the stereoselectivity. *Arkivoc* **2007**, *8*, 58-65.
- [283] Kollenz, G.; Terpetschnig, E.; Sterk, H.; Peters, K.; Peters, E. -M. Regio- and stereoselective photocycloadditions of heterocyclic 2,3-diones — Evidence for an unexpected 1,2-aroyl migration. *Tetrahedron* **1999**, *55*, 2973-2984.
- [284] Farid, S.; Hess, D.; Krauch, C. H. Strahlenchemische Bildung und Photolyse von α -Keto-oxetanderivaten aus Vinylencarbonat. *Chem. Ber.* **1967**, *100*, 3266-3272.

- [285] Vasudevan, S.; Brock, C. P.; Watt, D. S.; Morita, H. Diastereoselectivity in the Paternò-Büchi Reaction of Enol Acetates and Benzaldehydes. *J. Org. Chem.* **1994**, *59*, 4677-4679.
- [286] Kato, T.; Sato, M.; Kitagawa, Y. Studies on ketene and its derivatives. LXVII. Photoreaction of benzophenone and benzaldehyde with diketene. *Chem. Pharm. Bull.* **1975**, *23*, 365-370.
- [287] Bentrude, W. G.; Darnall, K. R. Oxetan intermediate in the photocondensation of acetone with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholen. *J. Chem. Soc. D, Chem. Commun.* **1969**, 862-863.
- [288] Krauch, C. H.; Farid, S. Competition between cyclobutane and oxetane formation in the photoaddition of 1,4-Naphthoquinone to benzocyclic olefins. *Tetrahedron Lett.* **1966**, 4783-4788.
- [289] Bach, T.; Jödicke, K. Diastereomerically Pure 3-(Silyloxy)oxetanes by a Selective Paternò-Büchi Reaction. *Chem. Ber.* **1993**, *126*, 2457-2466.
- [290] a) Abe, M.; Shirodai, Y.; Nojima, M. Regioselective formation of 2-alkoxyoxetanes in the photoreaction of aromatic carbonyl compounds with β,β -dimethyl ketene silyl acetals: notable solvent and silyl group effects. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3253-3260; b) Yoon, U. C.; Kim, M. J.; Moon, J. J.; Oh, S. W.; Kim, H. J.; Mariano, P. S. Photoaddition Reactions of Silyl Ketene Acetals with Aromatic Carbonyl Compounds: A New Procedure for β -hydroxyester Synthesis. *Bull. Korean Chem. Soc.* **2002**, *23*, 1218-1228; c) Abe, M.; Keda, M.; Shirodai, Y.; Nojima, M. Regio- and stereo-selective formation of 2-siloxy-2-alkoxyoxetanes in the photoreaction of cyclic ketene silyl acetals with 2-naphthaldehyde and their transformation to aldol-type adducts. *Tetrahedron Lett.* **1996**, *37*, 5901-5904.
- [291] Araki, Y.; Nagasawa, J.; Ishido, Y. Photochemical cycloaddition of 1,3-diacetoxy-2-propanone to (trimethylsilyloxy)ethylene. *Carbohydr. Res.* **1981**, *91*, 77-84.

- [292] Bach, T.; Eilers, F.; Kather, K. Regioselective Reductive Ring Opening of 2-(2-Hydroxyphenyl)-3-[(trimethylsilyloxy)oxetanes at the More Substituted C-2 Position. *Liebigs Ann./Recueil* **1997**, 1529-1536.
- [293] Abe, M.; Ikeda, M.; Nojima, M. A stereoselective, tandem [2+2] photocycloaddition–hydrolysis route to aldol-type adducts. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3261-3266.
- [294] Gan, C. Y.; Lambert, J. N. The tandem intermolecular Paternò–Büchi reaction: formation of tetrahydrooxepins. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2363-2372.
- [295] Kassir, A. F.; Ragab, S. S.; Nguyen, T. A. M.; Chamay-Pouget, F.; Guillot, R.; Scherrmann M. -C.; Boddaert, T.; Aitken, D. J. Synthetic Access to All Four Stereoisomers of Oxetin. *J. Org. Chem.* **2016**, *81*, 9983-9991.
- [296] Bach, T.; Brummerhop, H.; Harms, K. The Synthesis of (+)-Preussin and Related Pyrrolidinols by Diastereoselective Paternò–Büchi Reactions of Chiral 2-Substituted 2,3-Dihydropyrroles. *Chem. Eur. J.* **2000**, *6*, 3838-3848.
- [297] Bach, T.; Schröder, J. A Short Synthesis of (±)-Oxetin. *Liebigs Ann./Recueil* **1997**, 2265-2267.
- [298] Bach, T.; Brummerhop, H. Unprecedented Facial Diastereoselectivity in the Paternò–Büchi Reaction of a Chiral Dihydropyrrole—A Short Total Synthesis of (+)-Preussin. *Angew. Chem. Int. Ed.* **1998**, *37*, 3400-3402.
- [299] Döpp, D.; Fischer, M. -A. [2 + 2] Photoaddition of 2-aminopropenenitriles to diarylethanediones. A product study. *Rec. Trav. Chim. Pays-Bas* **1995**, *114*, 498-503.
- [300] Döpp, D.; Memarian, H. R.; Fischer, M. A.; van Eijk, A. M.; Varma, C. A. G. Paternò–Büchi Reaction of 2-Morpholinoacrylonitrile with Benzil. *Chem. Ber.* **1992**, *125*, 983-984.

- [301] van Wolven, C.; Döpp, D.; Fischer, M. A. α -Cyanoenamines in the Paternò-Büchi reaction. *J. Inf. Recording* **2000**, *25*, 209-14.
- [302] Jones, G. II; Gilow, H. M.; Low, J. Regioselective photoaddition of pyrroles and aliphatic carbonyl compounds. A new synthesis of 3(4)-substituted pyrroles. *J. Org. Chem.* **1979**, *44*, 2949-2951.
- [303] Matsuura, T.; Bamba, A.; Ogura, K. Photoinduced reactions—XLV : Photoaddition of ketones to methylimidazoles. *Tetrahedron* **1971**, *27*, 1211-1219.
- [304] Nakano, T.; Rivas, C.; Perez, C.; Larrauri, J. M. Photoaddition of ketones to imidazoles: Synthesis of oxetanes. *J. Heterocycl. Chem.* **1976**, *13*, 173-174.
- [305] Nakano, T.; Rodríguez, W.; de Roche, S. Z.; Larrauri, J. M.; Rivas, C.; Pérez, C. Photoaddition of ketones to imidazoles, thiazoles, isothiazoles and isoxazoles. Synthesis of their oxetanes. *J. Heterocycl. Chem.* **1980**, *17*, 1777-1780.
- [306] Griesbeck, A. G.; Franke, M.; Neudörff, J.; Kotaka, H. Photocycloaddition of aromatic and aliphatic aldehydes to isoxazoles: cycloaddition reactivity and stability studies. *Beilstein J. Org. Chem.* **2011**, *7*, 127-134.
- [307] Rivas, C.; Bolivar, R. A. Synthesis of oxetanes by photoaddition of carbonyl compounds to pyrrole derivatives. *J. Heterocycl. Chem.* **1976**, *13*, 1037-1040.
- [308] Rivas, C.; Velez, M.; Cucarella, M.; Bolivar, R. A.; Flores, S. E. Synthesis of an oxetane by photoaddition of benzophenone to a pyrrole derivative. *Acta Cient. Venezolana* **1971**, *22*, 145-146.
- [309] Sekretár, S.; Rudá, J.; Štibrányi, L. Photochemical reactions of 2-substituted furans with some carbonyl compounds. *Coll. Czech. Chem. Commun.* **1984**, *49*, 71-77.

- [310] Kitamura, T.; Kawakami, Y.; Imagawa, T.; Kawanisi, M. One-Pot Synthesis of 3-Substituted Furan: A Synthesis of Perillaketone. *Synth. Commun.* **1977**, *7*, 521-528.
- [311] Cantrell, T. S.; Allen, A. C.; Ziffer, H. Photochemical 2 + 2 cycloaddition of arenecarboxylic acid esters to furans and 1,3-dienes. 2 + 2 Cycloreversion of oxetanes to dienol esters and ketones. *J. Org. Chem.* **1989**, *54*, 140-145.
- [312] D'Auria, M.; Racioppi, R.; Viggiani, L. Paternò-Büchi reaction between furan and heterocyclic aldehydes: oxetane formation vs. metathesis. *Photochem. Photobiol. Sci.* **2010**, *9*, 1134-1138.
- [313] Tronchet, J. M. J.; Baehler, R. Glycosyl-6-dioxa-2,7-bicyclo[3,2,0]heptenes-3. *J. Carbohydr. Nucleosides Nucleotides* **1974**, *1*, 449-459.
- [314] Žagar, C.; Scharf, H. -D. Chiral Induction in Photochemical Reactions, XIII. The Paternò-Büchi Reaction of Achiral and Chiral Acyl Cyanides with Furan. *Chem. Ber.* **1991**, *124*, 967-969.
- [315] Jarosz, S.; Zamojski, A. Asymmetric photocycloaddition between furan and optically active ketones. *Tetrahedron* **1982**, *38*, 1453-1456.
- [316] Hambalek, R.; Just, G. A short synthesis of (±)-oxetanocin. *Tetrahedron Lett.* **1990**, *31*, 5445-5448.
- [317] Schreiber, S. L.; Hoveyda, A. H. Synthetic studies of the furan-carbonyl photocycloaddition reaction. A total synthesis of (±)-avenaciolide. *J. Am. Chem. Soc.* **1984**, *106*, 7200-7202.
- [318] Schenck, G. ●.; Hartmann, W.; Steinmetz, R. Vierringsynthesen durch photosensibilisierte Cycloaddition von Dimethylmaleinsäureanhydrid an ●efine. *Chem. Ber.* **1963**, *96*, 498-508.
- [319] Leitich, J. Photochemical cycloaddition of benzophenone to furans. *Tetrahedron Lett.* **1967**, 1937-1939.

- [320] Evanega, G. R.; Whipple, E. B. The photochemical addition of benzophenone to furan. *Tetrahedron Lett.* **1967**, 2163-2168.
- [321] Tsuge, ●.; ●e, K.; Tashiro, M. Photochemistry of heterocyclic compounds—II : The photochemical reaction of 2,5-disubstituted 1,3,4-oxadiazoles with furan. *Tetrahedron* **1973**, **29**, 41-46.
- [322] D'Auria, M.; Emanuele, L.; Racioppi, R. Diastereoselectivity in the Paternò-Büchi reaction on furan derivatives. *Tetrahedron Lett.* **2004**, **45**, 3877-3880.
- [323] D'Auria, M.; Emanuele, L.; Pace, V.; Racioppi, R. Diastereoselective Paternò-Büchi Reaction on Furan Derivatives-Reaction with Asymmetric Ketones. *Lett. Org. Chem.* **2006**, **3**, 350-355.
- [324] Vargas, F.; Rivas, C.; Navarro, M.; Alvarado, Y. Synthesis of an elusive oxetane by photoaddition of benzophenone to thiophene in the presence of a Lewis acid. *J. Photochem. Photobiol. A: Chem.* **1996**, **93**, 169-171.
- [325] Rivas, C.; Pacheco, D.; Vargas, F. Synthesis of an oxetane by photoaddition of benzophenone to a selenophene derivative. *Acta Sud Am. Quim.* **1982**, **2**, 1-3.
- [326] Griesbeck, A. G.; Bondock, S. Photocycloaddition of 5-Methoxyoxazoles to Aldehydes and ?-Keto Esters: A Comprehensive View on Stereoselectivity, Triplet Biradical Conformations, and Synthetic Applications of Paternò-Büchi Adducts. *Aust. J. Chem.* **2008**, **61**, 573-580.
- [327] D'Auria, M.; Racioppi, R.; Rofrano, F.; Stoia, S.; Viggiani, L. Investigation of the hydroxyl directing effect on the Paternò-Büchi reaction on 5-(2-triisopropylsilyloxazolyl)methanol derivatives. *Tetrahedron* **2016**, **72**, 5142-5148.
- [328] Abe, M.; Kawakami, T.; ●hata, S.; Nozaki, K.; Nojima, M. Mechanism of Stereo- and Regioselectivity in the Paternò-Büchi Reaction of Furan Derivatives with Aromatic Carbonyl Compounds:

- Importance of the Conformational Distribution in the Intermediary Triplet 1,4-Diradicals. *J. Am. Chem. Soc.* **2004**, *126*, 2838-2846.
- [329] Griesbeck, A. G.; Fiege, M.; Lex, J. Oxazole-Carbonyl photocycloadditions: selectivity pattern and synthetic route to erythro α -amino, β -hydroxy ketones. *Chem. Commun.* **2000**, 589-590.
- [330] Griesbeck, A. G.; Bondock, S.; Lex, J. Stereoselective generation of vicinal stereogenic quaternary centers by photocycloaddition of 5-methoxy oxazoles to α -keto esters: synthesis of erythro β -hydroxy dimethyl aspartates. *Org. Biomol. Chem.* **2004**, *2*, 1113-1115.
- [331] Schreiber, S. L.; Satake, K. Application of the furan carbonyl photocycloaddition reaction to the synthesis of the bis(tetrahydrofuran) moiety of asteltoxin. *J. Am. Chem. Soc.* **1983**, *105*, 6723-6724.
- [332] Schreiber, S. L.; Satake, K. Studies of the furan-carbonyl photocycloaddition reaction: The determination of the absolute stereostructure of asteltoxin. *Tetrahedron Lett.* **1986**, *27*, 2575-2578.
- [333] Rivas, C.; Pacheco, D.; Vargas, F.; Ascanio, J. Synthesis of oxetanes by photoaddition of carbonyl compounds to thiophene derivatives. *J. Heterocycl. Chem.* **1981**, *18*, 1065-1067.
- [334] Rivas, C.; Bolivar, R. A. Synthesis of oxetanes by photoaddition of carbonyl compounds to 2,5-dimethylthiophene. *J. Heterocycl. Chem.* **1973**, *10*, 967-971.
- [335] Rivas, C.; Velez, M.; Crescente, M. Synthesis of an oxetan by photoaddition of benzophenone to a thiophen derivative. *J. Chem. Soc. D, Chem. Commun.* **1970**, 1474.
- [336] Nakano, T.; Santana, M. Photoaddition of benzophenone to azaindole, synthesis of the oxetane of 7-azaindole. *J. Heterocycl. Chem.* **1976**, *13*, 585-587.

- [337] Julian, D. R.; Tringhan, G. D. Photoaddition of ketones to indoles: synthesis of oxeto[2,3-b]indoles *J. Chem. Soc., Chem. Commun.* **1973**, 13-14.
- [338] Krauch, C. H.; Farid, S. Photo-cycloadditionen mit Furocumarinen und Furochromonen. *Chem. Ber.* **1967**, *100*, 1685-1695.
- [339] Krauch, C. H.; Metzner, W.; Schenck, G. ●. Photochemische C4- und C3●-Cycloadditionen an Cumaron. *Chem. Ber.* **1966**, *99*, 1723-1731.
- [340] Capozzo, M.; D'Auria, M.; Emanuele, L.; Racioppi, R. Synthesis and photochemical reactivity towards the Paternò-Büchi reaction of benzo[b]furan derivatives: their use in the preparation of 3-benzofurylmethanol derivatives. *J. Photochem. Photobiol, A: Chem.* **2007**, *185*, 38-43.
- [341] Bondock, S.; Griesbeck, A. G. Diastereoselective Photochemical Synthesis of α -Amino- β -hydroxyketones by Photocycloaddition of Carbonyl Compounds to 2,5-Dimethyl-4-isobutyloxazole. *Monatsch. Chem.* **2006**, *137*, 765-777.
- [342] De Boer, C. ●. Oxetane formation from excited state olefin and ground state ketone. *Tetrahedron Lett.* **1971**, 4977-4980.
- [343] Ito, M.; Ji-Ben, M.; Suzuki, S.; Kusunaga, K.; Matsuura, T.; Fukuyama, K. Efficient photochemical oxetane formation from 1-methyl-2,4,5-triphenylimidazole and benzophenones. *Tetrahedron Lett.* **1985**, *26*, 2093-2096.
- [344] Klages, R. Über eine Verbesserung der additiven Berechnung von Verbrennungswärmen und der Berechnung der Mesomerie-Energie aus Verbrennungswärmen. *Chem. Ber.* **1949**, *82*, 358-375.
- [345] Katritzky, A. R.; Karelson, M.; Malhotra, N. Heterocyclic Aromaticity. *Heterocycles* **1991**, *32*, 127-161.
- [346] D'Auria, M. An Approach to the Aromaticity Based on the Energy of the Occupied π Orbitals. *Curr. Org. Chem.* **2016**, *20*, 971-983.

- [347] a) Cyrański, M.K.; Von Ragué Schleyer, P.; Krygowski, T.M.; Jiao, H. Facts and artifacts about aromatic stability estimation. *Tetrahedron* **2003**, *59*, 1657-1665; b) Omelchenko, I. V.; Shishkin, O. V.; Gorb, L.; Leszczynski, J.; Fias, S.; Bultinck, P. Aromaticity in heterocyclic analogues of benzene: comprehensive analysis of structural aspects, electron delocalization and magnetic characteristics. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20536-20548.
- [348] Thompson, M. P.; Agger, J.; Wong, L. S. Paternò-Büchi Reaction as a Demonstration of Chemical Kinetics and Synthetic Photochemistry Using a Light Emitting Diode Apparatus. *J. Chem. Educ.* **2015**, *92*, 1716-1720.
- [349] a) Kong, F. -F.; Wang, J. -B.; Song, Q. -H. Heavy atom effects in the Paternò-Büchi reaction of pyrimidine derivatives with 4,4'-disubstituted benzophenones. *Beilstein J. Org. Chem.* **2011**, *7*, 113-118; b) Song, Q. -H.; Zhai, B. -C.; Hei, X. -M.; Guo, Q. -X. The Paternò-Büchi Reaction of 1,3-Dimethyluracil and 1,3-Dimethylthymine with 4,4'-Disubstituted Benzophenones. *Eur. J. Org. Chem.* **2006**, 1790-1800; c) Song, Q. -H.; Wang, H. -B.; Li, X. -B.; Hei, X. -M.; Guo, Q. -X.; Yu, S. -Q. Notable substituent and temperature effects on the regioselectivity and the efficiency in Paternò-Büchi reaction of 4,4'-disubstituted benzophenones with 1,3-dimethyluracil and 1,3-dimethylthymine. *J. Photochem. Photobiol., A: Chem.* **2006**, *183*, 198-204.
- [350] a) Boussicault, F.; Robert, M. Electrochemical Approach to the Repair of Oxetanes Mimicking DNA (6-4) Photoproducts. *J. Phys. Chem. B* **2006**, *110*, 21987-21993; b) Prakash, G.; Falvey, D. E. Model studies of the (6-4) photoproduct DNA photolyase: Synthesis and photosensitized splitting of a thymine-5,6-oxetane. *J. Am. Chem. Soc.* **1995**, *117*, 11375-11376.
- [351] Hei, X. -M.; Song, Q. -H.; Li, X. -B.; Tang, W. -J.; Wang, H. -B.; Guo, Q. -X. Origin of a Large Temperature Dependence of Regioselectivity Observed for [2 + 2] Photocycloaddition (Paternò-Büchi Reaction) of 1,3-Dimethylthymine with Benzophenone and Its Derivatives: Conformational Property of the Intermediary Triplet 1,4-Diradicals. *J. Org. Chem.* **2005**, *70*, 2522-2527.

- [352] Zhai, B. -C.; Luo, S. -W.; Kong, F. -F.; Song, Q. -H. Notable solvent effects on the regioselectivity in the Paternò-Büchi reaction of 1,3-dimethylthymine with 4-methoxybenzophenone. *J. Photochem. Photobiol., A: Chem.* **2007**, *187*, 406-409.
- [353] a) Lhiaubet-Vallet, V.; Belmadoui, N.; Climent, M. J.; Miranda, M. A. Long-Lived Triplet Excited State of an Elongated Ketoprofen Derivative and Its Interactions with Amino Acids and Nucleosides. *J. Phys. Chem. B* **2007**, *111*, 8277-8282; b) Encinas, S.; Belmadoui, N.; Climent, M. J.; Gil, S.; Miranda, M. A. Photosensitization of Thymine Nucleobase by Benzophenone Derivatives as Models for Photoinduced DNA Damage: Paternò-Büchi vs Energy and Electron Transfer Processes *Chem. Res. Toxicol.* **2004**, *17*, 857-862.
- [354] Lhiaubet-Vallet, V.; Encinas, S.; Miranda, M. A. Excited State Enantiodifferentiating Interactions between a Chiral Benzophenone Derivative and Nucleosides *J. Am. Chem. Soc.* **2005**, *127*, 12774-12775.
- [355] von Wilucki, I.; Matthäus, H.; Krauch, C. H. Photosensibilisierte Cyoldimerisation von Thymim in Lösung. *Photochem. Photobiol.* **1967**, *6*, 497-500.
- [356] Joseph, A.; Prakash, G.; Falvey, D. E. Model Studies of the (6-4) Photoproduct Photolyase Enzyme: Laser Flash Photolysis Experiments Confirm Radical Ion Intermediates in the Sensitized Repair of Thymine Oxetane Adducts. *J. Am. Chem. Soc.* **2000**, *122*, 11219-11225.
- [357] Nakatani, K.; Yoshida, T.; Saito, I. Photochemistry of Benzophenone Immobilized in a Major Groove of DNA: Formation of Thermally Reversible Interstrand Cross-link. *J. Am. Chem. Soc.* **2002**, *124*, 2118-2119.
- [358] Vendrell-Criado, V.; Lhiaubet-Vallet, V.; Yamaji, M.; Cuquerella, M. C.; Miranda, M. A. Blocking cyclobutane pyrimidine dimer formation by steric hindrance. *Org. Biomol. Chem.* **2016**, *14*, 4110-4115.

- [359] Xin, H.; Zhu, X.; Yan, H.; Song, X. A novel photodimerization of 4-aryl-4H-pyrans for cage compounds. *Tetrahedron Lett.* **2013**, *54*, 3325-3328.
- [360] Bondarenko, L.; Hentschel, S.; Greiving, H.; Grunenberg, J.; Hopf, H.; Dix, I.; Jones, P. G.; Ernst, L. Intramolecular Reactions in Pseudo-Geminally Substituted [2.2]Paracyclophanes. *Chem. Eur. J.* **2007**, *13*, 3950-3963.
- [361] Gleiter, R.; Herb, T.; Borzyk, M.; Hyla-Kryspin, I. 2,7,9-trimethylenetricyclo[4.3.0.0^{3,8}]nonane and 2,9-dimethylenetricyclo[4.3.0.0^{3,8}]non-4-ene. Synthesis and properties. *Liebigs Ann.* **1995**, 357-364.
- [362] Herb, T.; Gleiter, R. 2,7,9-Trimethylenetricyclo[4.3.0.0^{3,8}]-non-4-ene. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2368-2369.
- [363] Gleiter, R.; Gaa, B.; Sigwart, C.; Lange, H.; Borzyk, M.; Rominger, F.; Irngartinger, H.; Meser, T. Preparation and properties of stelladiones. *Eur. J. Org. Chem.* **1998**, 171-176.
- [364] a) Sauers, R. R.; Rousseau, A. D.; Byrne, B. *J. Am. Chem. Soc.* **1975**, *97*, 4947; b) Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* **1969**, 79; c) Nakazaki, M.; Naemura, K.; Kondo, Y. *J. Org. Chem.* **1976**, *41*, 1229; d) Rawal, V. H.; Dufour, C. *J. Am. Chem. Soc.* **1994**, *116*, 2613.
- [365] Reddy, T. J.; Rawal, V. H. Expeditious Syntheses of (±)-5-oxosilphiperfol-6-ene and (±)-Silphiperfol-6-ene. *Org. Lett.* **2000**, *2*, 2711-2712.
- [366] Boxall, R. J.; Ferris, L.; Grainger, R. S. Synthesis of C-13 Oxidised Cuparene and Herbertane Sesquiterpenes via a Paternò-Büchi Photocyclisation-Oxetane Fragmentation Strategy: Total Synthesis of 1,13-Herbertenediol. *Synlett* **2004**, 2379-2381.

- [367] de la Torre, M. C.; Garga, I.; Sierra, M. A. Photochemical Access to Tetra- and Pentacyclic Terpene-like Products from R-(+)-Sclareolide. *J. Org. Chem.* **2003**, *68*, 6611-6618.
- [368] Iriondo-Alberdi, J.; Perea-Buceta, J. E.; Greaney, M. F. A Paternò-Büchi Approach to the Synthesis of Merrilactone A. *Org. Lett.* **2005**, *7*, 3969-3971.
- [369] Carless, H. A. J.; Fekarurhobo, C. K. A photochemical route to a thromboxane A₂ ring analogue. *J. Chem. Soc., Chem. Commun.* **1984**, 667-668.
- [370] a) Furih, B.; Daccord, G.; Kossanyi, J. Photochimie en solution. IX. Reactivite des allyl-2 cyclanones. *Tetrahedron Lett.* **1975**, 4259-4262; b) Kirschberg, T.; Mattay, J. Photoinduced Electron Transfer Reactions of α -Cyclopropyl- and α -Epoxy Ketones. Tandem Fragmentation-Cyclization to Bi-, Tri-, and Spirocyclic Ketones. *J. Org. Chem.* **1996**, *61*, 8885-8896.
- [371] Hammaecher, C.; Portella, C. New 6-oxa-2-silabicyclo[2.2.0]hexanes by photochemical conversion of acyl(allyl)(dimethyl)silanes. *Chem. Commun.* **2008**, 5833-5835.
- [372] Rochat, S.; Minardi, C.; de Saint Laumer, J. -Y.; Herrmann, A. Controlled Release of Perfumery Aldehydes and Ketones by Norrish Type-II Photofragmentation of α -Keto Esters in Undegassed Solution. *Helv Chim. Acta* **2000**, *83*, 1645-1671.
- [373] Hu, S.; Neckers, D. C. Photochemical Reactions of Alkenyl Phenylglyoxylates. *J. Org. Chem.* **1997**, *62*, 6820-6286.
- [374] Belmadoui, N.; Encinas, S.; Climent, M. J.; Gil, S.; Miranda, M. A. Intramolecular Interactions in the Triplet Excited States of Benzophenone-Thymine Dyads. *Chem. Eur. J.* **2006**, *12*, 553-561.
- [375] Thomas, M.; Guillaume, D.; Fourrey, J. -L.; Clivio, P. Further Insight in the Photochemistry of DNA: Structure of a 2-Imidazolone (5-4) Pyrimidone Adduct Derived from the Mutagenic Pyrimidine (6-4)

- Pyrimidone Photolesion by UV Irradiation. *J. Am. Chem. Soc.* **2002**, *124*, 2400-2401.
- [376] Yang, N. C.; Nussim, M.; Coulson, D. R. Photochemistry of δ,γ -unsaturated ketones in solution. *Tetrahedron Lett.* **1965**, 1525-1528.
- [377] Dalton, J. C.; Tremont, S. J. Photochemical synthesis of a 2,5-dioxabicyclo [2.2.0] hexane. *Tetrahedron Lett.* **1973**, 4025-4028.
- [378] Crandall, J. K.; Mayer, C. F. Photochemistry of 5,6-heptadien-2-one. *J. Org. Chem.* **1969**, *34*, 2814-2817.
- [379] Cormier, R. A.; Agosta, N. C. Abstraction of allylic hydrogen vs other processes in the photochemistry of three doubly unsaturated ketones. *J. Am. Chem. Soc.* **1974**, *96*, 1867-1873.
- [380] Morrison H. *cis-trans* Isomerization of Olefins by Intramolecular Energy Transfer. *J. Am. Chem. Soc.* **1965**, *87*, 932.
- [381] Meinwald, J.; Chapman, R. A. Solution photochemistry of some bicyclic ketones. *J. Am. Chem. Soc.* **1968**, *90*, 3218-3226.
- [382] Maruyama, K.; Kubo, Y. Formation of intramolecular oxetanes in the photolysis of N-2-alkenyl alicyclic imides. *J. Org. Chem.* **1977**, *42*, 3215-3216.
- [383] Bishop, R.; Hamer, N. K. Photochemical formation of 5-oxabicyclo[2,1,1]hexan-2-ones from unsaturated 1,2-diketones. *J. Chem Soc. D, Chem. Commun.* **1969**, 804.
- [384] Bishop, R.; Hamer, N. K. Photochemistry of some non-conjugated unsaturated 1,2-diketones. *J. Chem. Soc. (C)* **1970**, 1197-1202.
- [385] Bahurel, Y.; Pautet, F.; Descotes, G. Cétois. Réactions de cyclisation. IV. - Étude du comportement photochimique des ϵ -cétols insaturés et de leurs dérivés cyclopropaniques. *Bull. Soc. Chim. Fr.* **1971**, 2222-2227.

- [386] Dalton, J. C.; Tremont, S. J. Mechanistic photochemistry of γ,δ -unsaturated ketones. Discovery of a photo-Cope reaction of β -oxa- γ,δ -enones and its implications for the mechanisms of intramolecular photocycloaddition. *J. Am. Chem. Soc.* **1975**, *97*, 6916-6917.
- [387] Smith, A.B.; Brodsky, L.; Wolff, S.; Agosta, W.C. The photochemistry of two rigid β,γ -cyclopropyl ketones, *exo*- and *endo*-tricyclo[3,2,1,0^{2,4}]octan-6-one. *J. Chem. Soc., Chem. Comm.* **1975**, 509-510.
- [388] Meinwald, J.; Hamner, A. T. 7-Oxatricyclo[4,3,0,0^{5,8}]nonane and *exo*-bicyclo[3,2,1]octan-8-ol via an intramolecular Paterno-Büchi reaction. *Chem. Commun.* **1969**, 1302.
- [389] Kossanyi, J.; Guiard, B.; Furth, B. Photochimie an solution. V. - Réactivité des aldéhydes δ,ϵ -insaturés. *Bull. Soc. Chim. Fr.* **1974**, 305-309.
- [390] Kurowsky, S. R.; Morrison, H. Photochemistry of bichromophoric molecules. Solution phase photoisomerization of 5-hepten-2-one. *J. Am. Chem. Soc.* **1972**, *94*, 507-512.
- [391] Mattay, J. β -oxa- γ,δ -enones, II. Rearrangement and intramolecular cycloaddition of 1-cyclopentenyl-2-propanone. *Tetrahedron Lett.* **1980**, *21*, 2309-2312.
- [392] Sauers, R. R.; Kelly, K. W. Photochemistry of 5-norbornenylacetone and 5-norbornenylacetaldehyde. *J. Org. Chem.* **1970**, *35*, 498-501.
- [393] Sauers, R. R.; Whittle, J. A. Photocyclizations of 5-acylbicyclo[2.2.2]octenes. *J. Org. Chem.* **1969**, *34*, 3579-3582.
- [394] Duthaler, R. O.; Stingelin-Schmid, R. S.; Ganter, C. Photochemische Reaktionen. 86. Mitteilung [1]. Zur Photolyse von Bicyclo[3.3.1]nonan-2-on. *Helv. Chim. Acta* **1976**, *59*, 307-335.

- [395] Guiard, B.; Furth, B.; Kossanyi, J. Photochimie en solution. VIII (1). - Réactivité d'aldéhydes δ,ϵ -insaturés. *Bull. Soc. Chim. Fr.* **1976**, 1552-1560.
- [396] Berger, J.; Yoshioka, M.; Zink, M. P.; Wolf, H. R.; Jeger, O. Photochemische Reaktionen. 106. Mitteilung. Zur Photochemie tetraalkylsubstituierter γ -Keto-olefine. *Helv. Chim. Acta* **1980**, *63*, 154-190.
- [397] Sauers, R. R.; Lynch, D. C. Photochemistry of some heteroatom-substituted 5-aclynorbornenes. *J. Org. Chem.* **1980**, *45*, 1286-1290.
- [398] Sauers, R. R.; Bierenbaum, R.; Johnson, R. J.; Thich, J. A.; Potenza, J.; Schugar, H. J. Synthesis and chemistry of some polychlorinated oxetanes. *J. Org. Chem.* **1976**, *41*, 2943-2947.
- [399] Sauers, R. R.; Kelly, K. W. Photochemistry of 5-norbornenylacetone and 5-norbornenylacetaldehyde. *J. Org. Chem.* **1970**, *35*, 498-501.
- [400] Sauers, R. R.; Shurpik, A. Photochemistry of some dicyclopentadiene derivatives. *J. Org. Chem.* **1967**, *32*, 3120-3123.
- [401] Agosta, W. C.; Herron, D. K. Solution photolysis of camphor. *J. Am. Chem. Soc.* **1968**, *90*, 7025-7030.
- [402] Mori, T.; Yang, K. H.; Kimoto, K.; Nozaki, H. Photochemistry of bicyclo[3.3.1]nonanes having two functional groups at 3,7-positions. *Tetrahedron Lett.* **1970**, 2419-2420.
- [403] Scheffer, J. R.; Bhandari, K. S.; Ngan, Y. -M.; Schmidt, D. K. Solution photochemistry. XI. Irradiation of Some substituted butadiene-methyl vinyl ketone diels-alder adducts. *Tetrahedron Lett.* **1973**, 1413-1416.
- [404] Lange, G. L.; Bosch, M. Photochemistry of trans-5-cyclodecenone: a transamular paterno-buchi reaction. *Tetrahedron Lett.* **1971**, 315-316.

- [405] Jost, P.; Chaquin, P.; Kossanyi, J. Une nouvelle voie d'accès au squelette de l'azulène. *Tetrahedron Lett.* **1980**, *21*, 465-466.
- [406] Schexnayder, M. A.; Engel, P. S. Systematic structural modifications in the photochemistry of β,γ -unsaturated ketones. II. Acyclic olefins and acetylenes. *J. Am. Chem. Soc.* **1975**, *97*, 4825-4836.
- [407] Engel, P. S.; Schexnayder, M. A. Systematic structural modifications in the photochemistry by β,γ -unsaturated ketones. I. Cyclic olefins. *J. Am. Chem. Soc.* **1975**, *97*, 145-153.
- [408] Morrison, H.; Tisdale, V.; Wagner, P. J.; Liu, K. -C. Organic photochemistry. XXXIII. Intramolecular charge transfer quenching in excited β -vinyl phenyl ketones. *J. Am. Chem. Soc.* **1975**, *97*, 7189-7191.
- [409] Margaretha, P. Photochemistry of Tricyclo[3.3.1.0^{2,7}]nonan-6-ones. Preliminary communication. *Helv. Chim. Acta* **1976**, *59*, 2902-2905.
- [410] Zink, M. P.; Wolf, H. R.; Müller, E. P.; Schweizer, W. B.; Jeger, C. Photochemische Reaktionen. 83. Mitteilung. Verbindungen der 3,4-Dihydrojonon-Reihe als Modelle zur Photochemie γ , δ - bzw. δ , ϵ -ungesättigter Ketone und Aldehyde. *Helv. Chim. Acta* **1976**, *59*, 32-75.
- [411] Sakamoto, M.; Aoyama, H.; Motomoto, Y. Photochemical reactions of N-benzoylformyl α,β -unsaturated amides. *J. Chem. Soc. Perkin Trans. 1* **1986**, 1759-1762.
- [412] van Wageningen, A.; Cerfontain, H. Photochemistry of non-conjugated dienones III: photolysis of retro- γ -ionones. *Tetrahedron Lett.* **1972**, 3679-3682.
- [413] Schaffner, K.; Jeger, C. A chapter on ketone photochemistry. *Tetrahedron* **1974**, *30*, 1891-1902.
- [414] Dalton, J. C.; Chan, H. -F. Photochemistry of 2-aceto-2-methylmethylenecyclohexanes. *Tetrahedron Lett.* **1974**, 3351-3354.

- [415] Cookson, R. C.; Rogers, N. R. Photochemistry of 2-(cycloalk-1-enyl)cycloalkanones. A new photochemical reaction of β -unsaturated ketones. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1037-1043.
- [416] Hoshi, N.; Uda, H. Photoinduced 1,5-acyl shift of 3-acylated 3-methyloxepin-2(3H)-ones. *J. Chem. Soc., Chem. Commun.* **1981**, 1163-1164.
- [417] Valiulin, R. A.; Kutateladze, A. G. Harvesting the Strain Installed by a Paternò-Büchi Step in a Synthetically Useful Way: High-Yielding Photoprotolytic Oxametathesis in Polycyclic Systems. *Org. Lett.* **2009**, *11*, 3886-3889.
- [418] Rawal, V. H.; Fabré, A.; Iwasa, S. Photocyclization-fragmentation route to linear triquinanes: Stereocontrolled synthesis of (\pm)-endo-hirsutene. *Tetrahedron Lett.* **1995**, *36*, 6851-6854.
- [419] Gescheidt, G.; Neshchadin, D.; Rist, G.; Borer, A.; Dietliker, K.; Misteli, K. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1071.
- [420] Jindal, P.; Bhatia, R.; Khullar, S.; Mandal, S.; Kamboj, R. C. One-shot photochemical synthesis of 5-(thiophen-3-yl)pyrano[2,3-c]chromen-2(3H)-ones from 3-propynyloxy-chromenones: a case of an intramolecular Paternò-Büchi reaction. *Photochem. Photobiol. Sci.* **2014**, *13*, 488-491.
- [421] Valiulin, R. A.; Arisco, T. M.; Kutateladze, A. G. Photoinduced Intramolecular Cyclopentation vs Photoprotolytic Oxametathesis in Polycyclic Alkenes Outfitted with Conformationally Constrained Arylmethyl Chromophores. *J. Org. Chem.* **2013**, *78*, 2012-2025.
- [422] Sauers, R. R.; Rousseau, A. D. Intramolecular photocycloadditions of naphthyl ketones. *J. Am. Chem. Soc.* **1972**, *94*, 1776-1777.
- [423] Pérez-Ruiz, R.; Hinze, M.; Neudörfl, J. -M.; Gömer, H.; Griesbeck, A. G. Photochemistry of allyloxybenzophenones: a pseudo-Paternò-Büchi rearrangement accompanied by hydrogen transfer induced 1,5-cyclization. *Photochem. Photobiol. Sci.* **2008**, *7*, 782-788.

- [424] Yates, P.; Winnik, F. M. Bridged-ring steroids. II. The synthesis of bridged steroids with a bicyclo[2.2.1]heptane ring A system. *Can. J. Chem.* **1981**, *59*, 1641-1650.
- [425] Pepper, H. P.; Kuan, K. K. W.; George, J. H. Synthesis of a Liphagal-Frondosin C Hybrid and Speculation on the Biosynthesis of the Frondosins. *Org. Lett.* **2012**, *14*, 1524-1527.
- [426] Kondo, Y.; Waters, J. A.; Witkop, B.; Guenard, D.; Beugelmans, R. Fragmentation d'alcool allylique et homo-allylique en serie steroide. Oxymethylene- β , β a nor cholestane. *Tetrahedron* **1972**, *28*, 797-817.
- [427] Mihailović, M. L.; Lorenc, L.; Pavlović, V.; Kaldova, I. A convenient synthesis of 1 α - and 1 β -hydroxycholesterol. *Tetrahedron* **1977**, *33*, 441-444.
- [428] Miro, P.; Lhiaubet-Vallet, V.; Marin, M. L.; Miranda, M. A. Photosensitized Thymine Dimerization via Delocalized Triplet Excited States. *Chem. Eur. J.* **2015**, *21*, 17051-17056.
- [429] Carless, H. H. J. Mechanism of the thermal ring-cleavage of oxetans. *Tetrahedron Lett.* **1974**, 3425-3426.
- [430] Jones, G. II; Kleinman, H. H. The effects of medium on the rate and regiochemistry of thermally induced oxetane cycloreversions. *Tetrahedron Lett.* **1974**, 2103-2106.
- [431] Jones, G. II; Staires, J. C. The stereochemical course of thermally induced oxetane fragmentation. *Tetrahedron Lett.* **1974**, 2099-2102.
- [432] Shimizu, N.; Nishida, S. Distinctive thermal behaviour of geometrically isomeric oxetans. *J. Chem. Soc., Chem. Commun.* **1974**, 734-735.
- [433] Schaumann, E.; Ketcham, R. [2 + 2]-Cycloreversions. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 225-247.

- [434] Holbrook, K. A.; Scott, R. A. Gas-phase thermal unimolecular decomposition of oxetan. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1849-1856.
- [435] Holbrook, K. A.; Scott, R. A. Gas-phase unimolecular pyrolyses of cis- and trans-2,3-dimethyloxetan. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 43-50.
- [436] Pérez-Ruiz, R.; Miranda, M. A.; Alle, R.; Meerholz, K.; Griesbeck, A. G. An efficient carbonyl-alkene metathesis of bicyclic oxetanes: photoinduced electron transfer reduction of the Paternò-Büchi adducts from 2,3-dihydrofuran and aromatic aldehydes. *Photochem. Photobiol. Sci.* **2006**, *5*, 51-55.
- [437] Adames, G.; Bibby, C.; Grigg, R. Rhodium(I) catalysed rearrangements of vinyl epoxides and oxetans. *J. Chem. Soc., Chem. Commun.* **1972**, 491-492.
- [438] Carless, H. A. J. Stereochemistry of the reactions of oxetans with rhodium(I) and silver(I) catalysts. *J. Chem. Soc., Chem. Commun.* **1974**, 982.
- [439] Bach, T.; Schröder, J. Synthesis of syn- and anti-1,2-amino alcohols by regioselective ring opening reactions of cis-3-aminooxetanes. *Tetrahedron Lett.* **1997**, *38*, 3707-3710.
- [440] Kitagawa, Y.; Itoh, A.; Hashimoto, S.; Yamamoto, H.; Nozaki, H. Total synthesis of humulene. A stereoselective approach. *J. Am. Chem. Soc.* **1977**, *99*, 3864-3867.
- [441] Dvorak, C. A.; Dufour, C.; Iwasa, S.; Rawal, V. H. Rapid Synthesis of Di- and Triquinanes by Direct Reductive Fragmentation of Paternò-Büchi-Derived Oxetanes. *J. Org. Chem.* **1998**, *63*, 5302-5303.
- [442] Jarosz, S.; Zamojski, A. Rearrangement of 6-substituted 2,7-dioxabicyclo[3.2.0]hept-3-enes to furans. *J. Org. Chem.* **1979**, *44*, 3720-3723.

- [443] Gotthardt, H.; Hammond, G. S. Einige interessante Umlagerungen in der 2-Isopropylidenoxetan-Reihe. *Chem. Ber.* **1974**, *107*, 3922-3927.
- [444] Bach, T. Regioselective ring opening of oxetanes by hydrogenolysis. - A convenient method for the carbohydroxylation of enol ethers. *Liebigs Ann.* **1995**, 1045-1053.
- [445] Schroeter, S. H. Synthesis of 3-hydroxy aldehydes, 3-hydroxy acetals, and 3-hydroxy ethers from 2-alkoxy oxetanes. *J. Org. Chem.* **1969**, *34*, 1188-1191.
- [446] Koźluk, T.; Zamojski, A. The synthesis of 3-deoxy-dl-streptose. *Tetrahedron* **1983**, *39*, 805-810.
- [447] Schreiber, S. L.; Hoveyda, A. H.; Wu, H. -J. A photochemical route to the formation of threo aldols. *J. Am. Chem. Soc.* **1983**, *105*, 660-661.
- [448] Schreiber, S. L.; Porco, J. A. Studies of the furan-carbonyl photocycloaddition reaction: vinylic substitution reactions. *J. Org. Chem.* **1989**, *54*, 4721-4723.
- [449] Ma, X.; Xia, Y. Pinpointing Double Bonds in Lipids by Paternò-Büchi Reactions and Mass Spectrometry. *Angew. Chem. Int. Ed.* **2014**, *53*, 2592-2596.
- [450] a) Stinson, C. A.; Xia, Y. A method of coupling the Paternò-Büchi reaction with direct infusion ESI-MS/MS for locating the C=C bond in glycerophospholipids. *Analyst* **2016**, *141*, 3696-3704; b) Wäldchen, F.; Becher, S.; Esch, P.; Kompauer, M.; Heiles, S. Selective phosphatidylcholine double bond fragmentation and localization using Paternò-Büchi reactions and ultraviolet photodissociation. *Analyst* **2017**, *142*, 4744-4755; c) Murphy, R. C.; Okuno, T.; Johnson, C. A.; Barlkley, R. M. Determination of double bond position in polyunsaturated fatty acids using the photochemical Paternò-Büchi reaction with acetone and tandem mass spectrometry. *Anal. Chem.* **2017**, *89*, 8545-8553; d) Jack, V.; Korf, A.; Vosse, C.; Hayen, H. Localization of double-bond position in lipids by tandem mass

- spectrometry succeeding high-performance liquid chromatography with postcolumn derivatization. *Rapid Commun. Mass Spectrom.* **2018**, *10*, 1002/rcm.8262; e) Bednarik, A.; Boelsker, S.; Soltwisch, J.; Dreisewerd, K. An on-tissue Paterno-Büchi reaction for localization of carbon-carbon double bonds in phospholipids and glycolipids by matrix-assisted laser-desorption-ionization mass-spectrometry imaging. *Angew. Chem. Int. Ed.* **2018**, *57*, 12092-12096; f) Esch, P.; Heiles, S. Charging and charge switching of unsaturated lipids in apolar compounds using Paternò-Büchi reactions. *J. Am. Soc. Mass Spectrom.* **2018**, *29*, 1971-1980; g) Xu, T.; Pi, Z.; Song, F.; Liu, S.; Liu, Z. Benzophenone used as the photochemical reagent for pinpointing C=C locations in unsaturated lipids through shotgun and liquid chromatography-mass spectrometry approaches. *Anal. Chim. Acta* **2018**, *1028*, 32-44; h) Tang, F.; Guo, C.; Ma, X.; Zhang, J.; Su, Y.; Tian, R.; Shi, R.; Xia, Y.; Wang, X.; Ouyang, Z. Rapid in situ profiling of lipid C=C location isomers in tissue using ambient mass spectrometry with photochemical reactions. *Anal. Chem.* **2018**, *90*, 5612-5619.
- [451] Zhang, Y.; Zhang, H.; Ma, C.; Li, J.; Nishiyama, Y.; Tanimoto, H.; Morimoto, T.; Kakiuchi, K. Study of the Paternò-Büchi type photolabile protecting group and application to various acids. *Tetrahedron Lett.* **2016**, *57*, 5179-5184.
- [452] Conradi, M.; Ramakers, G.; Junkers, T. UV-Induced [2+2] Grafting-To Reactions for Polymer Modification of Cellulose. *Macromol. Rapid Commun.* **2016**, *37*, 174-180.
- [453] Schreiber, S. L.; Satake, K. Total synthesis of (±)-asteltoxin. *J. Am. Chem. Soc.* **1984**, *106*, 4186-4188.
- [454] Hambalek, R.; Just, G. Trisubstituted oxetanes from 2,7-dioxabicyclo-[3,2,0]-hept-3-enes. *Tetrahedron Lett.* **1990**, *31*, 4693-4696.
- [455] Aftab, T.; Carter, C.; Hart, J.; Nelson, A. A method for the stereospecific conversion of 1,3-diols into oxetanes. *Tetrahedron Lett.* **1999**, *40*, 8679-8683.

- [456] Aftab, T.; Carter, C.; Christlieb, M.; Hart, J.; Nelson, A. Stereospecific conversion of (1*R**,3*S**)- and (1*R**,3*R**)-3-cyclohexyl-1-phenylpropane-1,3-diol into the corresponding 2,4-disubstituted oxetanes. *J. Chem. Soc., Perkin Trans. 1* **2000**, 711-722.
- [457] Soai, K.; Niwa, S.; Yamanoi, T.; Hikima, H.; Ishizaki, M. Asymmetric synthesis of 2-aryl substituted oxetanes by enantioselective reduction of β -halogenoketones using lithium borohydride modified with *N,N*-dibenzoylcystine. *J. Chem. Soc., Chem. Commun.* **1986**, 1018-1019.
- [458] Roy, B. G.; Roy, A.; Achari, B.; Mandal, S. B. A simple one-pot entry to cyclic ethers of varied ring sizes from diols via phosphonium ion induced iodination and base catalyzed Williamson etherification. *Tetrahedron Lett.* **2006**, 47, 7783-7787.
- [459] Miao, C. -B.; Zhang, M.; Tian, Z. -Y.; Xi, H. -T.; Sun, X. -Q.; Yang, H. -T. Base-Controlled Selective Conversion of Michael Adducts of Malonates with Enones in the Presence of Iodine. *J. Org. Chem.* **2011**, 76, 9809-9816.
- [460] Vigo, D.; Stasi, L.; Gagliardi, S. Synthesis of 3,3-disubstituted oxetane building blocks. *Tetrahedron Lett.* **2011**, 52, 565-567.
- [461] Sevrin, M.; Krief, A. Regioselective and [C,C] connective routes to oxetanes and tetrahydrofuranes *Tetrahedron Lett.* **1980**, 21, 585-586.
- [462] Okuma, K.; Tanaka, Y.; Kaji, S.; Ohta, H. Reaction of dimethylxosulfonium methyllide with epoxides. Preparation of oxetanes. *J. Org. Chem.* **1983**, 48, 5133-5134.
- [463] Wender, P. A.; Badham, N. F.; Conway, S. P.; Floreancig, P. E.; Glass, T. E.; Houze, J. B.; Krauss, N. E.; Lee, D.; Marquess, D. G.; McGrane, P. L.; Meng, W.; Natchus, M. G.; Shuker, A. J.; Sutton, J. C.; Taylor, R. E. The Pinene Path to Taxanes. 6. A Concise Stereocontrolled Synthesis of Taxol. *J. Am. Chem. Soc.* **1997**, 119, 2757-2758.

- [464] Nicolau, K. C.; Yang, Z.; Liu, J. J.; Ueno, H.; Nantermet, P. G.; Guy, R. K.; Claiborne, C. T.; Renaud, J.; Couladouros, E. A.; Paulvaman, K.; Sorensen, E. J. Total synthesis of taxol. *Nature* **1994**, *367*, 630-634.
- [465] Hirai, S.; Otsugi, M.; Iwamoto, M.; Nakada, M. Formal Total Synthesis of (-)-Taxol through Pd-Catalyzed Eight-Membered Carbocyclic Ring Formation. *Chem. Eur. J.* **2015**, *21*, 355-359.
- [466] Dussault, P. H.; Trullinger, T. K.; Noor-e-Ain, F. Opening of Substituted Oxetanes with H₂O₂ and Alkyl Hydroperoxides: Stereoselective Approach to 3-Peroxyalcohols and 1,2,4-Trioxepanes. *Org. Lett.* **2002**, *4*, 4591-4593.
- [467] Kawahata, Y.; Takatsuto, S.; Ikekawa, N.; Murata, M.; Omura, S. Synthesis of a New Amino Acid-Antibiotic, Oxetin and Its Three Stereoisomers. *Chem. Pharm. Bull.* **1986**, *34*, 3102-3110.
- [468] Nishiyama, S.; Yamamura, S.; Kato, K.; Takita, T. A total synthesis of oxetanocin, a novel nucleoside with an oxetane ring. *Tetrahedron Lett.* **1988**, *29*, 4743-4746.
- [469] Davies, A. T.; Slawin, A. M. Z.; Smith, A. D. Enantioselective NHC-Catalyzed Redox [2+2] Cycloadditions with Perfluoroketones: A Route to Fluorinated Oxetanes. *Chem. Eur. J.* **2015**, *21*, 18944-18948.
- [470] Beherendt, J. M.; Bala, K.; Golding, P.; Hailes, H. C. Oxetane synthesis via cyclisation of aryl sulfonate esters on polystyrene and PEG polymeric supports. *Tetrahedron Lett.* **2005**, *46*, 643-645.
- [471] Boyd, S.; Davies, C. D. A new and versatile synthesis of 3-substituted oxetan-3-yl methyl alcohols. *Tetrahedron Lett.* **2014**, *55*, 4117-4119.
- [472] Ye, Y.; Zheng, C.; Fan, R. Solvent-Controlled Oxidative Cyclization for Divergent Synthesis of Highly Functionalized Oxetanes and Cyclopropanes. *Org. Lett.* **2009**, *11*, 3156-3159.

- [473] Jenkinson, S. F.; Fleet, G. W. J. Oxetanes from the Ring Contraction of α -Triflates of γ -Lactones: Oxetane Nucleosides and Oxetane Amino Acids. *Chimia* **2011**, *65*, 71-75.
- [474] Austin, G. N.; Fleet, G. W. J.; Peach, J. M.; Prout, K.; Son, J. C. Chiral oxetanes from sugar lactones: Synthesis of derivatives of 3,5-anhydro-1,2- α -isopropyl- α -D-glucuronic acid and of 3,5-anhydro-1,2- α -isopropylidene- β -L-iduronic acid. *Tetrahedron Lett.* **1987**, *28*, 4741-4744.
- [475] Dax, K.; Weidmann, H. Reactions of D-Glucofuranurono-6,3-Lactone. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 189-234.
- [476] Witty, D. R.; Fleet, G. W. J.; Vogt, K.; Wilson, F. X.; Wang, Y.; Storer, R.; Myers, P. L.; Wallis, C. J. Ring contraction of 2-*o*-trifluoromethanesulphonates of α -hydroxy- γ -lactones to oxetane carboxylic esters. *Tetrahedron Lett.* **1990**, *31*, 4787-4790.
- [477] Ehlinger, E.; Magnus, P. Silicon in Synthesis. **10**. The (Trimethylsilyl)allyl Anion: A β -Acyl Anion Equivalent for the Conversion of Aldehydes and Ketones into γ -Lactones *J. Am. Chem. Soc.* **1980**, *102*, 5004-5011.
- [478] Manabe, S.; Nishino, C. Stereochemistry of *cis*-clerodane diterpenes. *Tetrahedron* **1986**, *42*, 3461-3470.
- [479] Galatsis, P.; Milan, S. D.; Ferguson, G. Enantioselective Construction of Cyclic Ethers by An Aldol-Cyclization Sequence. *J. Org. Chem.* **1997**, *62*, 5048-5056.
- [480] Brown, W. L.; Fallis, A. G. Intramolecular rearrangements: Epimerization of bicyclic vinyl tertiary alcohols via a [2,3] sulfoxide sigmatropic rearrangement. *Can. J. Chem.* **1987**, *65*, 1828-1832.
- [481] Arjona, \bullet .; de la Pradilla, R. F.; Plumet, J.; Viso, A. Regioselective electrophilic additions to 2-oxygenated-7-oxabicyclo[2.2.1]Hept-5-enes: A simple entry into the 4,7-dioxatricyclo[3.2.1.0_{3,6}]octane skeleton. *Tetrahedron* **1989**, *45*, 4565-4578.

- [482] Evans, R. D.; Magee, J. W.; Schauble, J. H. Halocyclization of Unsaturated Alcohols and Carboxylic Acids Using Bis(*sym*-collidine)iodine(I) Perchlorate. *Synthesis* **1988**, 862-868.
- [483] Stepan, A. F.; Karki, K.; McDonald, W. S.; Dorff, P. H.; Dutra, J. K.; DiRico, K. J.; Won, A.; Subramanyam, C.; Efremov, I. V.; O'Donnell, C. J.; Nolan, C. E.; Becker, S. L.; Pustilnik, L. R.; Sneed, B.; Sun, H.; Lu, Y.; Robshaw, A. E.; Riddell, D.; O'Sullivan, T. J.; Sibley, E.; Capetta, S.; Atchison, K.; Hallgren, A. J.; Miller, E.; Wood, A.; Obach, R. S. Metabolism-Directed Design of Oxetane-Containing Arylsulfonamide Derivatives as γ -Secretase Inhibitors. *J. Med. Chem.* **2011**, 54, 7772-7783.
- [484] Jung, M. E.; Nichols, C. J. Highly stereoselective synthesis of *trans,trans*-4-aryl-2,3-oxetanedimethanols: Preparation of oxetanocin a analogues. *Tetrahedron Lett.* **1996**, 37, 7667-7670.
- [485] Rofoo, M.; Roux, M. -C.; Rousseau, G. Preparation of oxetanes by silicon-directed 4-*exo trig* electrophilic cyclisations of homoallylic alcohols. *Tetrahedron Lett.* **2001**, 42, 2481-2484.
- [486] Weller, A. Electron-transfer and complex formation in the excited state. *Pure Appl. Chem.* **1968**, 16, 115-123.
- [487] Kumarasamy, E.; Kandappa, S. K.; Raghunathan, R.; Jockusch, S.; Sivaguru, J. Realizing an aza Paternò-Büchi reaction. *Angew. Chem. Int. Ed.* **2017**, 56, 7056-7061.
- [488] a) Melis, N.; Luridiana, A.; Guillot, R.; Secci, F.; Frongia, A.; Boddaert, T.; Aitken, D. J. Stereoselective and regioselective pinacol-type rearrangement of a fused bicyclic oxetanol scaffold. *Eur. J. Org. Chem.* **2017**, 5896-5902; b) Ibba, F.; Capurro, P.; Garbarino, S.; Anselmo, M.; Moni, L.; Basso, A. Photoinduced multicomponent synthesis of α -silyloxy acrylamides, an unexplored class of silyl enol ethers. *Org. Lett.* **2018**, 20, 1098-1101.
- [489] a) Xue, J.; Abe, M.; Takagi, R. Paternò-Büchi photochemical [2 + 2] cycloaddition of aromatic carbonyl compounds with 2-siloxy-1H-

pyrrole derivatives. *J. Phys. Org. Chem.* **2017**, *30*, e3632; b) Xue, J.; Takagi, R.; Abe, M. Photochemical [2+2] cycloaddition reaction of enone derivatives with 2-siloxy-1*H*-pyrrole derivatives. *Arkivoc* **2018**, *ii*, 192-204.

- [490] Iyer, A.; Jockusch, S.; Sivaguru, J. A photo-auxiliary approach - enabling excited state classical phototransformations with metal free visible light irradiation. *Chem. Commun.* **2017**, *53*, 1692-1695.