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Electrocyclization reactions of vinyl, styryl, and butadienyl conjugated carbonyl/azomethine ylides

Olcay Anaç *, Füsun Şeyma Güngör

Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, Maslak, Istanbul, 34469, Turkey

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Contents

1. Introduction

According to Woodward and Hoffmann, a polyene (even-membered) or a polyenyl (odd-membered) system closes a ring in a process that can be described by a cyclic electron shift in an electrocyclic reaction. The net result is the conversion of a π-bond into a σ-bond.[1] As corresponding ring openings also take place via the same energy, both electrocyclic ring closures and ring openings belong to the same class, one-step 'pericyclic reactions'. Like all the pericyclic reactions, electrocyclic reactions are considered to be concerted with carbon–carbon σ bonds being formed/broken at the same time. In addition, they obey the principle of conservation of orbital symmetry benefiting from the energetically favored

* Corresponding author. Tel.: +90 212 285 3229; fax: +90 212 285 6386; e-mail address:anac@itu.edu.tr (O. Anaç).

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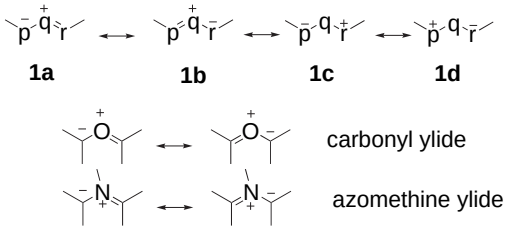
concertedness only by taking the steric course defined by the Woodward/Hoffmann rules (allowed process), but it should always be kept in mind that the opposite rotations are not totally 'forbidden' to take the place of the cyclization reactions. These 'forbidden' processes need higher activation energies and different pathways. For example, in the electrocyclization reactions of conjugated carbonyl ylide (CCY), mixtures of stereoisomers can also result from the isomerization of the ylide intermediate. Involvement of a singlet diradical or zwitterionic intermediates has not been debated.[2–8]

In the electrocyclic reactions, besides their theoretical interest, 1,3-dipole intermediates have been found to be very versatile for various syntheses, since Huisgen's reactions were reported.[9,10] A 1,3-dipole bound directly to an unsaturated moiety offers a powerful and reliable synthetic methodology to access three-, five-, and seven-membered heterocyclic rings in a regio- and stereocontrolled fashion. CCY and CAMY are very similar intermediates. In particular, the electrocyclization reactions of CCY/CAMY derived from 1,3-dipoles are practical methods for the synthesis of substituted and stereoisomerically pure dihydrofurans/dihydropyrroles and dihydrooxepines/dihydroazepines, which are important building blocks in the synthesis of many natural products and pharmaceuticals. In this review, the regioselectivities and stereoselectivities in the electrocyclization reactions of vinyl, styryl, and butadienyl CCY/CAMY are investigated.

Before describing the details of the electrocyclization reactions of carbonyl/azomethine ylides, it is pertinent to append a short and concise description of the structure, mechanism, and reactivities. Although there are no recent reviews relating to CCY, detailed aspects of CAMY are briefly summarized in a few recent reviews.[11,12] We do not intend to duplicate these reports about CAMY. Instead, only the most pertinent material will be covered here, as the chemistry of CCY usually parallels that of CAMY.

1,3-Dipoles (**1a**–**d**) possess carbon, nitrogen, oxygen, and sulfur in q centers including unsaturated moieties q=r as carbonyl, vinyl, imino, thiocarbonyl, azo, and nitroso groups (Scheme 1).



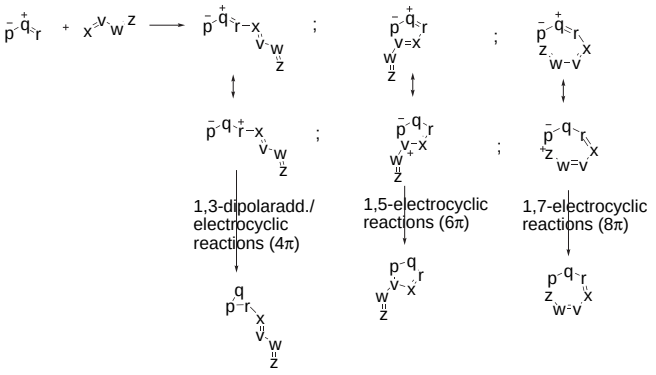
Scheme 1. Carbonyl and azomethine ylides are 1,3-dipoles of the allyl type.

These allyl-type 1,3-dipoles can be represented as a zwitterionic form of a p–q–r unit having four electrons in three parallel atomic *p* orbitals perpendicular to the plane of the dipole, providing a bent-type structure.[9] The characteristic stereochemical aspects of CCY/CAMY electrocyclizations are partly accounted for by this property. Four resonance forms can be drawn for this allyl-type 1,3-dipole (**1a**–**d**), as shown in Scheme 1.

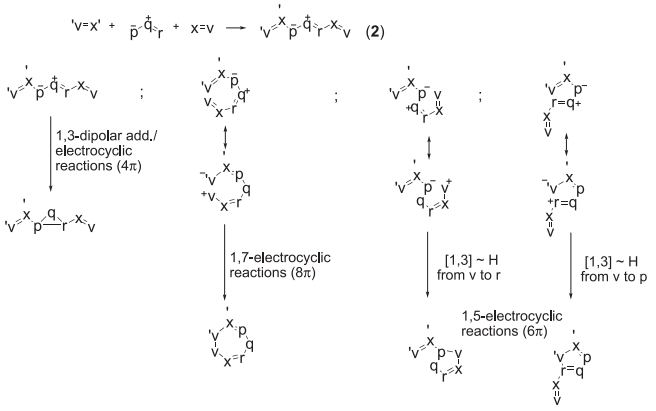
In the most common resonance representation, these dipoles have an octet structure in which the central q atom is positively charged and the negative charge is distributed over the two terminal carbon atoms (**1a**, **1b**). In an alternative representation, two of the four allylic π electrons are localized at the central q atom, thereby canceling the positive charge on it and creating electron sextets at the two terminal carbons (**1c**, **1d**). A butadienyl system may be anchored to the 1,3-dipole, as shown in Scheme 2.

The conjugated double bonds may be anchored to both the p and r atoms of a p–q=r system. Scheme 3 is focused on the electrocyclic reaction probabilities of 1,3-divinyl-1,3-dipoles (**2**).

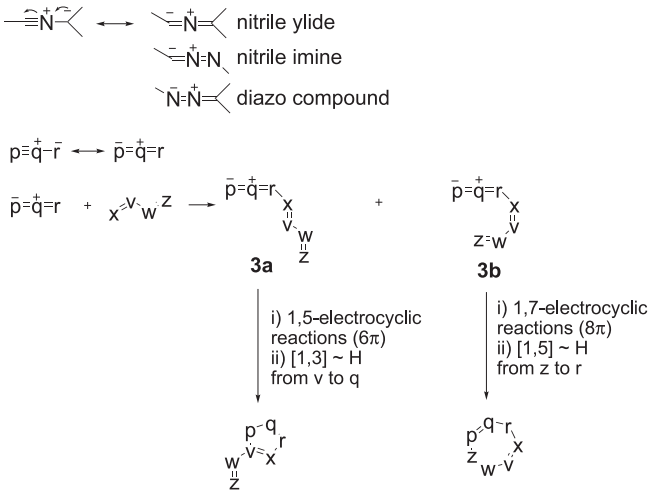
For the purpose of a brief comparison, nitrile ylides, nitrile imine ylides, and diazo compounds are also modeled (**3a** and **3b**) in Scheme 4.



Scheme 2. General pathways of electrocyclization of butadienyl conjugated carbonyl/azomethine ylides.



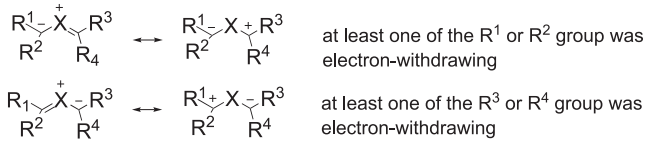
Scheme 3. General pathways of electrocyclization of divinyl conjugated carbonyl/azomethine ylides.



Scheme 4. General pathways of electrocyclization of butadienyl conjugated ylides derived from 1,3-dipoles of the propargyl/allenyl type (**3a** and **3b**).

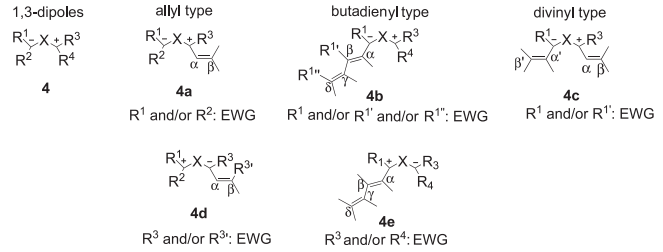
2. Importance of charge separations in the periselectivities of the cyclization reactions of CCY/CAMY

Distribution of the opposite charges of a 1,3-dipole of the allyl type may be affected by the substituents in the conjugated parts of both C1 and C3 atoms. The most effective substituents for the direction of the opposite charges are carbonyl and cyano groups (electron acceptors through resonance effects), which are bound on C1 or C3 (Scheme 5) and to some extent on the C(β) and C(δ) atoms



Scheme 5. Distribution of charges in a 1,3-dipole.

(Scheme 6, **4**, **4a**–**e**). If these groups are on the C1 or C3 atoms, they generally stabilise negative charges only on the C1 or C3 atoms and stabilize the negative charge of the CCY/CAMY better than the vinyl and phenyl groups.[13]



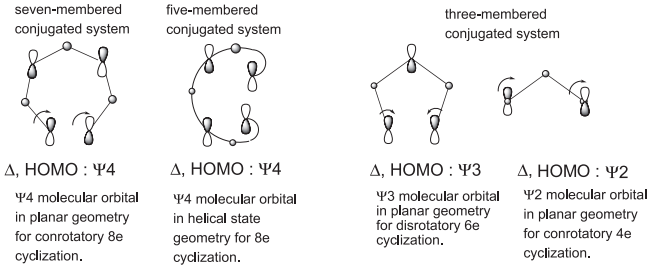
Scheme 6. Distribution of charges in a 1,3-dipole (allyl type) having extended conjugation.

However, predictions of the regioselectivity in the electrocyclization reactions of a conjugated carbonyl ylide and also an azomethine ylide can be made based on both the values of the orbital coefficients and the steric effects of the terminal carbons.

The studies of Eberbach and co-workers support the conclusion that, as compared with the vinylazomethine ylides, the vinylcarbonyl ylides exhibit greater configurative mobility and a smaller influence of orbital control on the ring closure.[14,15]

3. Importance of double-bond conformation in the periselectivities of the cyclization reactions of CCY/CAMY

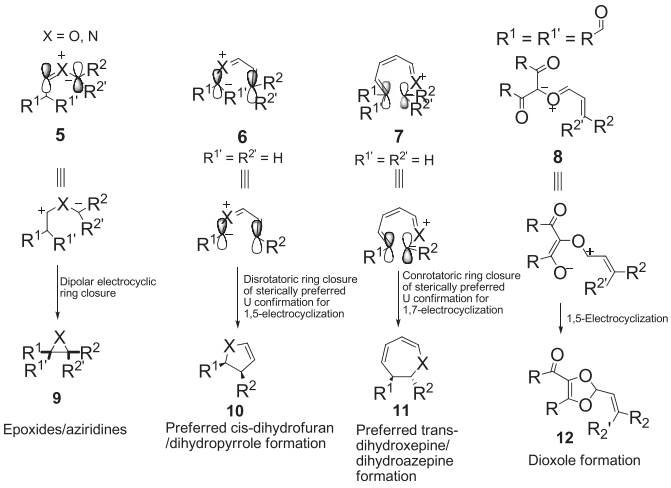
In order to understand a 1,7-electrocyclization reaction (seven p orbitals and eight π electrons), the presence of an appropriate construction of a totally *s-cisoid peri*-conformation and in some cases appropriate substituents at the terminals C(1) and C(7)=C(δ) atoms are important. The probable *s-cisoid peri*-conformation may lead to planar/helical transition state models (Scheme 7), both of which may undergo to 1,7-ring-closure reactions. In order to form this pre-ring system, placement of appropriate structural directors such as aromatic or cycloalkenyl groups is necessary in the middle or at least at one edge of the conjugated chain.



Scheme 7. Electrocyclization of conjugated systems.

In a similar way, the presence of an *s-cisoid peri*-conformation and steric requirements of the terminal carbons are also important for 1,5-cyclization reactions (five p orbitals and six π electrons) (Schemes 7 and 8).

The preferred formation of the *cis*-dihydrofuran/dihydropyrrole (**10**) would correspond to the allowed disrotatory ring closure of the vinylcarbonyl/azomethine ylide (**6**), i.e., the sterically preferred *U* configuration with terminal *exo*-substituents. In view of the exergonic nature of the 1,5-cyclization, one may presume an early transition state: the steric hindrance of the vinylcarbonyl/azomethine ylide affects the energy level of the transition state more strongly than the resulting dihydrofuran/dihydropyrrole steric factors (Scheme 8).



Scheme 8. 1,3-/1,5-/1,7-Electrocyclization of conjugated carbonyl/azomethine ylides.

As a similar approach, the preferred formation of the *trans*-dihydroxepine/dihydroazepine (**11**) would correspond to the allowed conrotatory ring closure of the butadienyl/styrylcarbonyl/azomethine ylide (**7**), i.e., the sterically preferred ***U*** configuration with terminal *exo*-substituents. The other possible electrocyclization pathways (**5**→**9** and **8**→**12**) are also represented at Scheme 8.

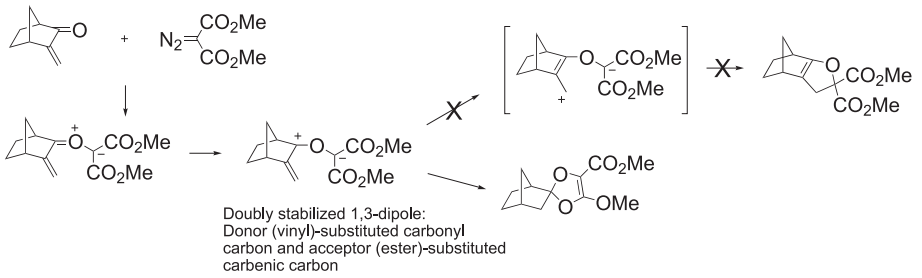
Mixture of stereoisomers can also result from the isomerization of the initially formed ylide. It is clear that the opposite rotations are not totally 'forbidden' to take place in the reactions. 'Forbidden' processes need higher activation energies.

As the main topic of this review is the electrocyclization reactions of CCY and CAMY, a few basic analogous mechanisms of the thermal reactions of diene-conjugated diazo compounds, cyclization of in situ-generated nitrile imines, and photochemical cyclization reactions of nitrile ylide intermediates will be discussed at the end of the report (Section 6–8).

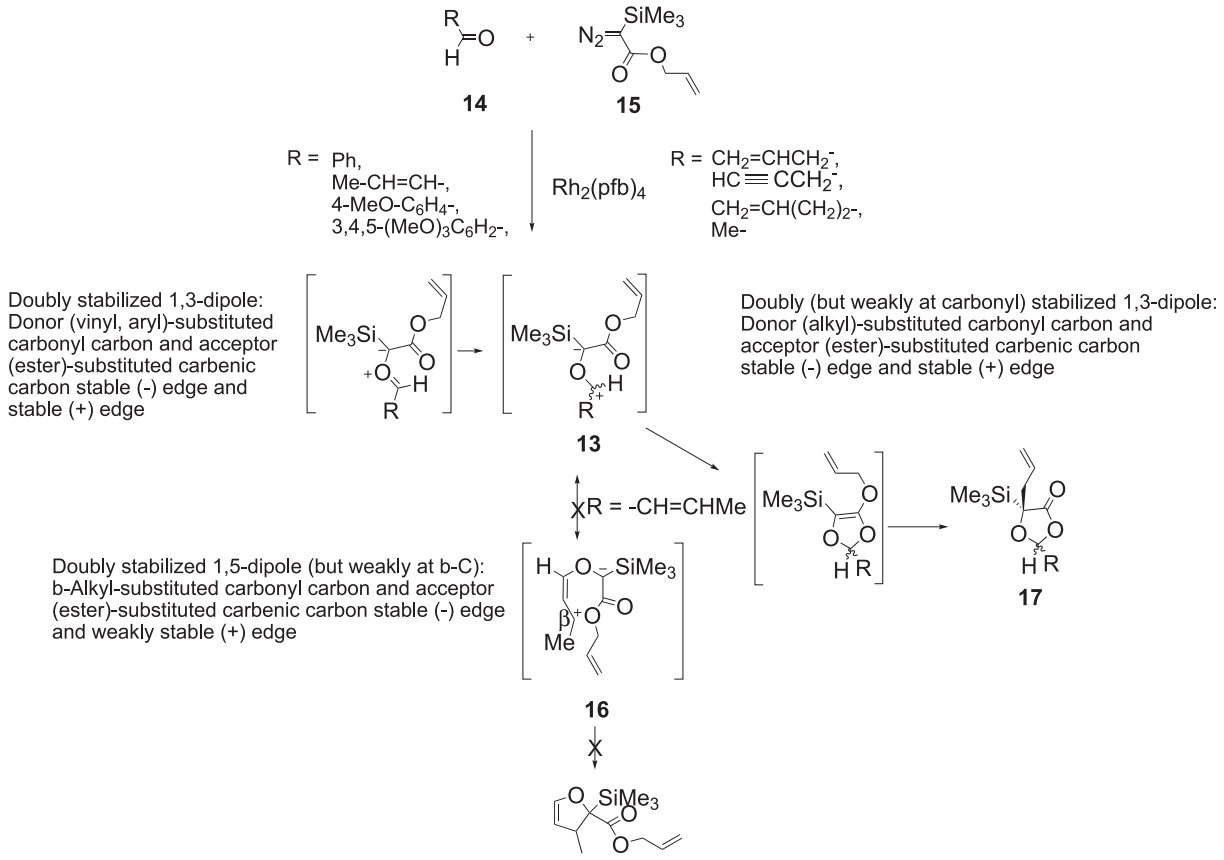
4. Electrocyclizations of CCY intermediates

The origins of the formation of conjugated vinyl, divinyl, styryl, and butadienyl carbonyl ylides may be either the catalyzed decomposition of diazo compounds with carbonyl compounds or the thermal/photochemical cleavage of vinyl/styryl and butadienyloxiranes. An alkenyl group can be attached to at least one of the carbon atoms of the carbonyl ylide. In order to produce conjugated carbonyl ylides being that are 1,3-dipoles, the starting compounds may be either conjugated carbonyl or conjugated diazo compound or both. In this reaction, the formation of a carbonyl ylide by an attack of a metallo-carbenoid intermediate onto the lone pair of electrons of the carbonyl group represents a particularly useful approach.

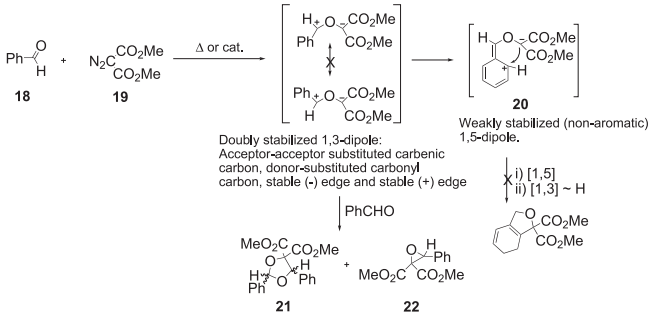
In recent years, Maas and co-workers and Huisgen and coworkers have shown that it is possible to trap carbonyl ylide adducts (**13**) intermolecularly, by the [3+2] reactions of unsaturated aldehydes (**14** and **18**) with some α-diazo-α-(trimethylsilyl)acetates (**15**)[16,17] (Scheme 10) and dimethyl diazomalonate (**19**)[18,19] (Scheme 11) with or without a metal catalyst to furnish the diastereomeric 1,3-dioxolanes (**17** and **21**) and oxirane (**22**). However,



Scheme 9. Reactions of 3-methylidene-2-norbornane with dimethyl diazomalonate.[19]



Scheme 10. Intermolecular [3+2] trapping reactions of ylides derived from unsaturated aldehydes (**14**) with some α-diazo-α-(trimethylsilyl)acetates.[16]

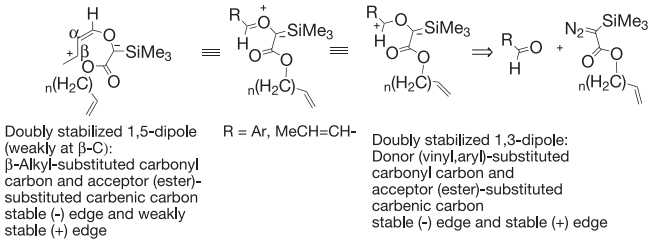


Scheme 11. Intermolecular [3+2] trapping reactions of ylides derived from benzaldehyde (**18**) with dimethyl diazomalonate.[18]

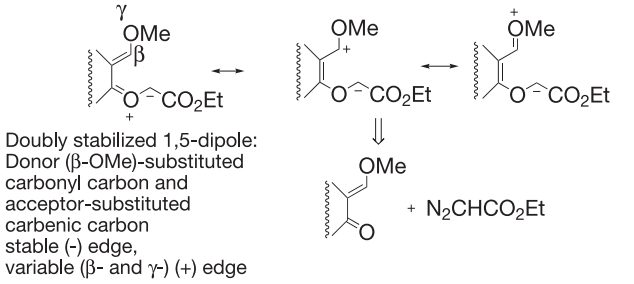
they did not observe any 1,5-cyclization of the carbonyl ylides in these trapping reactions. Probably, the initially formed 1,5-dipole was weakly stabilized (**16** and **20**) because of the non-aromatic terminal groups (Schemes 9–11). Several trapping agents (dipolarophiles) activated by electron-attracting group/groups were then used successfully to determine the stereointegrity of the carbonyl ylide, but in some cases the stereointegrity was lost.

Conjugated carbonyl ylides containing conjugation at carbonyl/diazo (or both) groups may represent different kinds of charge separation, depending on the present substituents, as generally shown in Scheme 6. If the possibility of both 1,5- and 1,7-electrocyclizations exists, the latter is often preferred because of the larger orbital coefficients at the termini of the conjugated system involving the 8π electrons. On the other hand the former 1,5-dipolar bond structure may also be stabilized by a charge-controlled step.

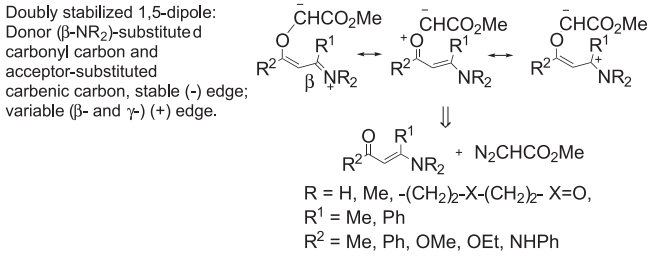
In addition, the donor/acceptor characters of the substituents present at the starting diazo and carbonyl compounds were also specified in Schemes 12–14 (the terms 'donor' and 'acceptor' refer, respectively, to electron donation or withdrawal through resonance effects).[20–25] In each category, the stabilities were reviewed, especially with respect to 1,3- and 1,5-charge separations and also steric crowding on the terminal carbons. Epoxy formation was a 1,3-dipolar addition and dihydrofuran formation over a 1,5-electrocyclization was very sensitive to the availability of a 1,5-dipole



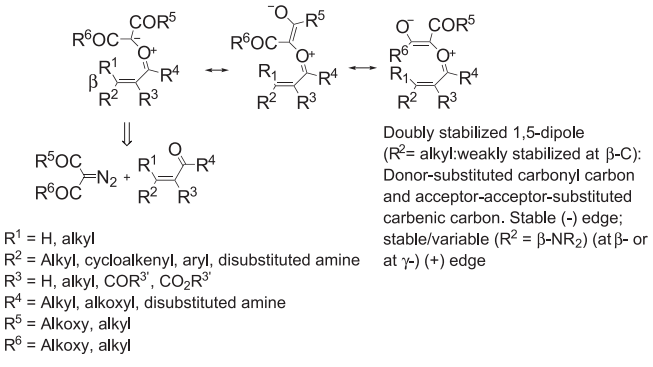
Scheme 12a. Conjugated carbonyl ylides containing alkenic/aromatic conjugation on carbonyl carbon.[17]



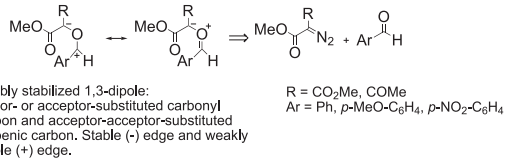
Scheme 12b. Conjugated carbonyl ylides containing alkenic conjugation on carbonyl carbon.[26–28]



Scheme 12c. Conjugated carbonyl ylide containing alkenic/aromatic conjugation on carbonyl carbon.[29–33]



Scheme 12d. Conjugated carbonyl ylide containing alkenic conjugation on carbonyl carbon.[34–41]



Scheme 12f. Conjugated carbonyl ylide containing aromatic conjugation on carbonyl carbon.[18,43,44]

(charge-controlled electrocyclic reaction). On the other hand, a 1,7-electrocyclization was very sensitive to the availability of a pre-ring conformation.

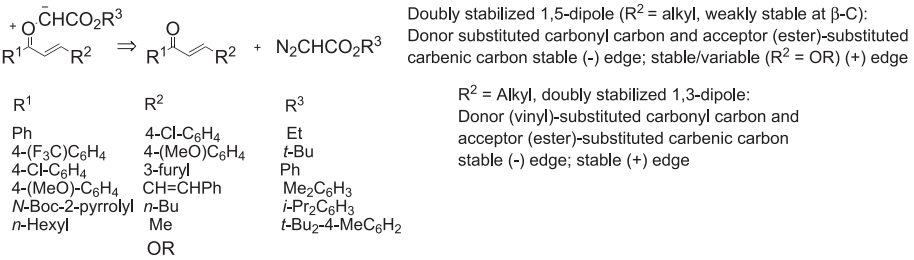
4.1. Electrocyclizations of carbonyl ylides derived from diazo and α,β-/α,β,γ,δ-conjugated carbonyl compounds to dihydrofurans and dihydrobenzoxepines

Conjugated carbonyl ylides derived from diazo compounds and α,β-/α,β,γ,δ-conjugated carbonyl compounds may be accepted as 1,3-, 1,5-, and 1,7-dipoles for the subsequent cycloaddition/electrocyclizations to yield oxiranes, dihydrofurans, and dihydrobenzoxepines, respectively.[2–8] In comparing these reactions, several different factors may be in operation for the relative importance of each model.

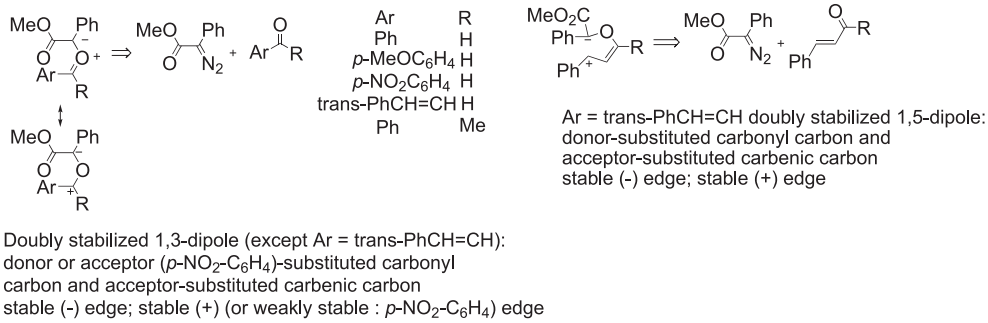
In their pioneering work, Spencer and co-workers have shown that, in the case of a few α-methoxymethylene ketones (**23**) (Scheme 15), where the carbonyl and olefin sites are fixed *cisoid* to each other, reaction with ethyl diazoacetate yields furancarboxylic acid esters (**24**), via carbonyl ylides, after methanol elimination (Scheme 15).[26–28]

This very interesting reaction was left aside for almost 35 years until Anaç and co-workers' first report in 1997,[34] and then a few groups have also been studying the formal 1,5-/1,7-electrocyclization reactions of carbonyl ylides derived from α,β-unsaturated carbonyl compounds and metallo-carbenoid species.[37–41]

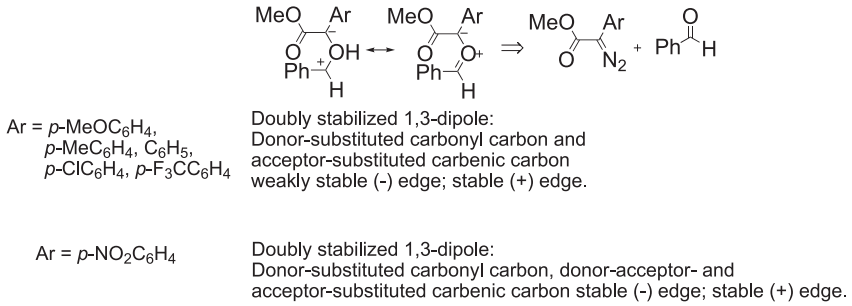
Anaç and co-workers showed that properly chosen *s-cis*-enketones/en-esters and biscarbonylcarbenoids (Scheme 12d) underwent electrocyclization reactions over *s-cis*-conjugated carbonyl ylides under mild conditions. In these conjugated carbonyl ylides, increasing electron withdrawal from the two carbonyl substituents of the carbenic carbon (acceptor/acceptor-substituted carbenoid) causes this 1,3-dipole to be stabilized due to the negative edge. This *s-cis*-conjugated carbonyl ylide, being sensitive to steric effects, cyclizes to form the dihydrofuran by a disrotatory 1,5-electrocyclization clearly and predominantly. They reacted several diazobiscarbonyls and α,β-enones/en-esters/en-diesters containing β-C–H, being sensitive to the terminal substituents, in the presence of a copper(II) acetylacetonate [Cu(acac)$_2$] catalyst. In their study, both the carbene carbon and the ligands of the catalyst are electrophilic enough to enhance the carbenoid electrophilicities, but, contrary to the expected lower selectivity (high reactivity/high electrophilicity), these reactions exhibited excellent chemo-control with the absence of any other competing reaction pathways. In addition, they also seemed to be stereo-controlled reactions



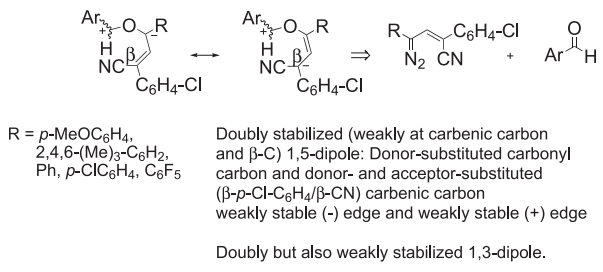
Scheme 12e. Conjugated carbonyl ylide containing alkenic/aromatic conjugation on carbonyl carbon.[42]



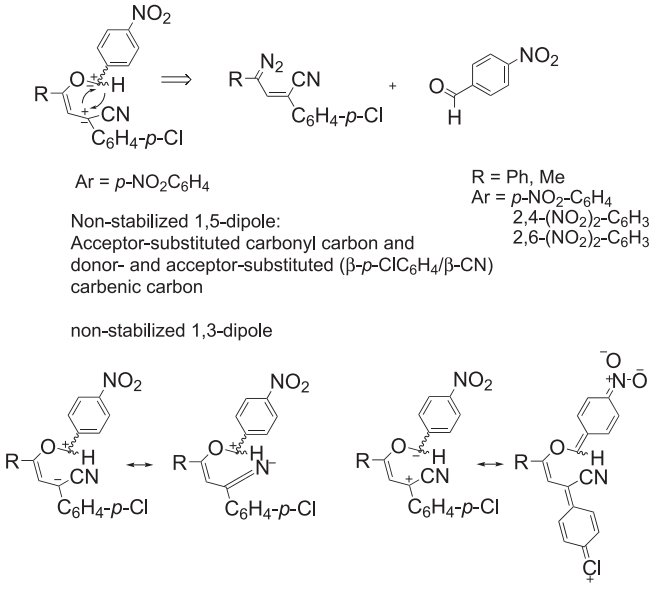
Scheme 12g. Conjugated carbonyl ylide containing alkenic/aromatic conjugation on carbonyl carbon.[45]



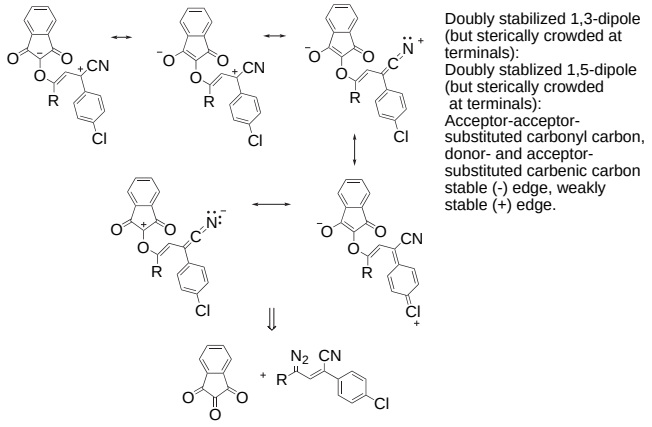
Scheme 12h. Conjugated carbonyl ylide containing phenyl conjugation on carbonyl carbon.[46]



Scheme 13a. Conjugated carbonyl ylide containing alkenic conjugation on carbenic carbon.[47–49]



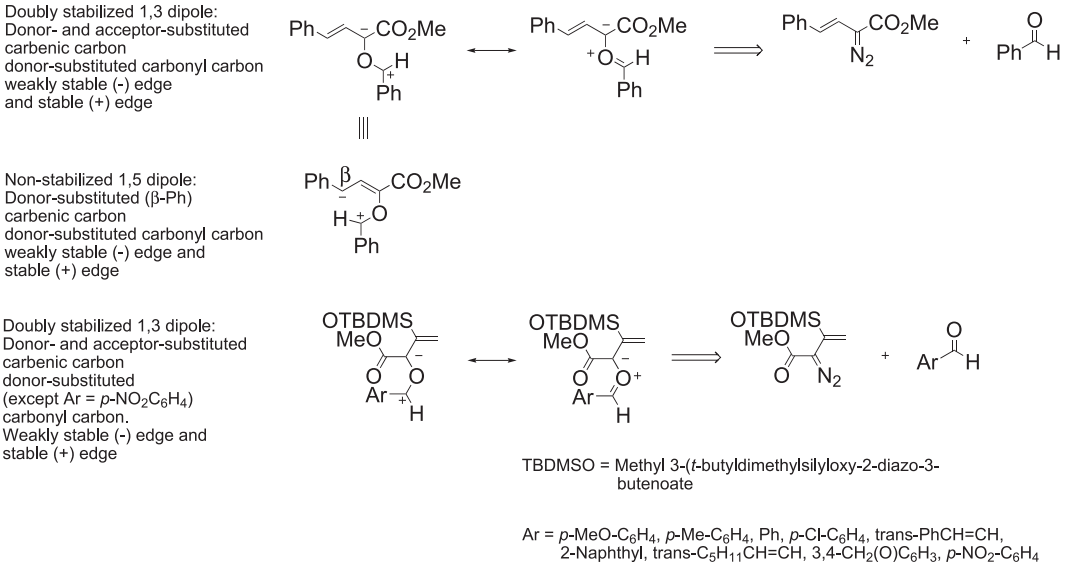
Scheme 13b. Conjugated carbonyl ylide containing alkenic conjugation on carbenic carbon.[47–49]



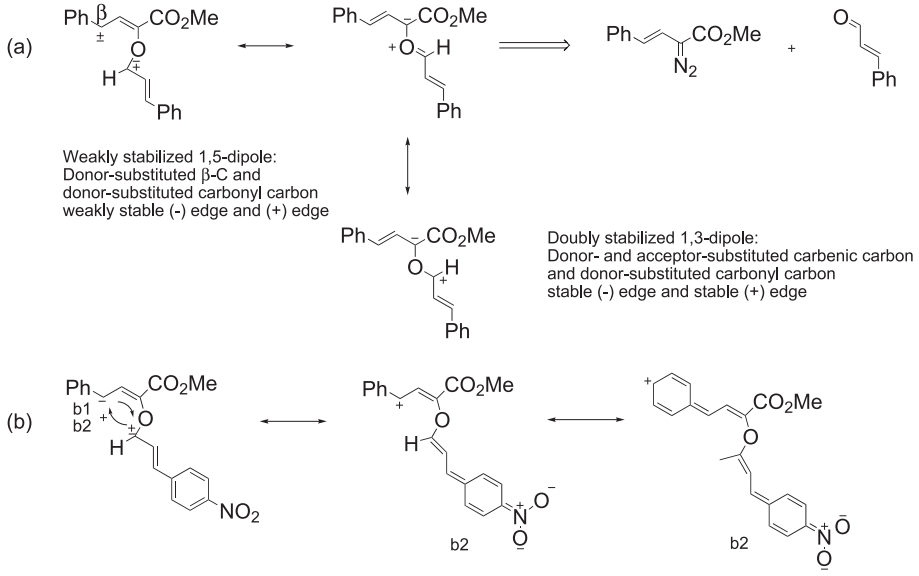
Scheme 13c. Conjugated carbonyl ylide containing alkenic conjugation on carbenic carbon.[50]

to some extent. On the other hand, the corresponding ylides arising from *s-trans*-conjugated α,β-enals yielded dioxole derivatives only. When α-ionone (**25**) was treated with dimethyl diazomalonate (dmdm) in a molar ratio of 1.5:1, under copper(II) acetylacetonate [$Cu(acac)_2$] catalysis, two diastereomeric major products, **26a**[35] and **26b**, were formed diastereoselectively in a 1:1.4 proportion (Scheme 16) along with a minor amount of a furofuran derivative (**27**).

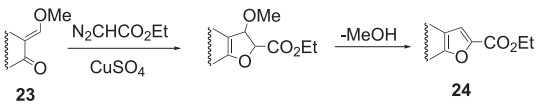
Dihydrofuroic ester (**29**) was obtained as the only diastereomer along with a minor furofuran derivative (**32**) from the stereospecific reaction of β-ionone (**28**) and dmdm. Furofuran compound (**32**) is derived from the addition of another mole of diazobiscarbonyl compound to the dihydrofuran initially formed. Recrystallization of dihydrofuran **29** from methanol resulted in the formation of the methanol and water adducts of the reactive enol ether moiety, yielding acetal/hemiacetal **31a**/**31b** (Scheme 16). Both compounds were determined as cis- isomers as a result of stereospecific addition. On the other hand, the reaction of ethyl acetodiazoacetate



Scheme 13d. Conjugated carbonyl ylide containing alkenic conjugation on carbenic carbon.[45]



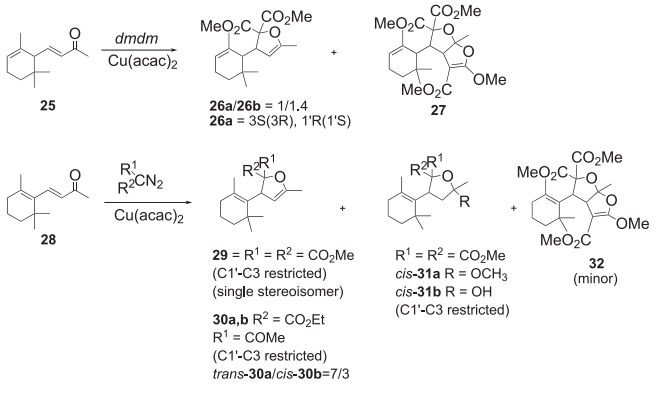
Scheme 14. Conjugated carbonyl ylide containing alkenic conjugations on carbonyl and carbenic carbons.[45–49]



Scheme 15. Catalyzed reaction of α-methoxymethylene ketones with ethyl diazoazetate.

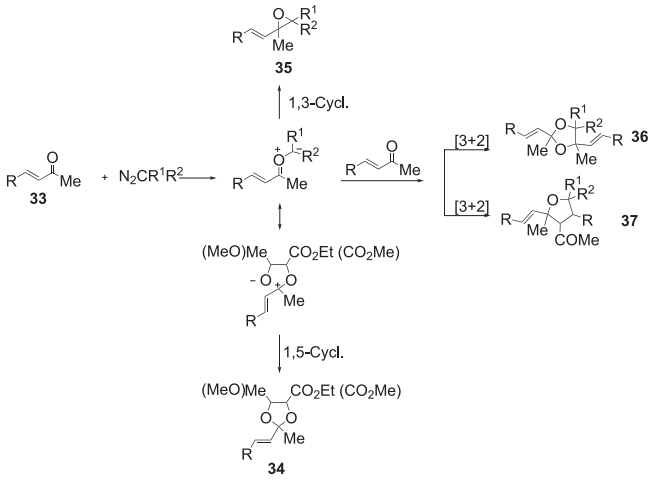
(*eada*) with β-ionone in the same reaction conditions yielded the diastereoselective mixture **30a**/**30b** in a ratio of 7:3.

This study[34] showed clearly that the carbonyl ylide intermediate derived from α,β-conjugated methyl ketone (**33**) and dimethoxycarbonyl carbenoid favors a chemo-controlled route of 1,5-cyclization to the dihydrofuran and its subsequent reactions represented in Scheme 15, instead of other possible reaction routes such as 1,5-cyclization to dioxole derivatives (**34**), insertions, cyclopropanations, ring closures by 1,3-cyclization (epoxidation) (**35**) and cycloaddition possibilities to other starting enones (**36** and **37**). Except for the formation of the dihydrofuran and its derivatives, all these other possible product distributions are summarized in Scheme 17.



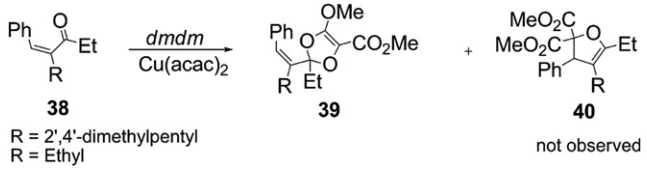
Scheme 16. Cu(acac)$_2$-catalyzed reaction of α- and β-ionone with diazo compounds.

Steric inhibition on the β-terminus *Z*-conformation in di/tri-substituted conjugated ketones (**38**, Scheme 18) or tetra-substituted conjugated ketone (**41**, Scheme 19) retards the reaction for dihydrofuran derivatives. The *Z*-enones (**38**) and the enone with

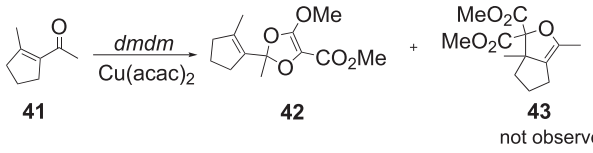


Scheme 17. Other possible reaction pathways in the $Cu(acac)_2$-catalyzed reactions of α, β-conjugated carbonyl and diazobiscarbonyl compounds.

two substituents on β-C (**41**) did not give any dihydrofuran derivatives (**40**, **43**), as expected from the pre-requisite of both termini, C(1) and C(5), being closest to each other in the transition state for an electrocyclic 1,5-ring-closure reaction to dihydrofuran; instead, an electrocyclic 1,5-ring-closure reaction to the dioxole derivatives (**39** and **42**), respectively occurred (Schemes 18 and 19) under mild conditions.

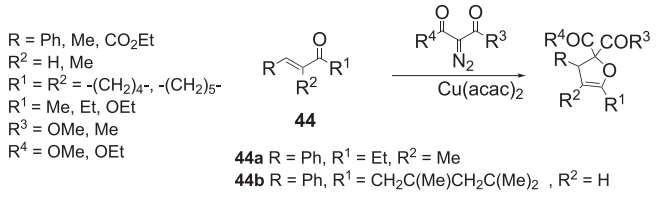


Scheme 18. An electrocyclic 1,5-ring-closure reaction to the dioxole derivatives from *Z*-enones.



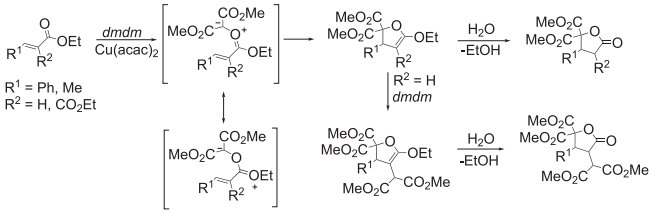
Scheme 19. Reaction of tetra-substituted conjugated ketone (**43**) with dimethyl diazomalonate.

On the other hand, steric crowding at R^1 and R^2 provides a beneficial effect to increase the yield of dihydrofuran by sterically preventing the possible follow-up reactions derived from the dihydrofuran, i.e., *E*-2-methyl-1-phenylpent-1-en-3-one (**44a**) and *E*-5,7-dimethyl-1-phenyloct-1-en-3-one (**44b**). When R is an aryl/alkenyl group, extended conjugation can stabilize the concerted transition state of the initially formed CCY (doubly stabilized 1,5-dipole) more and this may cause the reaction to occur more cleanly (Scheme 20).



Scheme 20. Dihydrofuran formation in the $Cu(acac)_2$-catalyzed reactions of α,β-conjugated carbonyls and diazo β-biscarbonyls.

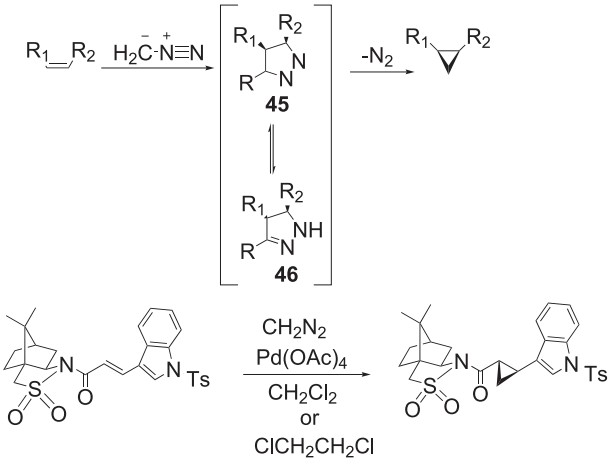
Anaç and co-workers also demonstrated that several conjugated esters/diesters gave only the dihydrofuran and its subsequent derivatives (lactones) more easily than conjugated ketones. The additional conjugation effect of the ester *O*-atom might facilitate the positive charge stability in the intermediary conjugated ester-ylide under their conditions and strengthened the charge-controlled step for 1,5-cyclization (Scheme 21).[39–41]



Scheme 21. Formation of dihydrofuran derivatives in the $Cu(acac)_2$-catalyzed reactions of α,β-conjugated esters and diazo β-dicarbonyls.

The existence of dihydrofuran derivative formation as the only reaction pathway in Scheme 21 was in contrast to the present literature data, in which mostly the formation of cyclopropane derivatives from conjugated esters and diazo compounds has been reported, as exemplified by Nichols and co-workers.[52]

In 1995, Nichols and co-workers[52] realized a stereoselective palladium-catalyzed cyclopropanation of the indole-3-acryloyl derivative of Oppolzer's chiral sultam (bornane[10,2]sultam) with diazomethane. Cyclopropanation occurred over unstable pyrazolines (**45**, **46**) that formed via 1,3-dipolar cycloaddition of the diazo compound (Scheme 22). In this reaction a singly stabilized (donor-substituted carbonyl and non-substituted carbene) 1,5-dipole did not exist to produce a dihydrofuran derivative.



Scheme 22. Stereoselective palladium-catalyzed propanation of indole-3-acryloyl derivative of Oppolzer's chiral sultam (bornane[10,2]sultam) with diazomethane.

Chiral auxiliaries that allow control of the facial selectivity of the 1,3-dipolar cycloaddition of diazomethane have also been developed for several specific substrates. Some representative examples (**47**,[53] **48**,[54,55] **49**,[56] **50**[57]) for α,β-conjugated carbonyl substrates are shown in Figure 1.

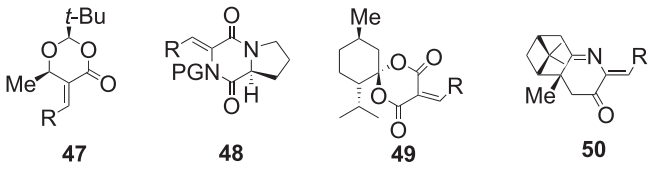
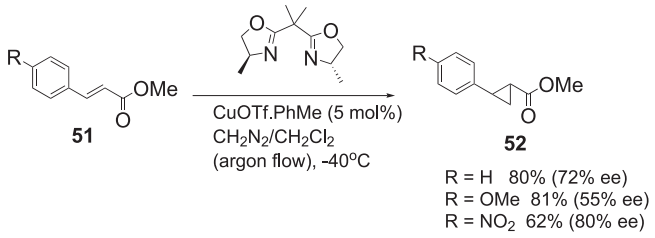


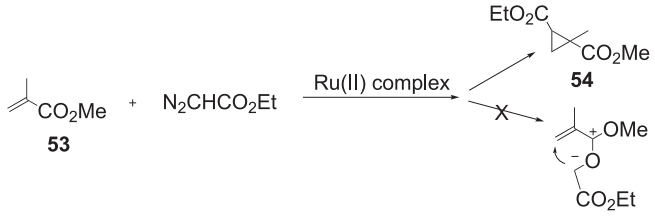
Figure 1. Examples of substrates containing chiral auxiliaries for stereoselective cyclopropanations.

In a similar way, Charette and co-workers[58] found chiral bis(oxazoline)/copper(I) complexes to be effective catalysts for the enantioselective cyclopropanation reactions of *trans*-cinnamate esters (**51**). They also obtained high yields and enantiomeric excesses of electron-poor methyl cinnamate derivatives (**52**) without forming dihydrofurans (Scheme 23). Although the carbonyl carbon had a stabilizing alkoxy-substituted aryl group (R=MeO), it was found that CCY was not stable enough to form a 1,5-dipole because of the absence of an electron-withdrawing stabilizers on the carbenic carbon.



Scheme 23. Chiral bis(oxazoline)/copper(I) complex-catalyzed enantioselective cyclopropanations of *trans*-cinnamate esters.

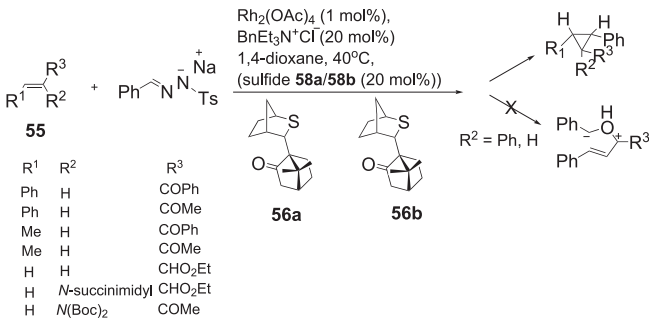
Doyle[59,60] and Nakamura[61,62] reported that α,β-unsaturated carbonyl compounds and nitriles could yield racemic cyclopropanes through the decomposition of pyrazoline intermediates, which result from the non-catalyzed 1,3-dipolar cycloaddition of olefins with diazo esters. Nguyen and co-workers[63] also reported that electron-poor methyl methacrylate (**53**) yielded highly enantioselective cyclopropanes (**54**) directly in the catalyzed reactions with ethyl diazoacetates in the presence of Schiff-base ruthenium(II) complexes as catalyst (Scheme 24). The absence of any product derived from a CCY again represented the inadequate stability of a probable 1,5-dipole.



Scheme 24. Schiff-base ruthenium(II) complex-catalyzed enantioselective cyclopropanations of methyl methacrylate.[63]

Aggarwal and co-workers have developed a catalytic asymmetric process for the cyclopropanation of electron-poor alkenes (**55**) such as phenyl ketones, methyl ketones, and α-amino-substituted acrylates by generating the diazo compound in situ. In all cases, high enantioselectivities and high yields were obtained and the sulfide (**56a** and **56b**) could be recovered in quantitative yield (Scheme 25).[64–67] No dihydrofuran derivative was observed in these reactions. These results again indicated the inadequate stability of a probable 1,5-dipole.

In Schemes 22–25,[51–67] the catalysts used are not $Cu(acac)_2$ and the diazo compounds are non-substituted, phenyl-substituted and monoester-substituted derivatives (weakly activated carbenic



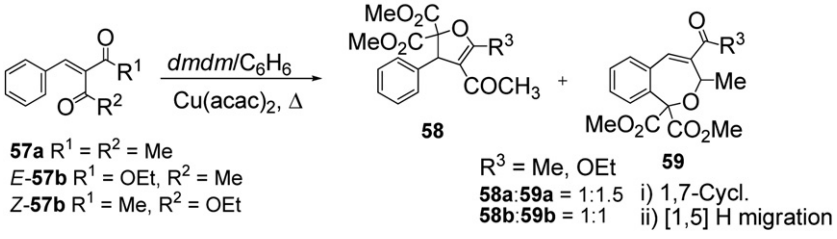
Scheme 25. Catalytic asymmetric process for the cyclopropanation of electron-poor alkenes.

carbon). In the studies of Anaç's group,[39–41] the use as diazobiscarbonyl compounds and copper(II) acetylacetonate as catalyst might support the formation of a conjugated ester/diester carbonyl ylide that represents enough stability to form a 1,5-dipole (charge-controlled step), leading to dihydrofurans rather than cyclopropane derivatives. In addition, oxirane derivatives probably being more strained rings and sensitive to steric effects were not observed under their conditions (Schemes 16 and 20) with relatively more crowded biscarbonyl carbenes.

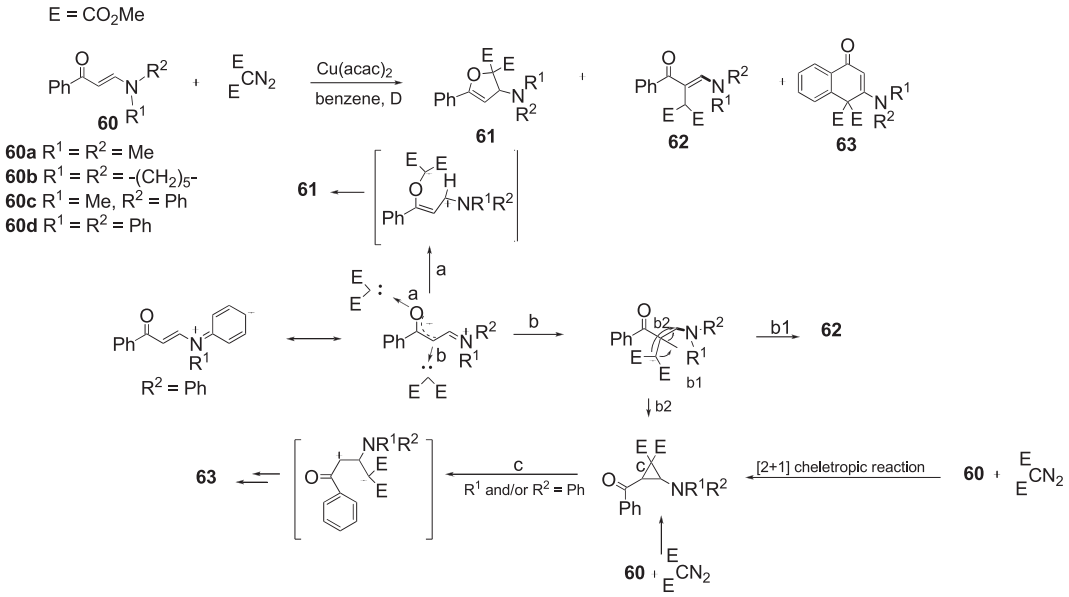
In their continuing report,[41] Anaç's group determined that sytryldicarbonyls having at least one keto function yielded also dihydrobenzoxepine derivatives (**59**, **59a**, and **59b**) by a 1,7-electrocyclization reaction in larger/equal amounts with respect to dihydrofuran derivatives (**58**, **58a**, and **58b**) by a 1,5-electrocylization (Scheme 26). Formation of the conjugated ester/dicarbonyl ylide in the catalytic reactions with sytryldicarbonyl compounds and diazobiscarbonyls represented again the stability of the dipole due to the charges on C1 and C5 but, additionally, signified that the orbital coefficients on the termini of the conjugated system involving the 8π electrons came into existence preferably.

In this study, benzylidene acetylacetone (**57a**) was treated with dimethyl diazomalonate in the presence of $Cu(acac)_2$ to yield the dihydrofuran and dihydrobenzoxepine in a 1:1.5 ratio. *Z*- and *E*-ethyl acetobenzylidene acetates *Z*-**57b**, *E*-**57b** were also reacted under the same conditions to compare the reactivities of conjugated ketone- and ester-ylides in order to obtain formal 1,7-/1,5-electrocyclization reactions in the same studies. In both attempts, the dihydrofuran from ester-ylide (**58b**) and dihydrobenzoxepine from keto-ylide (**59b**) were obtained approximately in the same ratios. They reported that the initially formed keto-/ester-ylides are highly polarized and do not need to undergo 1,5-/1,7-electrocyclization reactions directly, but may rather undergo a rotation around their C(α)–C(β) bonds in order to yield their regiospecific ring closures. According to this study, the ester-ylides did not prefer the formation of dihydrobenzoxepines, whereas the keto-ylides showed preference only for dihydrobenzoxepines by requiring the temporary loss of aromaticity of the involved phenyl ring.

In other words, it seemed that a competition (Scheme 26) took place between the 6π, 1,5- and the 8π, 1,7-cyclization of the conjugated carbonyl ylide intermediates derived from the ester and



Scheme 26. $Cu(acac)_2$-catalyzed reactions of styryldicarbonyl compounds with diazobiscarbonyls.



Scheme 27. Cu(acac)$_2$-catalyzed reactions of dimethyl diazomalonate with tertiary-enamino phenones (**60**).[40]

keto-ylides, respectively, to the β-carbon (dihydrofuran) or *ortho*-carbon of the phenyl ring (dihydrobenzoxepines). As discussed for azomethine ylide cyclizations,[68] if the possibility of both 1,5- and 1,7-electrocyclization existed, the latter is often preferred because of the larger orbital coefficients at the termini of the conjugated system involving the 8π electrons. On the other hand, the former, 1,5-dipolar bond structure may be more stabilized by an ester substituent (a charge-controlled step).

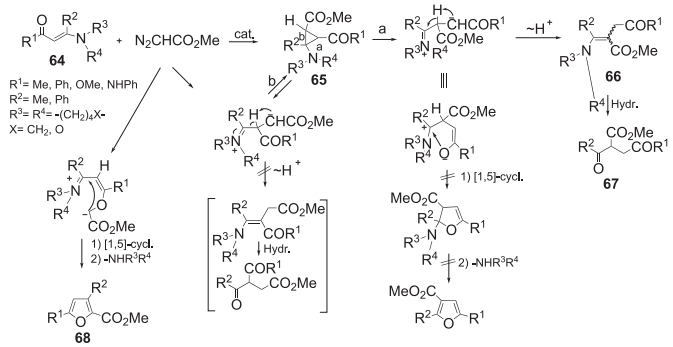
Anaç's group also studied the Cu(acac)$_2$-catalyzed reactions of dimethyl diazomalonate with tertiary enamino phenones (Scheme 27).[40] There are a few more reports on the reactions of β-amino-α, β-unsaturated compounds, which can be called enaminones and diazo compounds,[29–31,33] but the most relevant study was that of Maas and Müller[32] (Scheme 28).

Suprisingly, as noted by Maas and Müller (Scheme 28), furan formation (**68**) from enamino phenones (**64**) over elimination of an amine was detected in only a few of the reactions with trace amounts along with the compounds **65**, **66**, and **67**. On the contrary, Anaç's group obtained dihydrofuran derivatives as major products when the substituent on nitrogen was not phenyl, although the probability of a 1,5-dipole formation in the carbonyl ylide intermediate was decreased (variable+edge at β- and γ-atoms) because 1,6-dipole formation caused by the present enamine group was racing. In their reaction, a minor product of α-CH insertion was also obtained, as expected from the relatively stable resonance structure of **60b** (Scheme 27). Additionally, in the case of the anilino derivatives (R^1 or R^2=Ph), novel 3-anilino-4-oxo-1,4-dihydronaphthalene derivatives (**63**), by the loss of two hydrogens, were determined in their reaction conditions as the major products. They reported their further studies on the formation of those novel products as well as the effects of changing the catalyst on the product distribution. The formation of compound **63** was derived by the proper ring opening (pathway c) of a probable cyclopropane derivative (**65**) with the effect of the β-amino group (Table 1).[40]

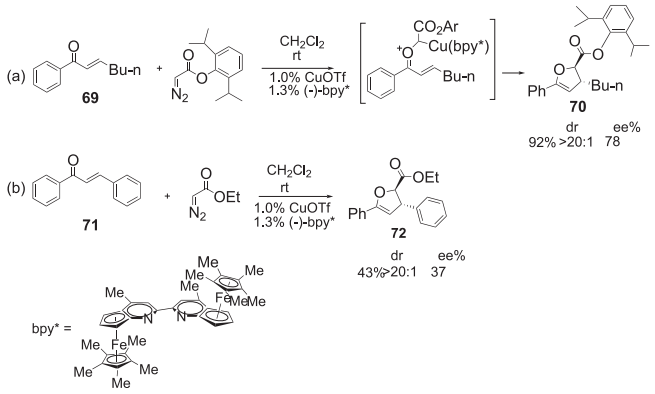
Table 1
Product distribution from the reactions of tertiary-enamino phenones with dmdm

Entry	R^1	R^2	**61**	**62**	**63**
a	Me	Me	1	0.56	—
b	−(CH$_2$)$_5$−		1	0.23	—
c	Me	Ph	1	—	3.52
d	Ph	Ph	1	—	2.47

It is noteworthy that Son and Fu, who recently worked with aromatic enones of acrylophenone (**69**, **71**), did not report the presence of such interactions with aromatic rings to form 4-oxo-1,4-dihydronaphthalene derivatives (**63**)[42] (Scheme 29). In this report, after exploring a variety of chiral ligands, Son and Fu described the use of a planar-chiral bipyridine ligand bpy*[69] copper- catalyst to achieve diastereo- and enantioselective [4+1] cycloadditions of enones with diazo compounds to produce highly substituted 2,3-



Scheme 28. Catalyzed reactions of enaminones with ethyl diazoacetate.[32]

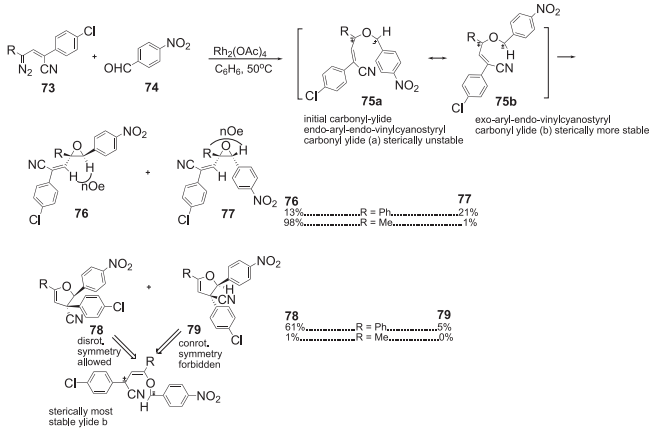


Scheme 29. Bpy* copper-catalyzed [4+1] cycloaddition of enones with diazo compounds.

dihydrofurans only. Although some of their CCYs were singly activated they only yielded dihydrofuran derivatives, due to the stabilities of the 1,5-dipoles (Scheme 12e, R^1=Ph; R^2=*n*-Bu, Me). They did not mention the presence of any other compound(s) when the yields of the dihydrofuran derivatives were low (Scheme 29).

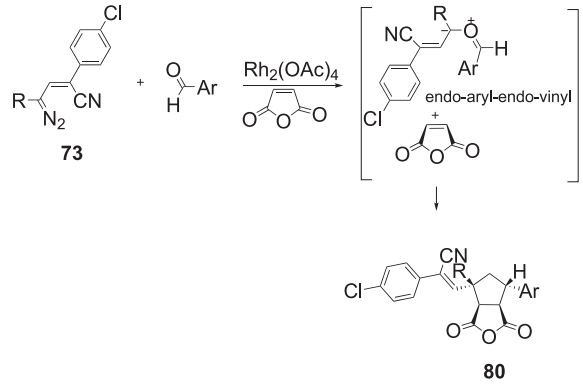
Son and Fu also applied their method to a catalytic asymmetric synthesis of a deoxy-C-nucleoside (R^1=Ph, R^2=OR, R^3=2,6-diisopropylphenyl, Scheme 12e) over the initially formed dihydrofuran derivatives. In this initial step, they did not obtain furan derivatives by elimination of an alcohol, in contrast to Spencer's pioneering work, but they obtained dihydrofuran derivatives, as in Anaç's work (Scheme 12c).[26–28]

In their reports in 2001, Hamaguchi's group described the $Rh_2(OAc)_4$-catalyzed reactions of aryl aldehydes with β,β′-cyano/*p*-Cl-phenyl (acceptor/donor) conjugated diazo compounds. They determined that electron-donating substituents (mesityl aldehyde) of benzaldehydes yielded doubly and weakly stabilized 1,5-dipoles (at both the carbenic carbon and β-C) and doubly and also weakly stabilized 1,3-dipoles (Scheme 13a). In the competition between the reactivities of these dipoles derived from **73** and **74**, the relative yields of *Z*-vinyloxiranes (**76**) were increased, but electron-withdrawing substituents (*p*-nitrobenzaldehyde) produced both non-stabilized 1,3- and 1,5-dipoles (Scheme 12b). In these reactions, the total yield of **77** and dihydrofurans (**78** and **79**) increased. More electronegative groups (2,4-dinitrobenzaldehyde) enriching the 1,5-dipole strength toward the reverse distribution (Scheme 13b), favored the formation of dihydrofurans[46,48] (Scheme 30). The stereoselectivities were also affected by crowding on the R substituent.



Scheme 30. $Rh_2(OAc)_4$-catalyzed reactions of aryl aldehydes (**74**) with β,β′-cyano/*p*-Cl-phenyl conjugated diazo compounds (**73**).

In this study, in order to trap the initial stereochemistry of the carbonyl ylide intermediates, reactive dipolarophiles were reacted with diazo compounds and substituted benzaldehydes (Scheme 31). In this trapping reaction, the formation of a single cycloadduct (**80**) among all of the possible diastereomeric cycloadducts confirmed the predominant stereochemistry of the initial carbonyl ylide as an *endo*-aryl-*endo*-vinyl- intermediate (Scheme 31).



Scheme 31. Trapping reactions of $Rh_2(OAc)_4$-catalyzed reactions of aryl aldehydes with β,β′-cyano/*p*-Cl-phenyl conjugated diazo compounds (**73**).

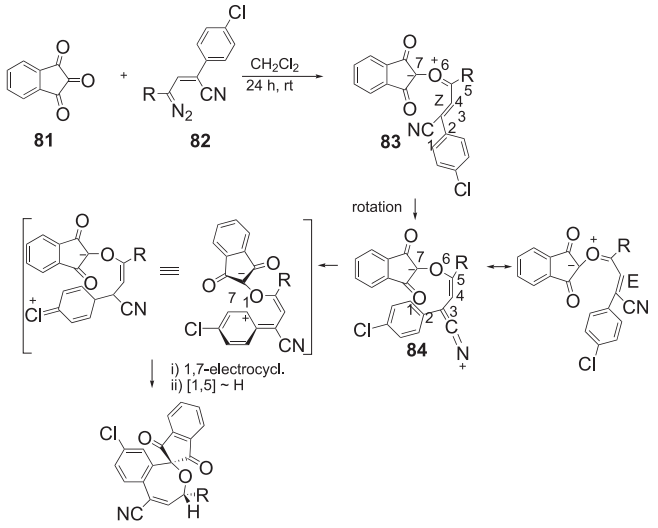
Moreover, the thermal conversion of vinyloxiranes into dihydrofurans via vinylcarbonyl ylides was also realized. It implies that the vinylcarbonyl ylides generated from thermal ring opening of the vinyloxiranes are different from those initially formed in the carbenic reaction, which must be very reactive toward maleic anhydride.

As shown in Scheme 30, the vinylcarbenoids derived from $Rh_2(OAc)_4$-catalyzed decomposition of the vinyldiazo compounds attack the carbonyl oxygen of benzaldehydes to form an unstable *endo*-aryl-*endo*-cyanostyryl carbonyl ylide (**75a**). This initial ylide undergoes a conrotatory cyclization to form the oxirane (**76**). The rotation around the C–O bond isomerizes the ylide (**75a**) to the sterically most favorable ylide **75b** (*endo*-vinyl-*exo*-aryl vinylcarbonyl ylide). A conrotatory cyclization of 75**b** yields the oxirane (**77**). The ylide (**75b**) also undergoes a disrotatory cyclization as a symmetry-allowed procedure to form the sterically unfavorable *cis*-diaryldihydrofurans (7**8**), whereas the same ylide undergoes a symmetry-forbidden conrotatory process to form the sterically favorable *trans*-diaryldihydrofurans (**79**). This symmetry-forbidden conrotatory ring-closure process should be concluded to be the more likely pathway for the formation of **79**.

Unlike azomethine ylides, carbonyl ylides, having more 'π-diradical character', allow a symmetry-forbidden process to a stable isomeric product in some cases, due to a configurational interaction. There was an analogous study that supports the rotation of the intermediate structure conformation in the ring closures of carbonyl ylide dipoles. In that study of the thermal cyclization reactions of diene-conjugated diazo compounds,[69] transformation of conformation of the intermediate structure under the reaction conditions was proposed. Reaction of 1,2,3-indanetrione (**81**) with **82** gave the spiroindan-1,3-dione-2,2-benzodihydrooxepine (**85**), but not the normal products, oxirane and dihydrofuran derivatives, as expected (Scheme 13c) from the intermediate vinylcarbonyl ylides (**83**). Oxiranes, dioxoles, and dihydrofurans seem to be either difficult to form, due to steric reasons, or to be electronically unstable derivatives, because of ring-opening reactions equilibrating with the carbonyl ylide intermediates.[50]

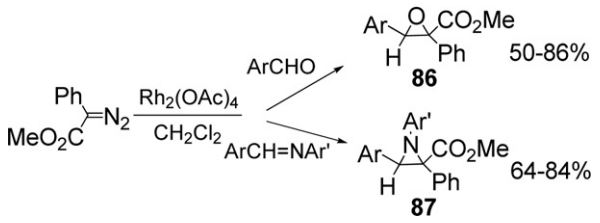
Formation of **85** requires isomerization of vinylcarbonyl ylides (**83**) bearing a *Z*-cyanostyryl group to the unstable *E*-form (**84**) and subsequent cyclization to oxepine (**85**) followed by a 1,5-hydrogen shift (Scheme 32).

In 2001, Doyle, Hu and Timmons realized rhodium(II) acetate-catalyzed stereospecific ring closure of aldehydes/imines and phenyldiazoacetate-derived carbonyl and iminium ylides (Scheme 12g)

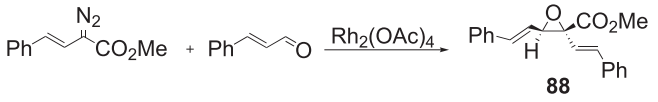


Scheme 32. Reaction of 1,2,3-indanetrione (**81**) with **82**.

and formed *Z*-epoxides (**86**) and *E*-configured aziridines (**87**), in high yields as the sole products[45] (Scheme 33). In a similar way, addition of styryldiazoacetate to an equivalent amount of cinnamaldehyde (Scheme 34) in the presence of $Rh_2(OAc)_4$ resulted in the production of epoxide (**88**) in a stereospecific way. When these reactions are performed with arylimines, stereospecific addition occurs to produce a single aziridine product (**87**) (Scheme 33).

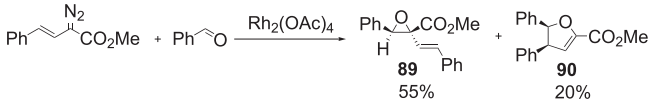


Scheme 33. $Rh_2(OAc)_4$-catalyzed reaction of some aldehydes/imines with phenyldiazoacetate.



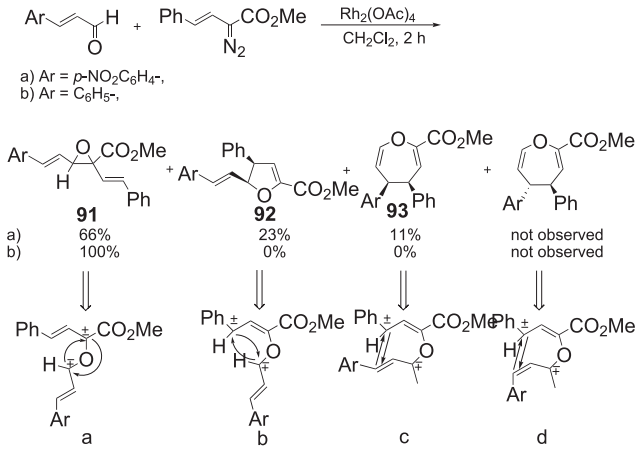
Scheme 34. $Rh_2(OAc)_4$-catalyzed reaction of styryldiazoacetate with cinnamaldehyde.

However, another report in 2001, from Davies and DeMeese,[71] claimed that this reaction was more complex than that previously described by Doyle's group, and they found that the *cis*-dihydrofuran (**90**) as a new product was formed in addition to the epoxide (**89**) (Scheme 35). They reported that the thermal rearrangement of vinylepoxide to *cis*-dihydrofuran was established, but, under rhodium-catalyzed reaction conditions, the epoxide **89** was stable and had a better yield. The mixture formed from the rhodium-catalyzed reaction likely arise due to competing cyclization of the ylide intermediate between epoxide formation and a 6π-electrocyclization to give the dihydrofuran. They reported that donor/acceptor-substituted carbenoids display very different reactivity to the traditional carbenoids derived from unsubstituted diazoacetates (Scheme 35).



Scheme 35. $Rh_2(OAc)_4$-catalyzed reaction of styryldiazoacetate with benzaldehyde.

After Davies and DeMeese's report (Scheme 35), Doyle's group presented another new analogous study[44] in which some modified cinnamaldehydes and styryldiazoacetates (Scheme 14) would have allowed the formation of three-, five-, and even newly seven-membered rings stereospecifically (Scheme 36a). They showed that extending conjugation in the intermediate ylide allowed also access to seven-membered ring heterocycles in this reaction. As anticipated, the reaction of styryldiazoacetate with *p*-nitrocinnamaldehyde (Scheme 36) gave also a mixture of products in which oxirane (**91a**), dihydrofuran (**92a**), and oxepine (**93a**) were formed in competition (Scheme 36, pathway a). For each product, only one stereoisomer was formed (≥20:1). The formed epoxides (**91a**) have extended conjugation at both cyclic edges. Increasing electron withdrawal from the carbonyl group (*p*-nitrobenzaldehyde) (Scheme 36) directed the product formation to dihydrofuran (**92a**) in preference to oxirane (**91a**), presumably through carbonyl ylide intermediates.



Scheme 36. $Rh_2(OAc)_4$-catalyzed reaction of methyl styryldiazoacetate with cinnamaldehyde derivatives **91a** and **91b**.

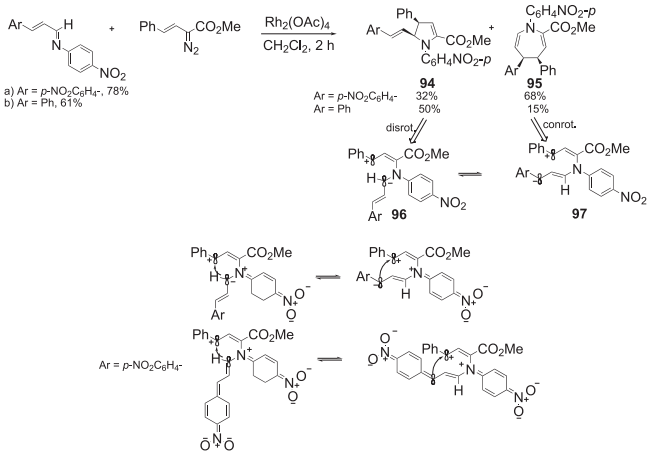
On the other hand, in the reactions of methyl styryldiazoacetate with cinnamaldehyde (Scheme 36, pathway b) they confirmed that only the oxirane derivative (**91b**) was obtained with the absence of **92b** and **93b**. They indicated once again the existence of a pronounced electronic effect.

In contrast to the results obtained with aldehydes, those with benzalanilines and imines derived from cinnamaldehydes/substituted cinnamaldehydes undergo catalytic reactions with styryldiazoacetate, resulting in a mixture of dihydropyrroles (**94**) and dihydroazepines (**95**) as particular stereoisomers. The aziridine product was not detected. These results are consistent with the preferred structures of the intermediate ylides and with their electrocyclic reactions (Scheme 37).

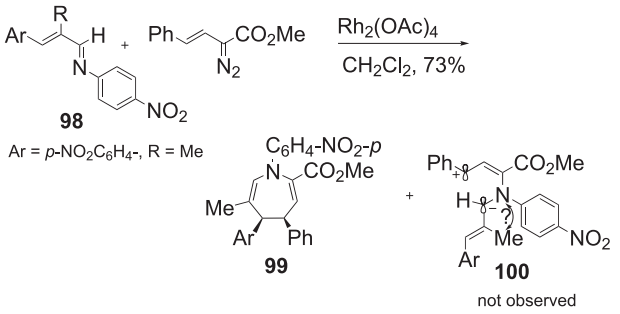
The absence of the trans isomer for the dihydropyrroles corresponds to a regiospecific conversion of **97** into **95**, and, of course, **94** can only be formed from **96**. Whether or not **94** and **95** are generated by initial aziridine formation followed by conversion into **94** and **95** could not be ascertained, as had been established for dihydrofuran and oxepines formed from cinnamaldehydes (Scheme 37).

The distribution of products between **94** and **95** was invariant of the catalyst, but could be modified substantially by the presence of a methyl group at the 3-position of the reacting imine (**98**). It was reasoned that this structural modification would decrease the stability of **96** (**100**) relative to **97**. In this case, the sole product, formed in 73% isolated yield, was the dihydroazepine **99** (Scheme 38).

In the same study, Doyle and co-workers indicated that there was no aziridine product due to the relative absence of the ylide

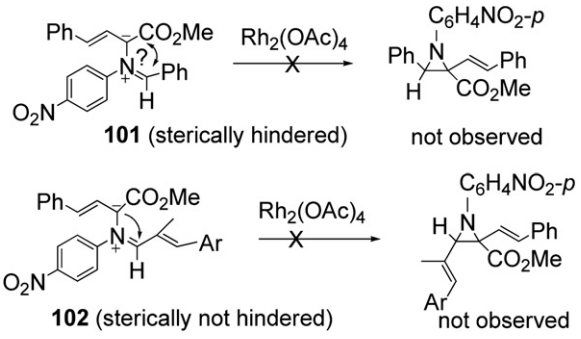


Scheme 37. $Rh_2(OAc)_4$-catalyzed reaction of methyl phenyldiazoacetate with benzalimines.



Scheme 38. $Rh_2(OAc)_4$-catalyzed reaction of styryldiazoacetate with **98**.

(**101**) as a result of steric preferences in the reaction of methyl styryldiazoacetate with benzaldehyde/imine (Scheme 39), but the absence of an aziridine product from the reaction of cinnamaldehyde/imine with styryldiazoacetate in Scheme 37 (**102**, Scheme 39) may be explained by the preferred structures of the intermediate ylides being dihydropyrroles and dihydroazepines, rather than the steric preferences.



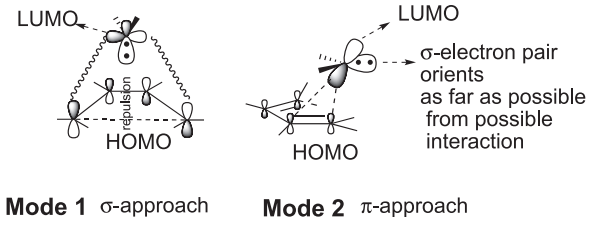
Scheme 39. Absence of aziridine products from the reactions of methyl styryldiazoacetate with benzaldehye/imine and cinnamaldehyde/imine.

4.2. 1,5-Electrocyclization of an α,β-conjugated ylide versus [4+1] cheletropic reaction of an α,β-conjugated carbonyl with a carbenoid

There is no experimental/theoretical report of a comparison between the 1,5-electrocyclization reaction mechanism of a conjugated carbonyl ylide and the [1+4] cheletrophic addition mechanism of an α,β-conjugated carbonyl with a carbenoid. However, a pioneering report from Hoffmann and Fujimoto relating to a comparison between the [2+1]/[4+1] additions of a singlet carbene to a butadiene may be overviewed.[72]

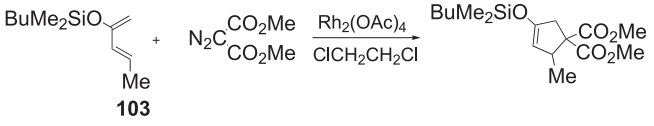
Although the application of the 'isolated-molecule-approximation' is limited to the case of relatively weak interactions, i.e., the early stage of chemical reactions, it can often be very informative in disclosing the governing factors of complicated chemical reactions. Hofmann and Fujimoto proposed a simple molecular orbital method to deal with the addition of singlet methylene to butadiene in terms of the molecular orbitals of the two isolated reactants. The electron population of a reacting system is partitioned into several orbital interaction terms, allowing a tracing of the origin of the intermolecular bond formation and of the intramolecular reorganization of the electron distribution. The method is applied to the interaction between singlet methylene and butadiene as the experiments on the reaction of singlet methylene with dienes have given no direct evidence of 1,4- concerted addition. Both 1,2- and 1,4-addition are electronically allowed, but the 1,4-addition is discriminated against by excessive closed-shell repulsive interactions. Normal 1,2-addition apparently prevails as the initial step. This is so, despite the least-motion cheletropic reaction of 1,4-addition clearly being a symmetry-allowed process.

In any reaction of methylene, the crucial orbital is its acceptor orbital, p. The primary interaction is between that acceptor, LUMO, p and whatever donor orbital is offered up by the substrate. That overlap, shown schematically in Mode 1 (Scheme 40), is basically inefficient. The methylene has to approach very close to the butadiene to make that overlap significant, and in doing so it encounters excessive closed-shell repulsions, but the repulsive nature of the closed-shell interaction between σ and π is 'remembered' to the extent that even when the primary attack of the methylene is through its p orbital, it still attempts to remove the σ electron pair as far as possible from possible interaction. In another way of thinking, the bonding situation, shown in Mode 2, represents a transition from the symmetry-enforced σ/π picture of methylene bonding to a hybridized state associated with the product cyclopropane (Scheme 40).

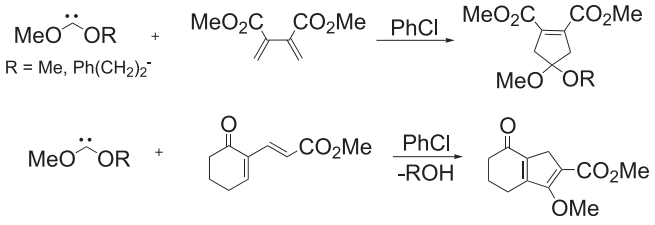


Scheme 40. Simple molecular orbital approaches of singlet methylene to butadiene.

Examples of [4+1]-cycloadditions between an electrophilic carbene and a simple diene are rare, because of the known propensity of carbenes and carbenoids to give cyclopropanation products with alkenes and 1,3-dienes.[73–83] Schnaubelt and co-workers[74] studied cycloadditions of the rhodium di(methoxycarbonyl) carbenoid to 2-siloxy-1,3-dienes such as **103** (Scheme 41). In this reaction, an electrophilic carbene and an electron-rich diene yielded a [4+1] product. Spino and co-workers[84] also added a few exceptions as formal [4+1]-cycloadditions of nucleophilic carbenes to electron-poor dienes (Scheme 42).



Scheme 41. [4+1]-Cycloadditions between rhodium (dimethoxycarbonyl) carbenoid and electron-rich 2-siloxy-1,3-dienes.[73]



Scheme 42. Formal [4+1]-cycloadditions of nucleophilic carbenes to electron-poor dienes.

When the 1,5-electrocyclization reaction mechanism of a conjugated carbonyl ylide and the [1+4] cheletrophic addition mechanism of an α,β-conjugated carbonyl to an electrophilic carbenoid are compared, it may concluded that [1+4] cheletrophic addition is not available. On the other hand, as mentioned before in this review, the [1+2] cheletrophic addition of an electrophilic carbenoid to an electron-poor α,β-double bond of the conjugated carbonyl compound is not a general case,[85,86] except the CCY is very unstable for forming a 1,5-dipole (Schemes 21–25).[52–67]

4.3. Alternative method of formal [4+1] ylide annulation for the synthesis of dihydrofurans

Ylides can react with C=X (X=C, N, O, etc.) double bonds to form betaine or oxetane intermediates, which further eliminate the heteroatom-containing group in one of two ways to give the corresponding olefination or cyclization product. This method is known as 'ylide-initiated Michael addition/cyclization reactions'. By altering the heteroatoms and the ligands of the ylides, the reactivity of the ylides may have been modulated. These modified ylides provide easy access to diverse cyclic compounds such as cyclopropanes and, in some cases, dihydrofurans, with the ability to control regioselectivity, chemoselectivity, diastereoselectivity, and enantioselectivity. Sulfur, phosphorus, arsenium, and telluronium ylides have been all used as cyclopropane precursors. Cyclopropanation reactions involving sulfonium salts were first reported in 1950.[87,88]

Nevertheless, the synthetic potential of this reaction was appreciated only in the 1960s, when Corey reported[89,90] that the addition of methylenedimethylsulfoxonium to chalcone gave *trans*-1-benzoyl-2-phenylcyclopropane. These studies were quickly followed by the development of several new sulfur ylide reagents. Representative examples of the four types of sulfonium ylides (**104**, **105**, **106**, **107**)[91–95] are shown in Figure 2. Other α,β-conjugated carbonyl derivatives (**108**) (Fig. 2) including esters,[96–103] diesters,[101,104,105] amides,[97] and ketones,[106–111] were reacted with substituted methylene reagents (ylides) and cyclopropane derivatives were obtained mainly.

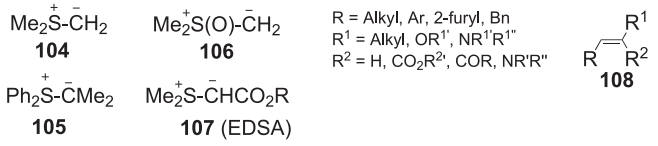
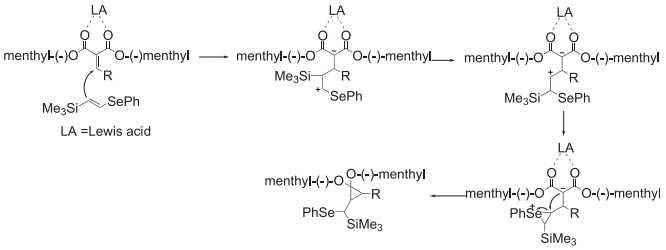


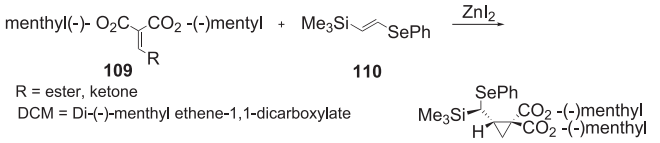
Figure 2. Four types of sulfonium ylides (**104**–**107**) and α,β-conjugated carbonyl derivatives (**108**).

In a similar way, Yamazaki and co-workers studied the development of novel carbocycle-forming reactions using vinyl selenides (**110**) and α,β-conjugated biscarbonyls (**109**) (Schemes 43 and 44).[112–121]

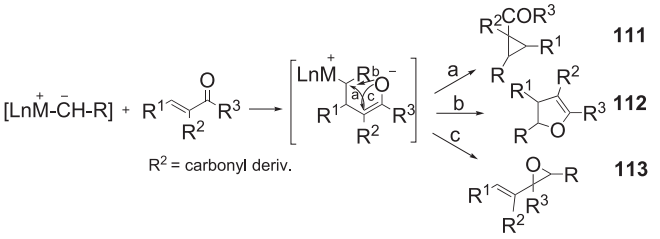
Recently, however it has been recognized that, if α,β-unsaturated biscarbonyl compounds were used as the starting compounds, nearby the formal [2+1] ylide addition to cyclopropane (**111**)[122] (a), enantioselective cycloaddition to construction of epoxides (**113**) (c), and the formal [4+1] ylide annulations (**112**) to create 5-membered heterocyclic compounds (b) are also possible (Scheme 45).[123–127]



Scheme 43. Lewis acid-promoted [2+1] cycloaddition reactions of 1-seleno-2-silylethene with di-(−)-menthyl ethene-1,1-dicarboxylates.

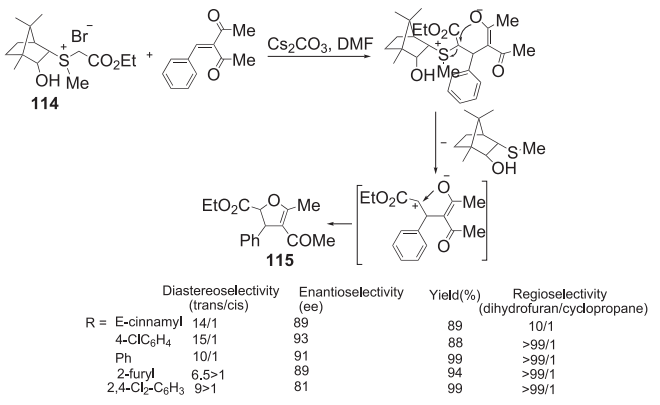


Scheme 44. Stereoselective [2+1] cycloaddition reactions of 1-seleno-2-silylethene with di-(−)-menthyl ethane-1,1-dicarboxylates.[112–121]



Scheme 45. Reaction pathways of α,β-unsaturated biscarbonyl compounds with metal carbenes.

While the reaction of ethyl (dimethylsulfuranylidene)acetate (EDSA) (**107**) with α,β-unsaturated ketones furnished cyclopropanes,[123] Tang and co-workers[128] found that the same ylide reacted with several alkylidene and 3-arylidene-2,4-pentanediones to afford dihydrofuran derivatives with high selectivities, rather than cyclopropanes. Probably, the steric hindrance of α-substituents of the carbonyl group retarded the 1,3-substitution to form cyclopropanes. By employing the camphor-derived sulfur ylide (**114**), instead of EDSA, they developed a diastereoselective (*trans*/*cis*) (dr>6.5/1) and highly enantioselective (>81% ee) cyclization reaction for the preparation of optically active highly substituted dihydrofurans (**115**). Various α-ylidene-β-diketones proved to be good substrates for this annulation (Scheme 46).

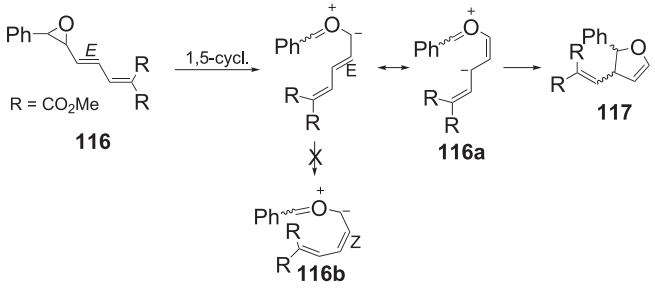


Scheme 46. Stereoselective synthesis of dihydrofurans via camphor-derivative sulfur ylide.

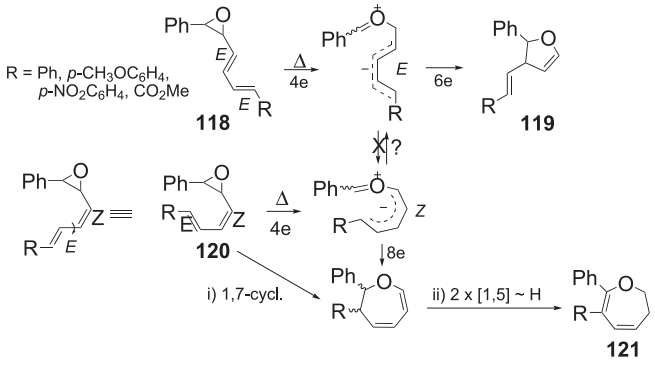
4.4. Electrocyclizations of carbonyl ylides derived from vinyl/styryl and butadienyloxiranes to dihydrofurans and dihydrooxepines[2,15,128–130]

Various thermal ring-expansion reactions of vinyl/styryl/butadienyloxiranes have been studied by Eberbach and co-workers. The substituent on the carbonyl of the conjugated carbonyl ylide, which is derived from the ring opening of conjugated oxiranes may direct to both possible (*E*/*Z*) orientations. Steric and electronic requirements direct the periselectivity of the ring-closure reaction route to either 1,5- or 1,7-cyclization or both.

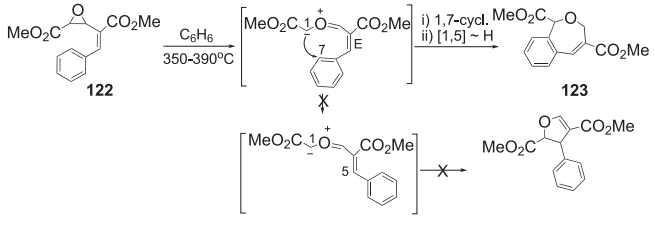
A discussion of the factors governing the periselectivity of the CCY cyclization (1,5- vs 1,7-cyclization) derived from oxiranes seems to be speculative, as shown in Schemes 47–55. Inspection studies on related conjugated dipoles in Schemes 47–55 give the impression that several different factors may be in operation, the relative importance of which changes from one particular system to another.



Scheme 47. Thermal ring-opening reaction of 3(*E*)-butadienyloxirane (**116**).[130]

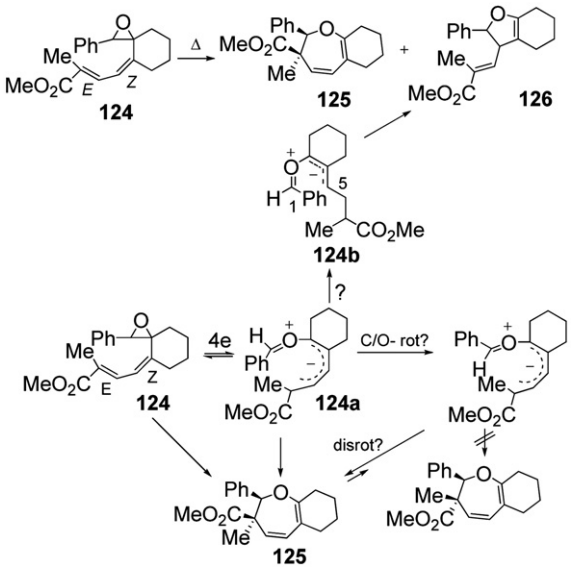


Scheme 48. Thermal ring-opening reaction of 3(*E*)/3(*Z*)-butadienyloxiranes to corresponding vinyl dihydrofurans and dihydrooxepines.[2]

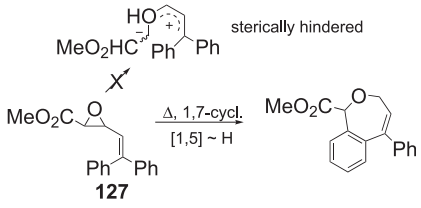


Scheme 49. Thermal ring-opening reaction of styrylepoxide (**122**).

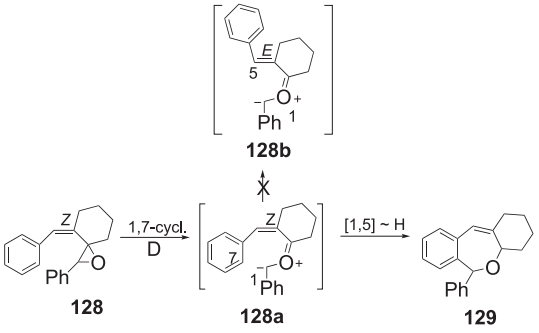
While butadienyloxirane (**116**) of which α,β-conjugation is *E*-conformation, prefers 1,5-dipole (**116a**) to yield dihydrofuran (**117**) and **116** does not undergo 1,7-cyclization that requires the ring closure of sterically crowded δ,δ′-disubstituted **116b** conformation (Scheme 47).[130]



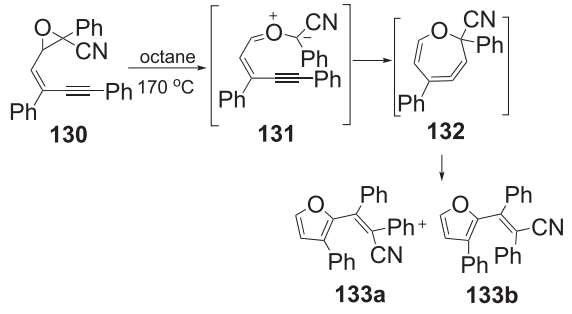
Scheme 50. Thermolysis of butadienyloxirane (**124**).



Scheme 51. Steric inhibition to dihydrofuran formation in the thermolysis of oxirane (**127**).

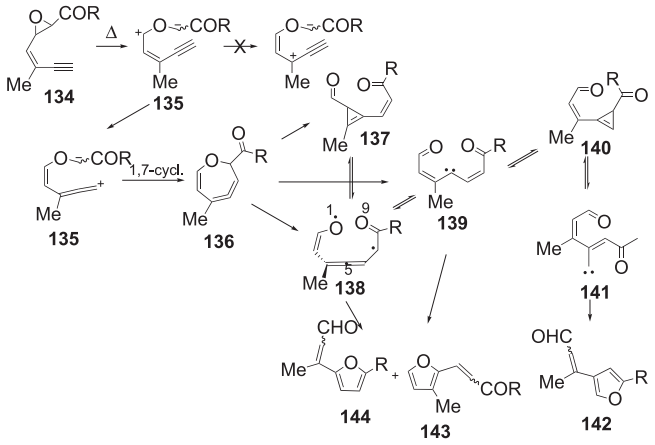


Scheme 52. Thermolysis of styryloxirane (**128**).

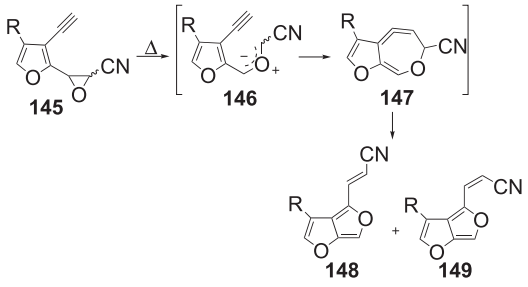


Scheme 53. Thermolysis of compound **130**.

As shown in Scheme 48, butadienyloxirane (**120**) yields dihydrofuran (**119**) and dihydrooxepine (**121**) over *Z*→*E* conversion of the α,β-double bond. However, butadienyloxirane (**118**) does not



Scheme 54. Thermolysis of compound **134**.



Scheme 55. Thermolysis of compound **145**.

show a conversion by the opposite route. On the other hand, the similar conversion does not occur for the sytrylepoxide (**122**) to undergo 1,5-cyclization (Scheme 49) and yields only oxepine **125**.[129]

In Scheme 50, *cis*-2,3-dihydrooxepine (**125**) is formed by thermolysis of **124** over conrotatory ring opening to **124a**. The formation of dihydrofuran derivative (**126**) represents the possibility of $Z \rightarrow E$ conversion from **124a** into **124b**.[130,131]

In Scheme 51, a 1,5-ring-closure reaction possibility seems sterically hindered because of the β,β′-diphenyl substitutents of the styryloxirane (**127**). Styryloxirane (**128**) yields only benzoxepine (**129**) in Scheme 52. The absence of any dihydrofuran derivative suggests that $Z \rightarrow E$ conversion (**128a**→**128b**) does not occur.

Schemes 49, 51, and 52 show that carbonyl ylides derived from *Z*-styryloxiranes undergo 1,7-electrocyclic ring closure onto the *ortho*-position of the phenyl ring, affording the benzoxepine derivatives. No dihydrofuran derivatives are detected. The periselectivite preference for the outer phenyl ring has been ascribed to the helical-type geometry of the starting substrates.

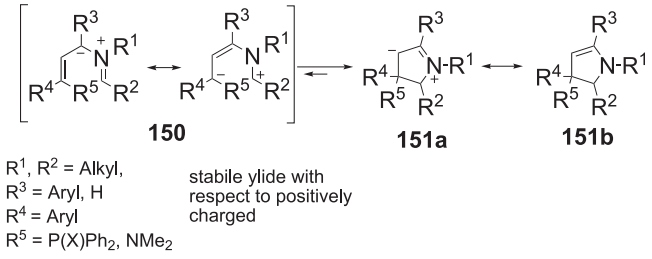
As shown in Schemes 53 and 54, *Z*-1,2-epoxy-3-hexen-5-ynes (**130** and **134**) firstly yield carbonyl ylides (**131** and **135**) and this ylide then undergoes an unprecedented 1,7-electrocyclic reaction onto the carbon–carbon triple bond. The resulting seven-membered cycloallenes (**132** and **136**) would then suffer ring contraction to the final dihydrofuran derivatives (**133a**, **133b**, **142**, **143**, **144**).

In Scheme 54, 1,3-dipolar cycloreversion of **134** leads to conjugated carbonyl ylides (**135**), which react via 1,7-electrocyclization affording the highly strained seven-membered cycloallenes (**136**). Although the formation of furans (**143** and **144**) might take place by simple recombination of the subsequently formed bis-oxopentadienyl radicals (**138**), the carbenes (**139**) represent other possible precursors. Convincing evidence for the intermediacy of structures like **137** and **139** has been obtained by the occurrence of furans (**142**) as the third thermolysis products. The specific substitution pattern can be satisfactorily explained by assuming (i) cyclization of **139** to the cyclopropenes **140**, (ii) reopening of **140** with formation of the isomeric vinylcarbenes **141**, which (iii) finally undergo 6e-ring-closure affording the furans (**142**). Similar to Schemes 47 and 48, the reaction pathway starting from **145** in Scheme 55 leading to **148** and **149** presumably proceeds via the carbonyl ylide (**146**) and its 1,7-dipolar cyclization to the cycloallene derivative (**147**), which is subsequently transformed into the furo[3,4-*b*]furans via a pathway involving diradical and/or carbene intermediates.[6]

5. Electrocyclizations of CAMY

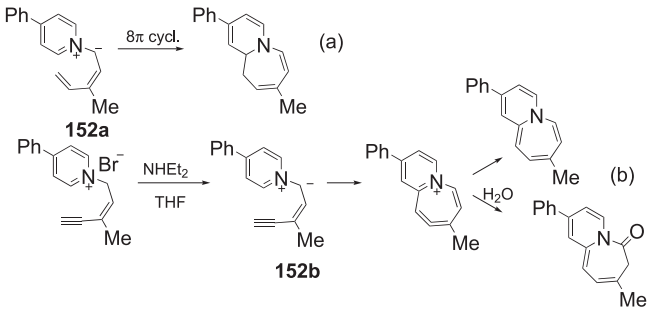
The *isoelectronic* replacement of CR in position 2 by NR in a pentadienyl species produces a conjugated 1,3-dipole, which cyclizes to a charge-free unsaturated five-membered ring.[9,132] Iminium zwitter ions delocalized the carbanionic charge in its three octet structures, depending on the electronegativities of the present substituents:

Mode A: R^2 is an alkyl group and an α-carbon bearing this alkyl group will be positively charged and will stabilize the ylide with respect to the positive edge. In the mode A, the ring closure is accompanied by the direction of negative charge compensation toward the aliphatic (alkenic) group as shown in Scheme 56. In Scheme 56, a neutral cyclic enamine (**151b**) arises over a zwitterionic form (**151a**), which reveals the allyl anion structure.



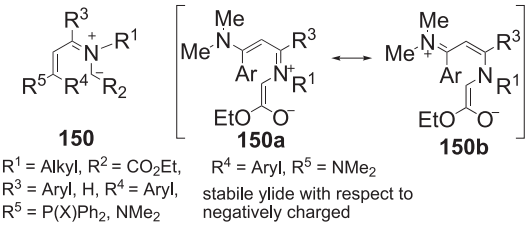
Scheme 56. Delocalization of anionic charge in a vinylogous iminium zwitter ion (**150**).

In earlier studies, Eberbach and Marx[68] synthesized a series of dihydropyridoazepines by stereoselective 1,7-electrocyclization of butadienylpyridinium ylides (**152a** and **152b**) (Scheme 57),[133] a subclass of azomethine ylides containing negative charge compensation toward the aliphatic (alkenic) group.

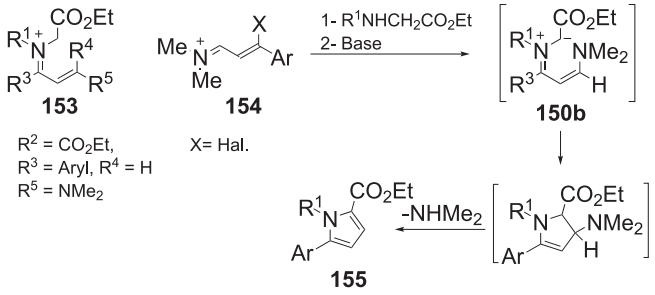


Scheme 57. Synthesis of dihydropyridoazepines by stereoselective 1,7-electrocyclization of butadienylpyridinium ylides (**152a** and **152b**).

Mode B: R^2 is a carbonyl group and an α-carbon bearing this carbonyl group will be negatively charged and will stabilize the ylide (**150**, **150a**, and **150b**) with respect to the negative edge. In the mode B, the ring closure is accompanied by the direction of positive charge compensation toward to the aliphatic (alkenic) group, as represented Schemes 58 and 59.



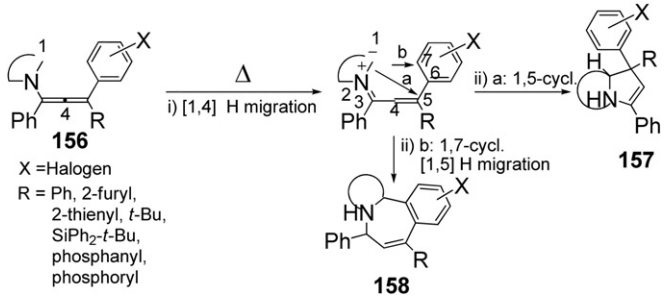
Scheme 58. Delocalization of anionic charge in **150a** and **150b**.[133]



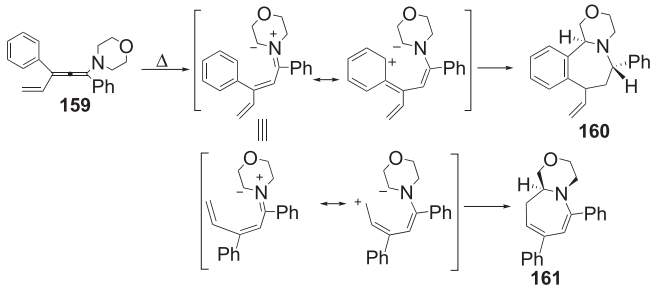
Scheme 59. 1,5-Electrocyclization of vinylogous iminium salts.

1,5-Electrocyclization of in situ-generated α,β-unsaturated azomethine ylides (R^2=CO_2Et) yield the pyrrole ring (**155**), either directly or requiring a subsequent β-elimination to establish the conjugated π system. Vinamidinium[134] and 3-chloropropene iminium salts (**154**)[135–139] are well-suited starting materials, which yield the conjugated azomethine ylides (**150b**) after reaction with *N*-alkylglycinates and deprotonation (Scheme 59).

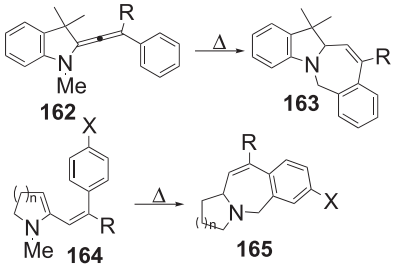
Maas and co-workers[140,141] (Schemes 60, 61, and 62) studied the thermal isomerizations of 1-amino-3-vinyl-3-allene/(het)arylallenes (**156**) to investigate the formation of dihydropyrrole (**157**) and dihydroazepine (**158**) derivatives related the nature of the present substituents over two steps: (i) a 1,4-H shift to form an α,β,γ,δ-unsaturated 1,3-dipole and (ii) six-electron 1,5- (**157**) or an eight-electron 1,7- (**158**) electrocyclic ring closure.



Scheme 60. Thermally induced cyclizations of aminoallenes to pyrrole (**157**) and azepine (**158**) derivatives.



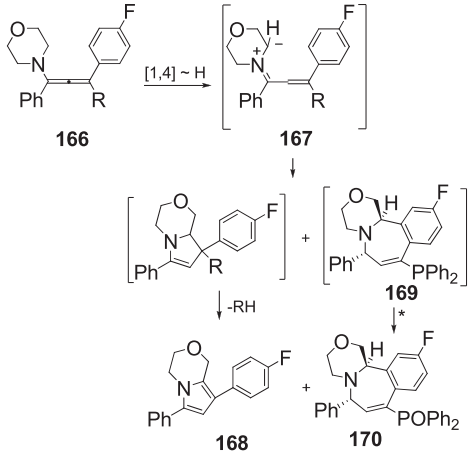
Scheme 61. Cyclization pathways of **159** to azepine derivatives in thermally induced reactions.



Scheme 62. Thermally induced cyclizations of aminoallenes (**162**, **164**) to azepine derivatives (**163**, **165**).

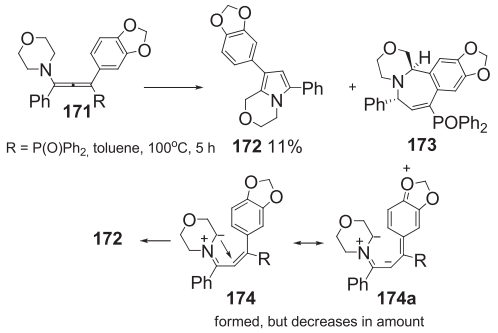
In these reports, to yield **158**, **160**, **161**, **163**, and **165**, where the 1,7-cyclization of the temporary loss of aromaticity of the involved (hetero)aryl rings **156** and **159** (Schemes 60 and 61), **162**, **164** (Scheme 62) were required, they never observed 1,5-cyclization products as might be expected from the steric inhibition at terminuses of the 1,5-dipole.

In another recent report[142] the same workers determined the decisive influence of the nature of the substituent R on the periselectivity of the electrocyclic ring closure of azomethine ylides (**167**) derived from **166** (Scheme 63). While they observed only 1,7-electrocyclization when R was a phenyl, 2-furyl, 2-thienyl, *t*-Bu, or $SiPh_2$–*t*-Bu substituent, 1,5-electrocyclization became a competitive or the dominant pathway when R was a phosphanyl (**166a**) or phosphoryl group (**166b**) (Scheme 63).



Scheme 63. Thermally induced cyclization of aminoallene (**166**) to pyrrole (**168**) and dihydroazepine (**170**) derivatives.

They converted several 1-dialkylamino-1,3-diaryl-3-diphenylphosphanylallenes (**166a**) into [*a*]-annulated 3,5-diarylpyrroles (**168**) and [*a*]-annulated benzo[*c*]azepines (**170**) from **169**. Although phosphanyl or phosphoryl groups are both capable of giving rise to the two cyclizations, the periselectivity is markedly shifted toward 1,5-cyclization when the diphenylphosphanyl substituent is replaced the diphenylphosphoryl group (Scheme 63). Thus, 1-dialkylamino-3-(diphenylphosphoryl)allenes yield pyrroles exclusively and with improved yields, unless the 3-aryl substituent of the allene is too electron-rich (i.e., benzodioxol-5-yl) (**171**) (Scheme 64). The preparation and thermal transformation of aminoallenes over three or four steps can be conducted as a one-pot procedure, thus providing a convenient synthesis of [*a*]-annulated 3,5-diarylpyrroles from enamino ketones. The trans configuration is determined in agreement with a conrotatory 8π electrocyclization

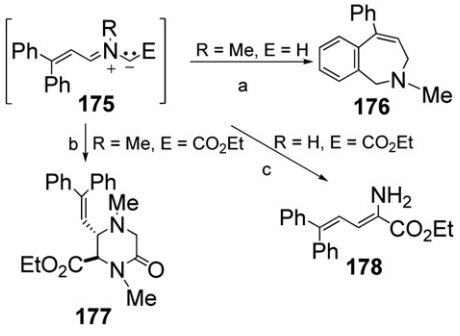


Scheme 64. Thermally induced cyclization of aminoallene (**171**) containing electron-rich substituent at 3-position.

mode of the azomethine ylide intermediates followed by a suprafacial [1,5] H migration.

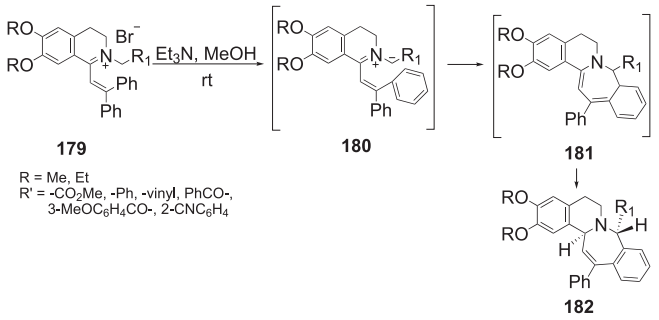
The factors governing the periselectivity of the azomethine ylide cyclization (1,5- vs 1,7-cyclization) may be explicable to some extent. Inspection of literature studies on related conjugated dipoles gives the impression that several different factors may be in operation, the relative importance of which changes from one particular system to another. The cyclization step could be orbital or charge controlled (i.e., a 'true' 6π vs 8π electrocyclization or a 1,5- vs 1,7-dipolar cyclization). Calculations by Eberbach and Marx[67] for butadienyl-substituted pyridinium ylides support the view that the orbital-controlled mode favors the 1,7-cyclization, because the helical transition-state geometry is particularly suited for a conrotatory 8π cyclization. On the other hand, although it was still an electrocyclization reaction (**174** and **174a**→**172**), stabilization by appropriate substituents for a 1,5-dipolar bond structure (a charge-controlled step) favors the 1,5-cyclization.

Nyerges and co-workers[143] found significant differences between the reactivity of α,β,γ,δ-unsaturated, non-stabilized (**175, a**) (E=H) and α,β,γ,δ- unsaturated, ester-stabilized azomethine ylides (**175, b**) (E=CO_2Et). The former dipoles react via a 1,7-electrocyclization, followed by a [1,5]-hydrogen shift, to give dihydroazepines (**176**, pathway a), while the latter (R=H (pathway c), R=Me (pathway b)) give other products (**177** or **178**) via novel rearrangements (reaction of ylide with i.e., amine) (Scheme 65).[144,145]



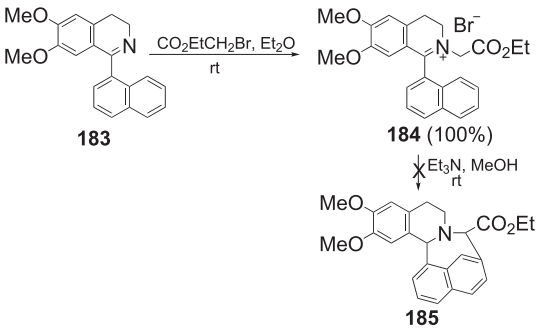
Scheme 65. Different reactivities of α,β,γ,δ-unsaturated azomethine ylides (**175**).

The same researchers[146,147] also showed the scope and limitations for the construction of the azepine ring system (**182**) via the 1,7-electrocyclization of these azomethine ylides (**180**) from **179**. The reactions with the diphenylethenyl side chains proceeded in good-to-excellent yield, depending upon the electron-withdrawing ability of the substituent on the azomethine ylide (Scheme 66). The steric restrictions caused by the additional bond between the two phenyl groups in the dipoles as shown in the reaction of compound **183** resulted in a significant decrease in the yields of the electrocyclization products (**185**) and the rigid nature of the



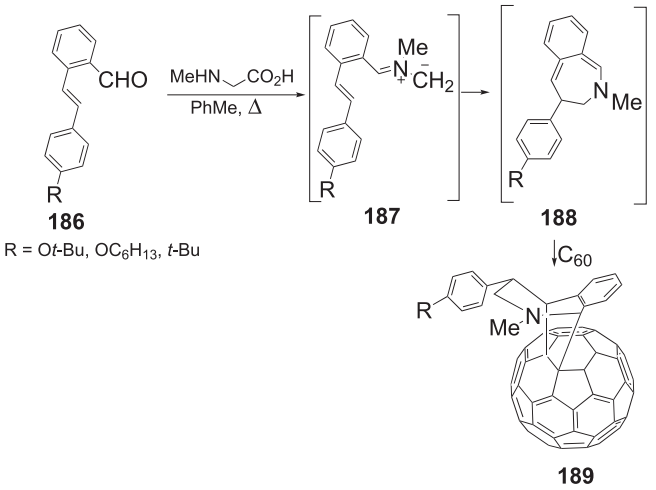
Scheme 66. 1,7-Electrocyclization of some diphenylethenyl-substituted azomethine ylides (**180**).

naphthalene side chain makes the reaction of **184** impossible (Scheme 67).



Scheme 67. Steric reactions in the 1,7-electrocyclization of compound **183**.

Another report from Eckert and co-workers [148] also showed that the reactivity pattern of conjugated azomethine ylides includes not only their reactivity as 1,3-dipoles for electrocyclization reactions, but also subsequent reactions such as Diels–Alder type cycloadditions. While an intermolecular reaction of an azomethine ylide derived from *trans*-2-stilbenecarboxaldehyde derivatives (**186**) with *N*-methylglycine onto C_{60} was attempted, Diels–Alder cycloaddition was obtained to yield fullerene derivatives (**189**). First, 1,7-cyclization does occur to give the diene (**188**), which acts as a 4π component in a subsequent Diels–Alder type cycloaddition (**188**) with C_{60} (Scheme 68).



Scheme 68. Fullerene derivatives (**189**) from Diels–Alder cycloaddition reaction of *trans*-2-stilbenecarboxyaldehydes (**186**) derivatives with *N*-methylglycine and C_{60}.

5.1. Regioselectivity in the formation of dihydropyrroles depending on catalyst

Like all metal-carbene transformations, electrocyclic reactions over CCY/CAMY derived from diazo and conjugated carbonyl/imine compounds take place via metal-carbene intermediates. Diazocarbonyl compounds that include esters, amides, aldehydes, and ketones are stabilized diazomethane derivatives and being ordinarily stable to temperatures above 100 °C, they undergo dinitrogen extrusion in the presence of a catalyst at considerably lower temperatures. The basic success of these catalysts is derived from their activities as Lewis acids for electrophilic addition to the diazo compound and in the stabilization of the metal carbene formed upon dinitrogen dissociation.

In the investigations of catalytic acceleration of diazo decomposition, copper and copper salts are the oldest and most studied that facilitate a variety of complex carbon–carbon bond-forming reactions, including addition, insertion, and also ylide generation.

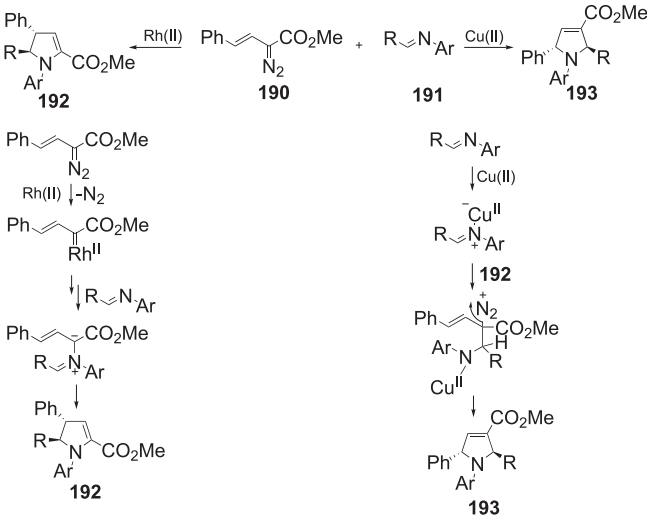
For the catalytic approaches to highly stereoselective ylide generation,[149,150] copper salts and dirhodium(II) complexes have been remarkably effective, leading to heterocyclic compounds, epoxides, aziridines, dihydropyrrolidines, dihydrofurans, dihydrooxepines, and dihydroazepines from aryl- and vinyldiazoacetates.[45,48,71] In early investigations, copper complex transformations were found to be relatively unselective, while reactions catalyzed by $Rh_2(OAc)_4$, and reactive chiral carboxylates and carboxamidates of dirhodium(II) were found to be highly stereoselective. However, Doyle and co-workers[151] produced the isomeric dihydropyrrole region- and stereoselectively by using copper(I) hexafluorophosphate, copper(I) triflate, and copper(II) triflate in the course of their investigations on the catalytic ylide-derived reactions of vinyldiazo compounds with imines. Catalytic ylide-derived reactions of vinyldiazo compounds with imines, including copper(I) hexafluorophosphate, copper(I) triflate, and copper(II) triflate were investigated in the same study. Whereas $Rh_2(OAc)_4$ and reactive chiral carboxylates and carboxamidates of dirhodium (II) gave the anticipated dihydropyrrole (**192**) from the reaction between styryldiazoacetate (**190**) and imine (**191**) (R=*trans*-PhCH=CH) with high stereocontrol (100:0, *cis*:*trans*), the use of copper catalysts, including $CuPF_6$ and CuOTf that normally operate through the same mechanistic pathway as rhodium(II) catalysts, produced the isomeric dihydropyrrole (**193**) competitively. Cu $(OTf)_2$ was optimum for this transformation (**192**:**193**; 0:100, 74% yield). The alternative copper(II)-catalyzed pathway to obtain **193** is a Lewis acid-catalyzed process, that is, reminiscent of the efficient construction of aziridines with ethyl diazoacetate reported by Wulff.[152,153] Other Lewis acids were employed in efforts to develop the generality of the process, but only $Sn(OTf)_2$ a showed comparable product yield (*trans*:*cis*, 84:16).

Accordingly, **192** is formed from an ylide originating with a metal-carbene intermediate, whereas **193** is formed by a process in which the metal catalyst, acting as a Lewis acid, activates the imine for electrophilic addition to the diazo compound (Scheme 69). In previous investigations of copper-catalyzed aziridination reactions of ethyl diazoacetate, copper/carbene species were the proposed intermediates.[154,155] However, activation of imines for electrophilic addition by copper salts has recently been utilized in cycloaddition reactions.[156–159]

There are also studies recent studies related to the regio/stereocontrolled 1,3-dipolar cycloadditions of azomethine ylides using copper catalysts.[160–162]

6. Thermal cyclization reactions of diene-conjugated diazo compounds

Sharp and co-workers generated diene-conjugated diazo compounds by the thermal decomposition of the sodium salts of the



Scheme 69. Catalyst-directed selective pathways to dihydropyrroles.

corresponding tosylhydrazones of 1-acyl-1,3-dienes.[163–173] Some examples for diene-conjugated diazo compounds (**194**–**198**)[70] are shown in Figure 3. All these compounds representing a cis relationship of the diazo group and the γ,δ-double bond and having a *cis* hydrogen atom at the diene terminus cyclize only with the 8π electron, 1,7-ring-closure reaction to give 3*H*-1,2-diazepines. In order to meet the requirements for the pre-ring conformation, compounds **194**–**198** also have to contain suitable substituents to constitute the helical transition state for a 1,7-cyclization reaction to yield **199** (Scheme 70).

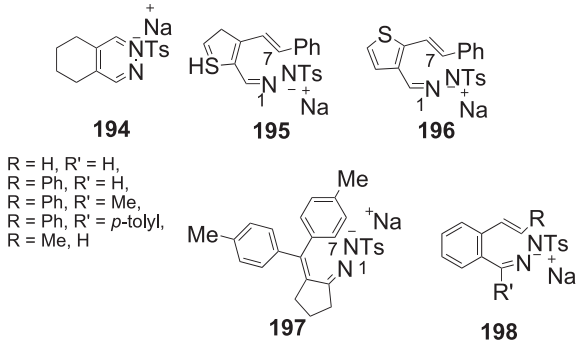
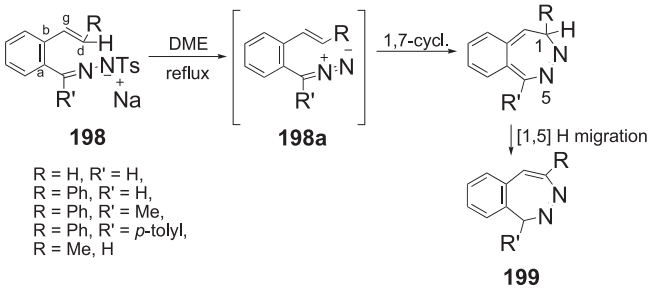


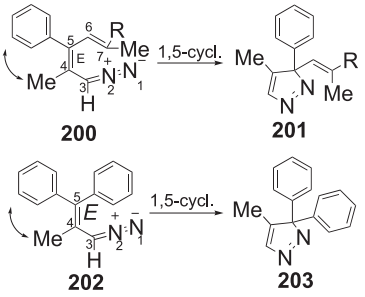
Figure 3. Examples of tosylhydrazones of 1-acyl-1,3-dienes for the synthesis of diene-conjugated diazo compounds.



Scheme 70. Reaction mechanism of thermal cyclization of diene-conjugated diazo compounds.

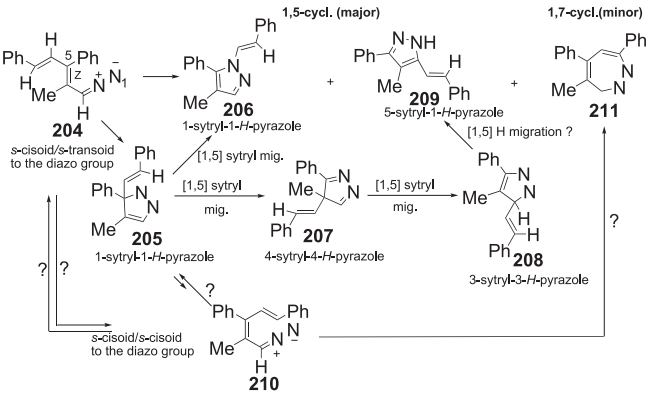
In the thermal cyclization reactions of diene-conjugated diazo compounds (**200** and **202**), 1,7-cyclization was inhibited by the presence of *cis*-methyl/phenyl substituents present at the diene

terminus (δ-C). These types of diene-conjugated diazo compounds cyclized to give 3-alkenyl-3*H*-pyrazoles (**201** and **203**) by an alternative 1,5-ring-closure (6π electron) reaction as the primary products (Scheme 71).

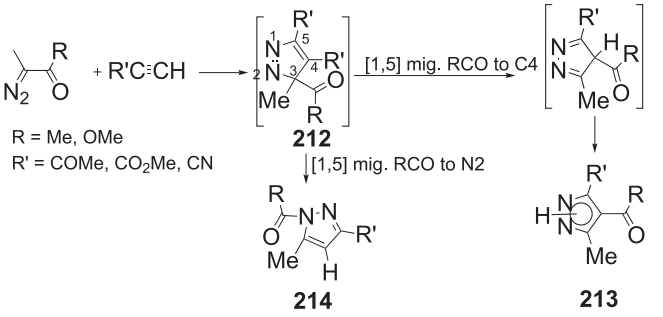


Scheme 71. Inhibition of 1,7-electrocyclization by *cis*-methyl/phenyl substituents present at diene terminus.

The compound **204** has an *s-cisoid*/*s-transoid* conformation and the cyclization reaction of **204** yields pyrazole derivatives (**206**, 33% and **209**, 20%) as major products. Besides, the *s-cisoid*/*s-cisoid* intermediate (**210**), a diazepine derivative (**211**, 20%) was obtained as a minor product (Schemes 72 and 73).



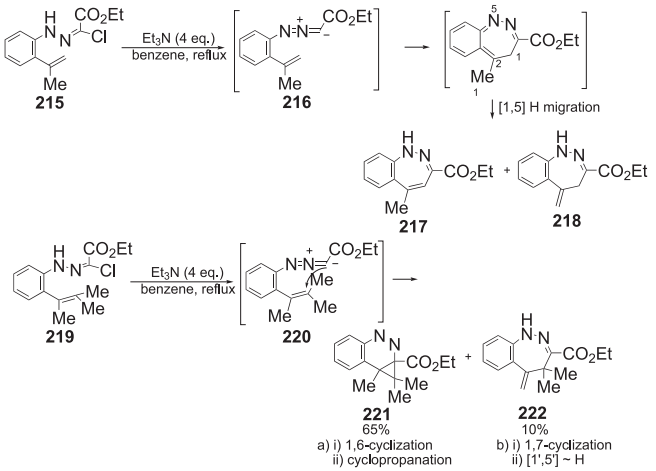
Scheme 72. 1,5-/1,7-Electrocyclizations over *s-cisoid*/*s-transoid* and *s-cisoid*/*s-cisoid* conformations of diene-conjugated diazo compounds of **204** and **210**.



Scheme 73. Different types of migrations on a pyrazole derivative (**212**).[174]

7. Cyclization of in situ-generated nitrile imines[175–185]

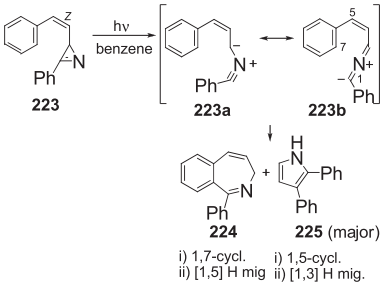
As a typical example, *N*-(2-vinylphenyl)-substituted nitrile imines (**216**–**220**), generated in situ upon base treatment of the corresponding hydrazonyl chlorides (**215** and **219**), cyclize to 1,2-benzodiazepines (**217**, **218**, and **219**) and/or cyclopropa[*c*]cinnoline (**221**), depending on the substituents at the ethylenic bond, as well as on the experimental conditions (Scheme 74).



Scheme 74. Cyclization reactions of *N*-(2-vinylphenyl)-substituted nitrile imines (**216** and **220**) to 1,2-benzodiazepines (**217**, **218**, **222**) and/or cyclopropa[*c*]cinnoline (**221**).

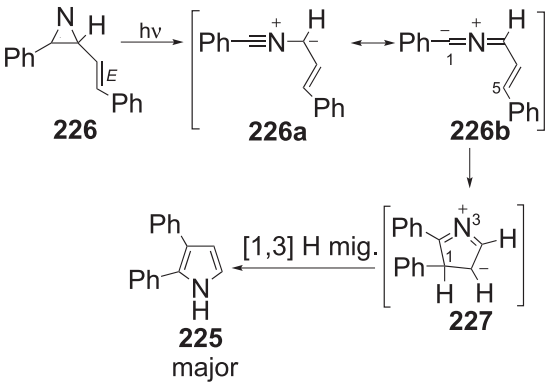
8. Photochemical cyclization reactions of nitrile ylides

The azirine derivatives undergo photochemical rearrangement to give 2,3-disubstituted pyrroles and benzazepine derivatives via transient nitrile ylide intermediates, which can be trapped with external dipolarophiles. Photochemical reaction of *Z*-3-phenyl-2-styryl-2*H*-azirine (**223**) affords 1-phenyl-3*H*-2-benzazepine (**224**) in high yield (80%), along with a trace amount of 2,3-diphenylpyrrole (**225**, 4%) in terms of competitive 1,7- and 1,5-electrocyclic reactions of the transient nitrile ylides (**223a** and **223b**) (Scheme 75).[186]



Scheme 75. Photochemical reactions of *Z*-3-phenyl-2-styryl-2*H*-azirine (**223**).

These transformations (Schemes 75 and 76) are both explicable on the basis of a ring opening of **223** and **226** to nitrile ylide intermediates (**223a**/**b** and **226a**/**b**), which subsequently undergo intramolecular reorganizations to seven- and/or five-



Scheme 76. Photochemical reactions of *E*-3-phenyl-2-styryl-2*H*-azirine (**226**).

membered rings followed by 1,5- and 1,3-sigmatropic shifts. A study of the quantum yield for product formation as a function of added dipolarophile shows that the photocyclization to give a seven-membered azepine is significantly faster than cyclization to the five-membered pyrrole ring.

While *Z*-3-phenyl-2-styryl-2*H*-azirine (**223**) yields benzazepine derivative (**224**) as the major product, *E*-3-phenyl-2-styryl-2*H*-azirine (**226**) takes an entirely different course, giving 2,3-diphenylpyrrole (**225**) as the major product, as expected from the stereochemistry of the starting compound. It should be pointed out that this pyrrole (**225**) was also formed in low yield in the irradiation of the ***Z***-isomer (**223**). The formation of a 2,3-disubstituted pyrrole (**225**) from the irradiation of a 2-vinyl-substituted 2*H*-azirine (**226**) can also be interpreted in terms of a mechanism, which involves a nitrile ylide intermediate (**226a** and **226b**). Intramolecular reorganization of the nitrile ylide intermediate (**227**) followed by a 1,3-sigmatropic hydrogen shift of the initially formed five-membered ring (**227**) readily rationalizes the formation of the final product (**225**). This mechanism is supported by the observation that the nitrile ylide can be trapped by the addition of an external dipolarophile.

9. Summary

Three-, five-, and seven-membered heterocycles containing oxygen and nitrogen atoms are very valuable for the synthesis of many natural products, and 1,5-, 1,7-, and 1,3-electrocyclizations of conjugated carbonyl ylides (CCY) and conjugated azomethine ylides (CAMY) are efficient and versatile tools for the construction of these heterocycles (dihydofurans/dihydropyrroles, dihydroxepines/dihydroazepines, and oxiranes/aziridines). Conjugated carbonyl ylides and conjugated azomethine ylides are very similar intermediates having parallel chemistries. Their chemo- and stereoselective electrocyclizations depend on the starting compounds and the catalysts used. The double-bond conformations and charge separations of the intermediates of CCY/CAMY are stabilized/non-stabilized by the placement and the acceptor/donor effects of the substituents.

Consequently, orbital coefficients and/or dipolar structures designed at the termini of the conjugated carbonyl ylide systems direct the regio-/stereo-selectivities of the electrocyclization reaction to resulting heterocycles.

Chiral auxiliaries in the reactants/catalysts are often used for the facial selectivities of the asymmetric electrocyclization reactions.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.05.058. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395.
2. Eberbach, W.; König, G.; Trostmann, U. *Tetrahedron Lett.* **1979**, *20*, 4649.
3. Eberbach, W.; Roser, J. *Heterocycles* **1985**, *23*, 2797.
4. Eberbach, W.; Roser, J. *Tetrahedron* **1986**, *42*, 2221.
5. Eberbach, W.; Roser, J. *Tetrahedron Lett.* **1987**, *28*, 2685.
6. Eberbach, W.; Fritz, H.; Laber, N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 568.
7. Eberbach, W.; Fritz, H.; Laber, N. *Angew. Chem.* **1988**, *100*, 599.
8. Eberbach, W.; Trostmann, U. *Chem. Ber.* **1985**, *118*, 4035.
9. Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565.
10. Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 1753.
11. Pandey, G.; Banerjee, P.; Gadre, S. R. *Chem. Rev.* **2006**, *106*, 4484.
12. Pinho e Melo, T. M. V. D. *Eur. J. Org. Chem.* **2006**, *2006*, 2873.
13. Moisan, B.; Robert, A.; Foucaud, A. *Tetrahedron* **1974**, *30*, 2867.
14. Eberbach, W.; Seiler, W. *Tetrahedron Lett.* **1978**, *49*, 4875.
15. Eberbach, W.; Burchardt, B. *Chem. Ber.* **1978**, *111*, 3665.
16. Alt, M.; Maas, G. *Tetrahedron* **1994**, *50*, 7435.
17. Alt, M.; Maas, G. *Chem. Ber.* **1994**, *127*, 1537.
18. Demarch, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952.
19. Çelik, M. A.; Yurtsever, M.; Tüzün, N. S.; Güngör, F. Ş.; Sezer, Ö.; Anaç, O. *Organometallics* **2007**, *26*, 2978.
20. Houk, K. N.; Sims, J.; Duke, R. E.; Strozier, W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287.
21. Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.
22. Vedejs, E. In *Advances in Cycloaddition Chemistry*; Curran, D. P., Ed.; JAI Press: Greenwich, CT, 1988; Vol. 1, p 33.
23. Padwa, A. In *Comprehensive Organic Synthesis*; Trost, L. F. B. M., Ed.; Pergamon: Oxford, 1991; Vol. 4, p 1069.
24. Wade, P. A. In *Comprehensive Organic Synthesis*; Trost, L. F. B. M., Ed.; Pergamon: Oxford, 1991; Vol. 4, p 1111.
25. Hansen, J.; Autschbach, J.; Davies, H. M. L. *J. Org. Chem.* **2009**, *74*, 6555.
26. Spencer, T. A.; Villarica, R. M.; Storm, D. L.; Weaver, T. D.; Friary, R. J.; Posler, J.; Shafer, P. R. *J. Am. Chem. Soc.* **1967**, *89*, 5497.
27. Storm, D. L.; Spencer, T. A. *Tetrahedron Lett.* **1967**, *8*, 1865.
28. Murayama, S. T.; Spencer, T. A. *Tetrahedron Lett.* **1969**, *10*, 4479.
29. Eberlin, M. N.; Kascheres, C. *J. Org. Chem.* **1988**, *53*, 2084.
30. Eberlin, M. N.; Takahata, Y.; Kascheres, C. *J. Org. Chem.* **1990**, *55*, 5150.
31. Augusti, R.; Eberlin, M. N.; Kascheres, C. *J. Heterocycl. Chem.* **1995**, *32*, 1355.
32. Maas, G.; Müller, A. *J. Prakt. Chem.* **1998**, *340*, 315.
33. Kascheres, C. M. *J. Brazil. Chem. Soc.* **2003**, *14*, 945.
34. Anac, O.; Daut, A. *Lieb. Ann. Rec.* **1997**, 1249.
35. Daut-Ozdemir, A.; Anac, O.; Borrmann, H.; Somer, M. *Z. Kristallogr.* **2002**, *217*, 607.
36. Daut-Ozdemir, A.; Anac, O.; Borrmann, H.; Somer, M. *Z. Kristallogr.* **2002**, *217*, 609.
37. Anaç, O.; Sezer, Ö.; Daut Özdemir, A. *Helv. Chim. Acta* **2003**, *86*, 290.
38. Anac, O.; Gungor, F. S.; Kahveci, C.; Cansever, M. S. *Helv. Chim. Acta* **2004**, *87*, 408.
39. Anac, O.; Gungor, F. S.; Merey, G. *Helv. Chim. Acta* **2006**, *89*, 1231.
40. Gungor, F. S.; Anac, O.; Sezer, O. *Tetrahedron Lett.* **2007**, *48*, 4883.
41. Anac, O.; Sezer, O.; Candan, O.; Gungor, F. S.; Cansever, M. S. *Tetrahedron Lett.* **2008**, *49*, 1062.
42. Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 1046.
43. Huisgen, R.; Demarch, P. *J. Am. Chem. Soc.* **1982**, *104*, 4953.
44. Doyle, M. P.; Forbes, D. C.; Protopopova, M. N.; Stanley, S. A.; Vasbinder, M. M.; Xavier, K. R. *J. Org. Chem.* **1997**, *62*, 7210.
45. Doyle, M. P.; Hu, W. H.; Timmons, D. J. *Org. Lett.* **2001**, *3*, 933.
46. Russell, A. E.; Brekan, J.; Gronenberg, L.; Doyle, M. P. *J. Org. Chem.* **2004**, *69*, 5269.
47. Hamaguchi, M.; Matsubara, H.; Nagai, T. *Tetrahedron Lett.* **2000**, *41*, 1457.
48. Doyle, M. P.; Hu, W. H.; Timmons, D. J. *Org. Lett.* **2001**, *3*, 3741.
49. Hamaguchi, M.; Matsubara, H.; Nagai, T. *J. Org. Chem.* **2001**, *66*, 5395.
50. Hamaguchi, M.; Takahashi, K.; Oshima, T.; Tamura, H. *Tetrahedron Lett.* **2003**, *44*, 4339.
51. Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339.
52. Vangveravong, S.; Nichols, D. E. *J. Org. Chem.* **1995**, *60*, 3409.
53. Bartels, A.; Jones, P. G.; Liebscher, J. *Synthesis* **1998**, 1645.
54. Alcaraz, C.; Fernandez, M. D.; Defrutos, M. P.; Marco, J. L.; Bernabe, M. *Tetrahedron* **1994**, *50*, 12443.
55. Alcaraz, C.; Herrero, A.; Marco, J. L.; Fernandezalvarez, E.; Bernabe, M. *Tetrahedron Lett.* **1992**, *33*, 5605.
56. Sato, M.; Hisamichi, H.; Kaneko, C.; Suzaki, N.; Furuya, T.; Inukai, N. *Tetrahedron Lett.* **1989**, *30*, 5281.
57. Alami, A.; Calmes, M.; Daunis, J.; Escale, F.; Jacquier, R.; Roumestant, M. L.; Viallefont, P. *Tetrahedron: Asymmetry* **1991**, *2*, 175.
58. Charette, A. B.; Janes, M. K.; Lebel, H. *Tetrahedron: Asymmetry* **2003**, *14*, 867.
59. Doyle, M. P.; Colsman, M. R.; Dorow, R. L. *J. Heterocycl. Chem.* **1983**, *20*, 943.
60. Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H. *J. Org. Chem.* **1982**, *47*, 4059.
61. Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443.
62. Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449.
63. Miller, J. A.; Jin, W. C.; Nguyen, S. T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2953.
64. Aggarwal, V. K.; Alonso, E.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Porcelloni, M.; Studley, J. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1430.
65. Aggarwal, V. K.; Smith, H. W.; Hynd, G.; Jones, R. V. H.; Fieldhouse, R.; Spey, S. E. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3267.
66. Aggarwal, V. K.; Smith, H. W.; Jones, R. V. H.; Fieldhouse, R. *Chem. Commun.* **1997**, 1785.
67. Aggarwal, V. K.; Thompson, A.; Jones, R. V. H.; Standen, M. C. H. *J. Org. Chem.* **1996**, *61*, 8368.
68. Marx, K.; Eberbach, W. *Tetrahedron* **1997**, *53*, 14687.
69. Rios, R.; Liang, J.; Lo, M. M. C.; Fu, G. C. *Chem. Commun.* **2000**, 377.
70. Robertson, I. R.; Sharp, J. T. *Tetrahedron* **1984**, *40*, 3095.
71. Davies, H. M. L.; DeMeese, J. *Tetrahedron Lett.* **2001**, *42*, 6803.
72. Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167.
73. Davies, H. M. L.; Clark, T. J. *Tetrahedron* **1994**, *50*, 9883.
74. Schnaubelt, J.; Marks, E.; Reissig, H. U. *Chem. Ber.* **1996**, *129*, 73.
75. Burger, U.; Gandillon, G. *Tetrahedron Lett.* **1979**, 4281.
76. Mayr, H.; Heigl, U. W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 579.
77. Sugita, H.; Mizuno, K.; Mori, T.; Isagawa, K.; Otsuji, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 984.
78. Jefford, C. W.; Mareda, J.; Gehret, J. C. E.; Kabengele, N. T.; Graham, W. D.; Burger, U. *J. Am. Chem. Soc.* **1976**, *98*, 2585.
79. Birney, D. M.; Ham, S.; Unruh, G. R. *J. Am. Chem. Soc.* **1997**, *119*, 4509.
80. Loebach, J. L.; Bennett, D. M.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9690.
81. Davies, H. M. L.; Stafford, D. G.; Doan, B. D.; Houser, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 3326.
82. Reddy, R. P.; Davies, H. M. L. *J. Am. Chem. Soc.* **2007**, *129*, 10312.

83. Schwartz, B. D.; Denton, J. R.; Lian, Y.; Davies, H. M. L.; Williams, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 8329.
84. Spino, C.; Rezaei, H.; Dupont-Gaudet, K.; Belanger, F. *J. Am. Chem. Soc.* **2004**, *126*, 9926.
85. Lilienblum, W.; Hoffmann, R. W. *Chem. Ber.* **1977**, *110*, 3405.
86. Rigby, J. H.; Wang, Z. Q. *Org. Lett.* **2003**, *5*, 263.
87. Friedrich Krollpfeiffer, H. H. *Chem. Ber.* **1950**, *83*, 90.
88. Takahashi, T.; Yamashita, Y.; Doi, T.; Tsuji, J. *J. Org. Chem.* **1989**, *54*, 4273.
89. Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
90. Corey, E. J.; Jautelat, M. *J. Am. Chem. Soc.* **1967**, *89*, 3912.
91. Trost, B. M.; Melvin, L. S. *Sulfur Ylides, Emerging Synthetic Intermediates*; Academic: New York, NY, 1975.
92. Johnson, C. R. In *Comprehensive Organic Synthesis*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 247.
93. Gololobov, Y. G.; Nesmeyanov, A. N.; Lysenko, V. P.; Boldeskul, I. E. *Tetrahedron* **1987**, *43*, 2609.
94. Li, A. H.; Dai, L. X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341.
95. La Porta, E.; Piarulli, U.; Cardullo, F.; Paio, A.; Provera, S.; Seneci, P.; Gennari, C. *Tetrahedron Lett.* **2002**, *43*, 761.
96. Ahmad, S.; Doweyko, L. M.; Dugar, S.; Grazier, N.; Ngu, K.; Wu, S. C.; Yost, K. J.; Chen, B. C.; Gougoutas, J. Z.; DiMarco, J. D.; Lan, S. J.; Gavin, B. J.; Chen, A. Y.; Dorso, C. R.; Serafino, R.; Kirby, M.; Atwal, K. S. *J. Med. Chem.* **2001**, *44*, 3302.
97. Tang, Y.; Huang, Y. Z.; Dai, L. X.; Chi, Z. F.; Shi, L. P. *J. Org. Chem.* **1996**, *61*, 5762.
98. Jubault, P.; Goumain, S.; Feasson, C.; Collignon, N. *Tetrahedron* **1998**, *54*, 14767.
99. Goumain, S.; Jubault, P.; Feasson, C.; Quirion, J. C. *Tetrahedron Lett.* **1999**, *40*, 8099.
100. Duquenne, C.; Goumain, S.; Jubault, P.; Feasson, C.; Quirion, J. C. *Org. Lett.* **2000**, *2*, 453.
101. Elinson, M. N.; Feducovich, S. K.; Starikova, Z. A.; Olessova, O. S.; Vereshchagin, A. N.; Nikishin, G. I. *Tetrahedron Lett.* **2000**, *41*, 4937.
102. Matsumura, Y.; Inoue, M.; Nakamura, Y.; Talib, I. L.; Maki, T.; Onomura, O. *Tetrahedron Lett.* **2000**, *41*, 4619.
103. Bruncko, M.; Crich, D. *J. Org. Chem.* **1994**, *59*, 4239.
104. Tang, Y.; Chi, Z. F.; Huang, Y. Z.; Dai, L. X.; Yu, Y. H. *Tetrahedron* **1996**, *52*, 8747.
105. Elinson, M. N.; Feducovich, S. K.; Lizunova, T. L.; Nikishin, G. I. *Tetrahedron* **2000**, *56*, 3063.
106. Guo, X.; Shen, W. B.; Shao, J. G.; Zhong, Q. *Synth. Commun.* **2000**, *30*, 3275.
107. Guo, X.; Shen, W. B.; Zheng, M.; Zhong, Q. *Synth. Commun.* **2000**, *30*, 3363.
108. Tang, Y.; Huang, Y. Z.; Dai, L. X.; Sun, J.; Xia, W. *J. Org. Chem.* **1997**, *62*, 954.
109. Hoppe, H. A.; Lloyd-Jones, G. C.; Murray, M.; Peakman, T. M.; Walsh, K. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1545.
110. Wender, P. A.; Glass, T. E.; Krauss, N. E.; Muhlebach, M.; Peschke, B.; Rawlins, D. B. *J. Org. Chem.* **1996**, *61*, 7662.
111. Dauben, W. G.; Hendricks, R. T.; Pandy, B.; Wu, S. C.; Zhang, X. M.; Luzzio, J. M. *Tetrahedron Lett.* **1995**, *36*, 2385.
112. Yamazaki, S.; Katoh, S.; Yamabe, S. *J. Org. Chem.* **1992**, *57*, 4.
113. Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356.
114. Yamazaki, S.; Tanaka, M.; Inoue, T.; Morimoto, N.; Kumagai, H.; Yamamoto, K. *J. Org. Chem.* **1995**, *60*, 6546.
115. Yamazaki, S.; Kumagai, H.; Takada, T.; Yamabe, S.; Yamamoto, K. *J. Org. Chem.* **1997**, *62*, 2968.
116. Yamazaki, S. *Rev. Heteroatom Chem.* **1999**, *21*, 43.
117. Yamazaki, S.; Inoue, T.; Hamada, T.; Takada, T.; Yamamoto, K. *J. Org. Chem.* **1999**, *64*, 282.
118. Yamazaki, S.; Kataoka, H.; Yamabe, S. *J. Org. Chem.* **1999**, *64*, 2367.
119. Yamazaki, S.; Yanase, Y.; Tanigawa, E.; Yamabe, S.; Tamura, H. *J. Org. Chem.* **1999**, *64*, 9521.
120. Yamazaki, S.; Sakamoto, M.; Suzuri, M.; Doi, M.; Nakazawa, T.; Kobayashi, Y. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1870.
121. Yamazaki, S.; Yamabe, S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 164.
122. Clagett, M.; Gooch, A.; Graham, P.; Holy, N.; Mains, B.; Strunk, J. *J. Org. Chem.* **1976**, *41*, 4033.
123. Payne, G. B. *J. Org. Chem.* **1967**, *32*, 3351.
124. Hubner, J.; Liebscher, J.; Patzel, M. *Tetrahedron* **2002**, *58*, 10485.
125. Yang, Z. J.; Fan, M. J.; Mu, R. Z.; Liu, W. M.; Liang, Y. M. *Tetrahedron* **2005**, *61*, 9140.
126. Bernard, A. M.; Frongia, A.; Piras, P. P.; Secci, F.; Spiga, M. *Org. Lett.* **2005**, *7*, 4565.
127. Jiang, Y. W.; Ma, D. W. *Tetrahedron: Asymmetry* **2002**, *13*, 1033.
128. Zheng, J.-C.; Zhu, C.-Y.; Sun, X.-L.; Tang, Y.; Dai, L.-X. *J. Org. Chem.* **2008**, *73*, 6909.
129. Eberbach, W.; Burchardt, B.; Trostmann, U. *Tetrahedron Lett.* **1979**, 4049.
130. Eberbach, W.; Hadicke, E.; Trostmann, U. *Tetrahedron Lett.* **1981**, *22*, 4953.
131. Eberbach, W.; Trostmann, U. *Tetrahedron Lett.* **1977**, 3569.
132. Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403.
133. Maier, W.; Eberbach, W.; Fritz, H. *Helv. Chim. Acta* **1991**, *74*, 1095.
134. Gupton, J. T.; Krolikowski, D. A.; Yu, R. H.; Riesinger, S. W.; Sikorski, J. A. *J. Org. Chem.* **1990**, *55*, 4735.
135. Gupton, J. T.; Hicks, F. A.; Wilkinson, D. R.; Petrich, S. A.; Sikorski, J. A. *Heterocycles* **1994**, *37*, 487.
136. Gupton, J. T.; Krolikowski, D. A.; Yu, R. H.; Vu, P.; Sikorski, J. A.; Dahl, M. L.; Jones, C. R. *J. Org. Chem.* **1992**, *57*, 5480.
137. Gupton, J. T.; Krumpe, K. E.; Burnham, B. S.; Dwornik, K. A.; Petrich, S. A.; Du, K. X.; Bruce, M. A.; Vu, P.; Vargas, M.; Keertikar, K. M.; Hosein, K. N.; Jones, C. R.; Sikorski, J. A. *Tetrahedron* **1998**, *54*, 5075.
138. Gupton, J. T.; Petrich, S. A.; Hicks, F. A.; Wilkinson, D. R.; Vargas, M.; Hosein, K. N.; Sikorski, J. A. *Heterocycles* **1998**, *47*, 689.
139. Gupton, J. T.; Petrich, S. A.; Smith, L. L.; Bruce, A.; Vu, P.; Du, K. X.; Dueno, E. E.; Jones, C. R.; Sikorski, J. A. *Tetrahedron* **1996**, *52*, 6879.
140. Mayer, T.; Maas, G. *Tetrahedron Lett.* **1992**, *33*, 205.
141. Reinhard, R.; Glaser, M.; Neumann, R.; Maas, G. *J. Org. Chem.* **1997**, *62*, 7744.
142. Reisser, M.; Maas, G. *J. Org. Chem.* **2004**, *69*, 4913.
143. Nyerges, M.; Arany, A.; Fejes, I.; Groundwater, P. W.; Zhang, W. M.; Bendell, D.; Anderson, R. J.; Toke, L. *Tetrahedron* **2002**, *58*, 989.
144. Groundwater, P. W.; Sharif, T.; Arany, A.; Hibbs, D. E.; Hursthouse, M. B.; Nyerges, M. *Tetrahedron Lett.* **1998**, *39*, 1433.
145. Groundwater, P. W.; Sharif, T.; Arany, A.; Hibbs, D. E.; Hursthouse, M. B.; Garnett, I.; Nyerges, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2837.
146. Nyerges, M.; Viranyi, A.; Pinter, A.; Toke, L. *Tetrahedron Lett.* **2003**, *44*, 793.
147. Toth, J.; Dancso, A.; Blasko, G.; Toke, L.; Groundwater, P. W.; Nyerges, M. *Tetrahedron* **2006**, *62*, 5725.
148. Eckert, J. F.; Bourgogne, C.; Nierengarten, J. F. *Chem. Commun.* **2002**, 712.
149. Dave, V.; Warnhoff, E. W. *Organic Reactions*; Wiley: New York, NY, 1970; Vol. 18, p 217.
150. Marchand, A. P.; Brockway, N. M. *Chem. Rev.* **1974**, *74*, 431.
151. Doyle, M. P.; Yan, M.; Hu, W. H.; Gronenberg, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 4692.
152. Loncaric, C.; Wulff, W. D. *Org. Lett.* **2001**, *3*, 3675.
153. Antilla, J. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 5099.
154. Hansen, K. B.; Finney, N. S.; Jacobsen, E. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 676.
155. Rasmussen, K. G.; Jorgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1287.
156. Knudsen, K. R.; Risgaard, T.; Nishiwaki, N.; Gothelf, K. V.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2001**, *123*, 5843.
157. Kel'in, A. V.; Sromek, A. W.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 2074.
158. Lee, S. H.; Yang, J.; Han, T. D. *Tetrahedron Lett.* **2001**, *42*, 3487.
159. Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3558.
160. Rovis, D. A. E. T. In *Prog. Inorg. Chem.*; Karlin, K. D., Ed.; John Wiley and Sons: 2001; Vol. 50, p 1.
161. Kim, H. Y.; Shih, H.-J.; Knabe, W. E.; Oh, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 7420.
162. López-Pérez, A.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 340.
163. Dingwall, J.; Sharp, J. T. *J. Chem. Soc., Chem. Commun.* **1975**, 128.
164. Findlay, R. H.; Sharp, J. T.; Thorogoo, P. B. *J. Chem. Soc., Chem. Commun.* **1970**, 909.
165. Miller, T. K.; Sharp, J. T.; Sood, H. R.; Stefaniuk, E. *Tetrahedron Lett.* **1980**, *21*, 1379.
166. Miller, T. K.; Sharp, J. T.; Sood, H. R.; Stefaniuk, E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 823.
167. Munro, D. P.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1718.
168. Munro, D. P.; Sharp, J. T. *Tetrahedron Lett.* **1980**, *21*, 4109.
169. Munro, D. P.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. 1* **1984**, 849.
170. Reid, A. A.; Sharp, J. T.; Sood, H. R.; Thorogoo, P. B. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2543.
171. Sharp, J. T.; Findlay, R. H.; Thorogood, P. B. *J. Chem. Soc., Perkin Trans. 1* **1975**, 102.
172. Sharp, J. T.; Thorogoo, P. B. *J. Chem. Soc., Chem. Commun.* **1970**, 1197.
173. Stanley, K. L. M.; Dingwall, J.; Sharp, J. T.; Naisby, T. W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1433.
174. Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1976**, *17*, 2069.
175. Garanti, L.; Scandroglio, A.; Zecchi, G. *Tetrahedron Lett.* **1975**, 3349.
176. Garanti, L.; Vigevani, A.; Zecchi, G. *Tetrahedron Lett.* **1976**, 1527.
177. Garanti, L.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2092.
178. Chiodini, L.; Garanti, L.; Zecchi, G. *Synthesis* **1978**, 603.
179. Garanti, L.; Zecchi, G. *J. Heterocycl. Chem.* **1979**, *16*, 377.
180. Padwa, A.; Nahm, S. *J. Org. Chem.* **1979**, *44*, 4746.
181. Garanti, L.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 116.
182. Padwa, A.; Nahm, S. *J. Org. Chem.* **1981**, *46*, 1402.
183. Bruche, L.; Delbuttero, P.; Garanti, L.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2041.
184. Bruche, L.; Garanti, L.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1983**, 539.
185. Alemagna, A.; Garanti, L.; Licandro, E.; Zecchi, G. *Tetrahedron* **1984**, *40*, 2165.
186. Padwa, A.; Smolanoff, J.; Tremper, A. *J. Am. Chem. Soc.* **1975**, *97*, 4682.

Biographical sketch

Olcay Anaç was born in Mersin, Turkey in 1951. She received her M.Sc. and Ph.D. degrees from Istanbul Technical University in 1975 and 1983. Her research interests include new synthetic methodologies based on copper/carbenoid intermediates, synthesis, and reactions of diazo aldehyde compounds, and analysis of essential oils of Turkish plants.

Füsun Şeyma Güngör was born in Ordu, Turkey in 1978. She obtained her undergraduate degree in 1999, master's degree in 2003 (organic chemistry), and Ph.D. degree in 2010 (organic chemistry) from Istanbul Technical University. Her research interests include electrocyclization of β-amino conjugated carbonyl compounds with metallocarbenes.