THERMAL AND PHOTOCHEMICAL 1,3-ELECTROCYCLIC REACTIONS IN THE CHEMISTRY OF THREE-MEMBERED HETEROCYCLIC COMPOUNDS (REVIEW)

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Recent data on thermal and photochemical 1,3-electrocyclic reactions are examined and systematized.

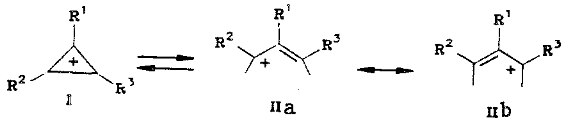
Electrocyclic reactions (ER), together with cycloaddition, sigmatropic shifts, and cheleotropic transformations, are processes, the regioselectivity and stereoselectivity of which can be predicted on the basis of the rules of retention of orbital symmetry [1]. 1,3-Electrocyclic reactions are widespread in the chemistry of three-membered heterocyclic compounds. However, data on these reactions are presented in literature sources that are, as a rule, devoted to other special questions and have not been systematized. Data only up to 1979 have been presented in a monograph [2]; moreover, the most interesting types of ER — photochemical reactions — have not been described. These processes are of particular theoretical interest in connection with the high degree of strain of three-membered rings and are important from a practical point of view.

In the present review we examined data on the synthesis and transformations of three-membered heterocyclic compounds that include at least one 1,3-ER. The material is divided into three parts: ER of derivatives and isoelectronic analogs of the cyclopropyl cation, ER of the anion, and ER of cyclopropene. Particular attention was directed to heterocyclic systems.

The cyclopropyl cations and anions undergo disrotatory and conrotatory opening, respectively [1]. Only one methylene group rotates in the conversion of cyclopropene to vinylcarbene [1, 2]. In heteroaromatic systems, owing to the presence at the heteroatoms of unshared pairs, one of which is located in the plane of the molecule, there is no longer any need for rotation about the carbon—heteroatom bond (see Fig. 1, structures 1b-3b); finally, in the case of 3b rotation about both the C—C bonds and the carbon—heteroatom bonds is absent. Cyclizations that proceed via mechanisms 1b-3b should have lower energy barriers than reactions in purely carbon systems. For these processes we have proposed the term "heteroelectrocyclization."

1. TWO-ELECTRON PROCESSES

The interconversions of cyclopropyl (I) and allyl (II) cations and their heteroanalogs are examples of a two-electron electrocyclic process. The thermal reaction is realized via a disrotatory mechanism [1-6].



R^1, R^2, R^3 = Alk, Ar, Het

Allyl cations are more stable than cyclopropyl cations [2-5].

The introduction of electron-acceptor groups into the 2 and 3 positions of the ring and of electron-donor groups into the 1 position increases the stabilities of I [2, 4, 7]. Isoionic replacement of the carbon atoms by heteroatoms also increases the stability of the ring [8]. The conversion of these compounds to heteroanalogs of the allyl cation is postulated to explain the rearrangements of α-formylmethyl cations to acetyl cations [9-11] and the formation of carbonyl compounds from oxiranyl and aziridinyl halides [12, 13].

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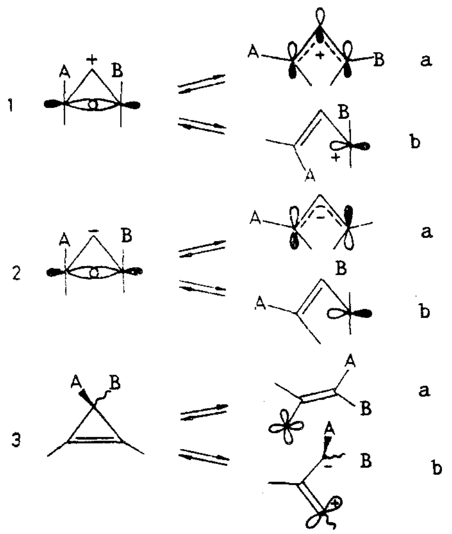


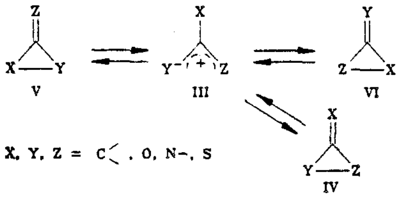
Fig. 1. Possible mechanisms of the cyclization of the cyclopropyl cation (1), the cyclopropyl anion (2), and vinylcarbene (3).

It must be noted that reactions between cations I and II are judged from the structures of the substances formed as a result of subsequent transformations of these compounds.

The introduction of groups with a negative charge into the 1 position of the ring increases the stabilities of both cyclic and ring structures and makes it possible to investigate the transformations of real substances rather than hypothetical particles.

Replacement of the ring carbon atoms by heteroatoms leads to diverse carbo- and heterocyclic compounds — α-lactams, alkylideneaziridines, diaziridineimines, thiiraneimines, etc.

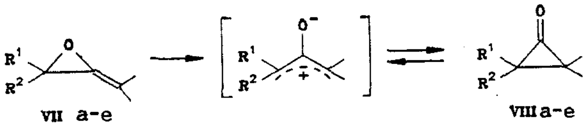
Some zwitter-ionic compounds of the III type have been isolated and characterized [14, 15], and the existence of others has been proved by chemical transformations [14-24].



It is assumed that the cyclization of ions III to IV-VI is realized via a disrotatory mechanism [2-16]. However, in our opinion, a heteroelectrocyclization mechanism in the formation of the carbon—heteroatom bond is more preferred [25].

Transformations in the cyclopropane—hydroxyallyl—allene oxide triad have been investigated in greater detail [15, 24, 26]. Allene oxide VIIa or its monoalkyl derivative VIIb reacts more readily with nucleophiles or undergoes polymerization more readily than isomerization to cyclopropanones VIIIa, b.

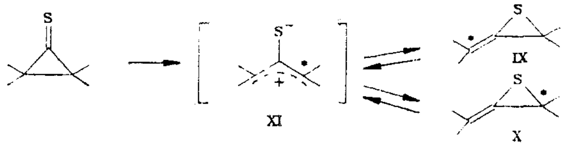
A decrease in the energy barrier to isomerization is observed when bulky tert-butyl substituents are introduced, and allene oxide VIIc is converted to cyclopropanone VIIIc on heating. Aryl-substituted allene oxides VIId, e undergo isomerization to cyclopropanones even at room temperature.



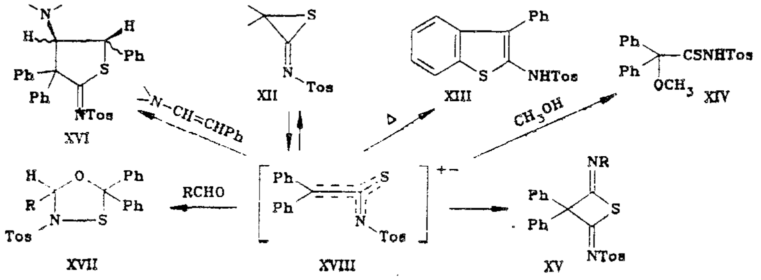
VII, VIII a $R^1=R^2=H$; b $R^1=H$, $R^2=CH_3$; c $R^1=R^2=t\text{-Bu}$; d $R^1=Ar$, $R^2=H$; e $R^1=R^2=Ar$

Replacement of the exocyclic methylene group in allene oxides by an oxygen atom leads to oxiranones, which open up to give ions III much more readily than allene oxides [14, 15, 19, 27].

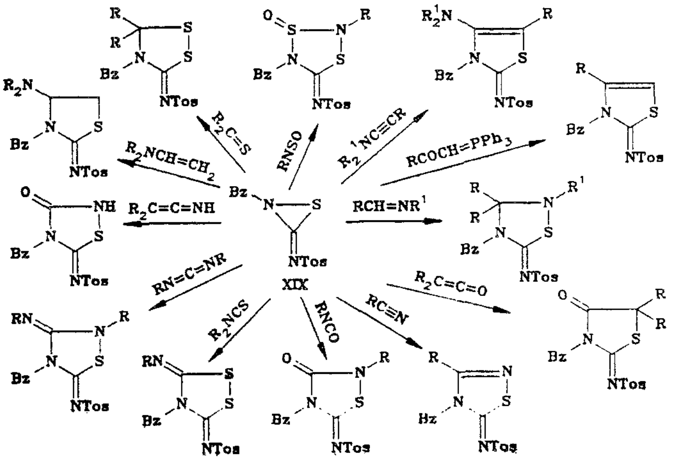
In contrast to oxygen analogs VIIIa-e, cyclopropanethione is extremely unstable and is converted to thiiranylidene (allene sulfide) [16-19, 25], evidently through thioallyl ions XI. This process contradicts the well-known rule for the rearrangements of heterocyclic compounds, according to which the pathway with departure of the endocyclic heteroatom into the side chain predominates [28].



As demonstrated in the case of radioactively labeled compounds, the interconversions of allene sulfides IX and X also proceed through thioallyl ions XI [16]. The first representative of thiiuraneimines XII was synthesized in 1978. Its conversion to benzothiophene XIII on heating and to thioamide XIV on reaction with methanol and its cycloaddition reactions evidently proceed through ion XVIII [14].



Reactions involving opening of the rings of thiiranones, alkylideneaziridines, aziridineimines, diaziridinones, diaziridineimines, and thiaziridineimines are also heteroelectrocyclic reactions [14]. The possibilities of syntheses based on these heterocycles are illustrated by the transformations of thiaziridineimine XIX. In our opinion, electrocyclic opening of the ring is the first step in all of these processes [14, 29].



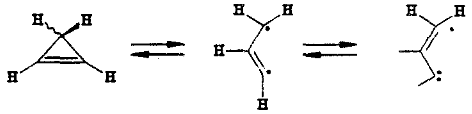
The relative reactivities of heteroanalogs of allyl cations in heterocyclization reactions have not been thoroughly studied, since the principal aim of research on this topic is not so much the investigation of the cyclization of ions III as it is the study of their reactivities with various dipolarophiles.

2. FOUR-ELECTRON PROCESSES

The interconversions of cyclopropene and vinylcarbene, cyclopropyl and allyl anions, and cyclopropylidene and allene, as well as their heteroanalogs, proceed with the participation of four electrons. The latter system (cyclopropylidene and allene) is not examined in our review, since it is not of great significance for the chemistry of heterocyclic compounds.

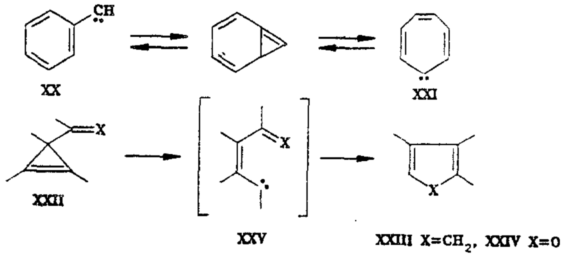
2.1. Interconversions of Cyclopropene and Vinylcarbene, as well as Their Heteroanalogs

The opening of the cyclopropene ring to give vinylcarbene reduces to only rotation of the methylene group, and the terms conrotatory and disrotatory therefore lose their significance for this case.



The cyclopropene ring has a high strain energy; nevertheless, heating above 160°C is required for its thermal rearrangements. The use of catalysts (Ag [30] and Cu [31] salts or trifluoroacetic acid [32]) makes it possible to carry out these reactions at room temperature.

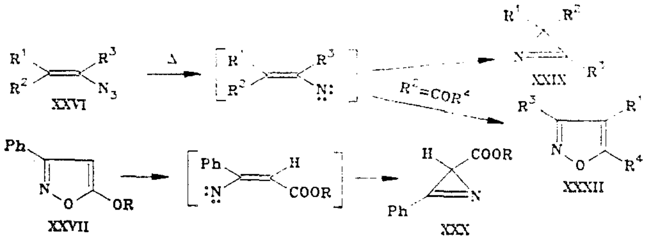
Opening of the cyclopropene ring to give a vinylcarbene is one of the steps in the isomerization of carbenes XX and XXI and carbonyl- and vinylcyclopropenes XXII to give cyclopentadienes XXIII and furans XXIV [33-35], as well as in the cycloaddition of cyclopropenes [35, 36].


XX XXI XXII XXV XXIII $X=CH_2$, XXIV $X=O$

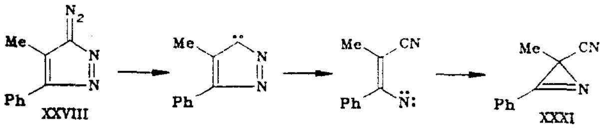
It is not clear whether XXIII and XXIV are formed as a result of a concerted 1,3-sigmatropic shift or via a two-step process through intermediate vinylcarbene XXV.

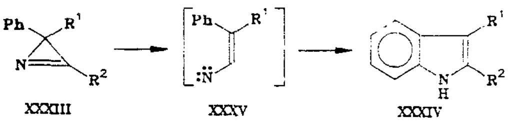
The introduction of heteroatoms into cyclopropene expands the sphere of electrocyclic reactions significantly. The interconversions of azirine and vinylnitrene, diazirine and diazomethane, as well as oxirene and thiirene and the corresponding carbene particles, are reactions of this sort.

One of the steps in the thermal conversion of vinyl azides XXVI [37-42], isoxazoles XXVII [43], and diazopyrazoles XXVIII [44] to the corresponding azirines XXIX, XXX, and XXXI is 1,3-ER of vinylnitrenes. In the case of carbonyl-containing vinyl azides, in addition to 1,3-ER, one observes 1,5-ER, as a result of which isoxazole XXXII is formed [41].



XXVI XXIX XXXII XXVII XXX

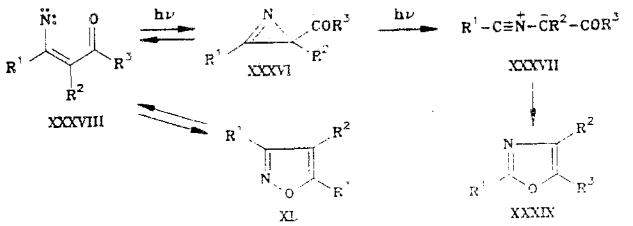

XXVIII XXXI


XXXIII XXXV XXXIV

A retro-1,3-ER is observed in the thermal conversion of azirine XXXIII to indole XXXIV [2]. This reaction resembles the conversion of a cyclopropene to an indene [2].

Reactions involving the cyclization of phenylnitrenes to benzazirines are also used to obtain o-substituted benzenes [45, 46], pyridines [47], azepines [48-51], and benzimidazolones [52]. Data on the conversion of vinylazirines to pyrroles are correlated in [53].

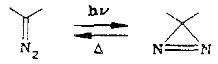
In contrast to thermolysis, the irradiation of azirines with UV light generally leads to the formation of nitrile ylids. It is interesting to note that in the case of azirines XXXVI, depending on the wavelength, one observes cleavage of either the C—C or C—N bonds and the formation of nitrile ylids XXXVII or vinylnitrenes XXXVIII, which undergo cyclization to, respectively, oxazoles XXXIX and isoxazoles XL [54].



XXXVI—XL R^1, R^2, R^3=H, Alk, Ar, COR^4; R^4=Alk, Ph, OAlk, NHPh

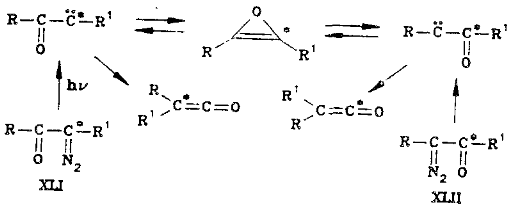
The formation of a nitrile ylid is another type of azirine-nitrile ylid retro-ER. This process is irreversible; the nitrile ylids formed can be intercepted by diverse dipolarophiles [55-59].

A retro-1,3-ER also occurs when diazirines are heated. It is interesting to note that the diazo compounds formed are converted to the starting diazirines on UV irradiation [60].



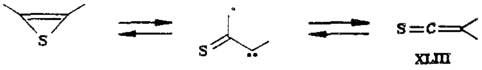
Replacement of the methylene group in cyclopropene by oxygen and sulfur atoms leads to antiaromatic 4π-electron heterocycles — oxirene and thiirene. As a result of a retro-1,3-ER, these compounds are converted to more stable carbene particles.

Interconversions of ketocarbenes to oxirenes occur in the photochemical Wolff rearrangement of α-diazo ketones [61], which confirms experiments with diazo compounds XLI and XLII labeled with ^{13}C [62] and ^{14}C [63] isotopes.



R, R^1= alkyl, aryl

Reversible opening of the thiirene ring occurs in the photolysis of 1,2,3-thiadiazoles [64], in the addition of singlet sulfur to acetylenes [65, 66], and in the isomerization of allyl derivatives of thioketenes XLIII [67].



Attempts to isolate thiirene in the form of a metal complex led only to complexes of isomeric α-thiocarbonylcarbene XLIII. It is assumed that a benzothiirene is an intermediate in the formation of a dithiin from o-bromobenzene thiolates [68].

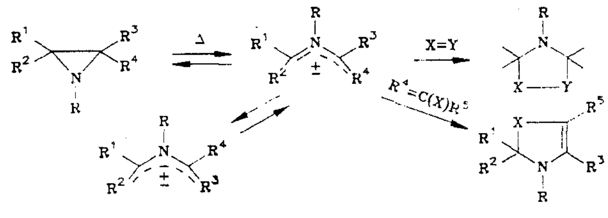
2.2. Interconversions of Cyclopropyl and Allyl Anions

The first example of a four-electron electrocyclic process in which the rotation of two methylene groups occurs is the conversion of the cyclopropyl anion to an allyl anion. Thermal ring opening occurs via a conrotatory mechanism [1, 69]. Isoelectronic replacement of the C atom in the 1 position of the cyclopropyl anion by heteroatoms, on the one hand, substantially expands the sphere of ER and, on the other, gives subjects that are more convenient for the theoretical investigation of 1,3-ER than purely carbon systems.

Heteroanalogs of the cyclopropyl anion can be divided into those that contain one heteroatom — aziridines, oxiranes, and thiiranes — two heteroatoms — diaziridines, oxaridines, dioxiranes, and oxathiiranes — and three heteroatoms — thia- and azadioxiranes.

2.2.1. Systems with One Heteroatom.

The opening of the aziridine ring to give an azomethine ylid and the reverse process are realized via a conrotatory mechanism in conformity with the predictions of the rules of orbital symmetry [1, 70-74]. If the dipolar particle reacts with the dipolarophile more rapidly than it undergoes isomerization, the stereochemistry of the process can be judged from the structures of the products formed. Pyrrolidines, pyrrolines, pyrroles, oxazolines, thiazolines, and other heterocyclic compounds are obtained, depending on the conditions and the dipolarophile used [2, 74-79].

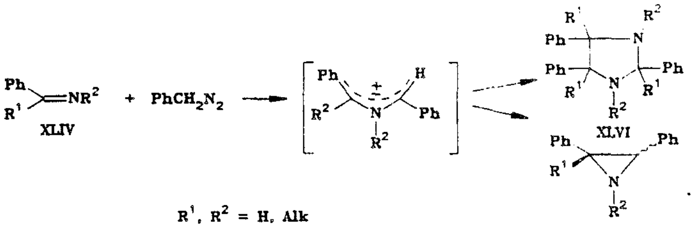


R, R¹, R², R³, R⁴, R⁵=Alk, Ar, Het; X=Y=CH, CH₂, NR, S

The multiple bonds at the terminal carbon atom of an azomethine ylid may act as an internal dipolarophile [79, 81-83]. These reactions are 1,5-dipolar electrocyclizations (DPE) [54].

The presence of a carbonyl group attached to the carbon atom of the aziridine ring promotes cleavage of the C—C bond, while the presence of electron-donor alkylthio and alkoxy groups promotes cleavage of the C—N bond [80]. Competition between 1,5-DPE and intermolecular cycloaddition arises when carbonyl and vinyl derivatives of aziridines are heated in the presence of a dipolarophile [79, 81]. Opening of aziridines to give azomethine ylids and 1,5-DPE of carbonyl azomethine ylids (X = 0) lie at the foundation of the rearrangement of isoxazolines to oxazolines [84].

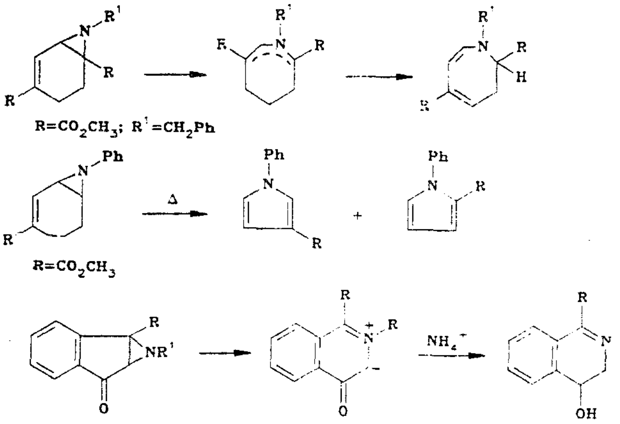
Azomethine ylids that are formed as a result of the reaction of phenyldiazomethane and imine XLIV are converted to mixtures of aziridines XLV and imidazolines XLVI [85]. In this case competition between 1,3-ER and [2 + 3]-cycloaddition is observed.



XLIV XLVI XLV

R¹, R² = H, Alk

In the absence of dipolarophiles the cis isomer of diethyl N-arylaziridine-2,3-dicarboxylate undergoes isomerization to the trans isomer on heating to 100°C [86]. Examples of the formation of azomethine ylids from bicyclic aziridines, the disrotatory opening of which is predetermined by the geometry, have been described [2, 87]. In addition to their theoretical interest, these reactions have great significance as a method for the synthesis of nitrogen-containing heterocycles with expansion of the aziridine ring [2, 87].



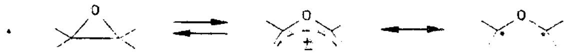
R=CO₂CH₃; R'=CH₂Ph

R=CO₂CH₃

R=H, CH₂Ph

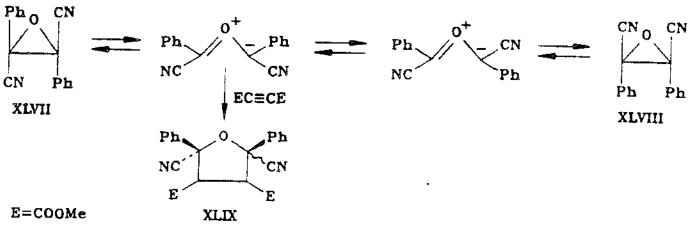
The next isoelectronic analog of the cyclopropyl anion is oxirane. According to the rules of retention of orbital symmetry, its conversion to a carbonyl ylid under the conditions of photochemical experiments should proceed via a disrotatory mechanism, while the thermally induced process should take place via a conrotatory mechanism [1].

It has been shown by quantum-chemical calculations using both semiempirical [88] and ab initio [89-91] methods that the high-lying filled and low-lying vacant molecular orbitals of



the carbonyl ylid have close energies and are localized on the heavy atoms, while the molecule has a considerable degree of biradical character (38% [9] and 55% [93]). The energies required to cleave the C—C and C—O bonds of oxirane are close — 213 and 226 kJ/mole [89]. The introduction of both electron-donor and electron-acceptor substituents stabilizes carbonyl ylids and promotes their formation from oxiranes [89]. The greatest effect was obtained in the so-called push—pull systems, in which electron-donor and electron-acceptor substituents are found at different ends of the carbonyl ylid.

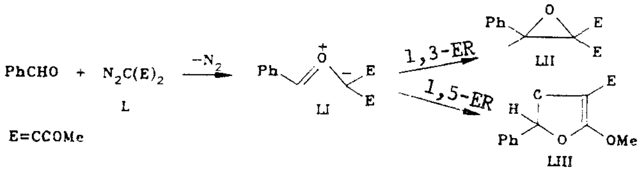
The conrotatory opening of oxiranes to give carbonyl ylids under the conditions of thermal experiments is in agreement with the faster isomerization of trans-2-phenyl-3-(p-tolyl)-oxirane as compared with the cis isomer [2, 93]. However, it was shown in a series of experiments that the agreement between theory and experiment may be disrupted by the introduction of certain substituents [2, 94, 95]. Thus, for example, trans- and cis-2,3,-dicyano-2,3-diphenyloxirane (XLVII and XLVIII) react with dimethyl acetylenedicarboxylate to give the same cycloadduct XLIX.



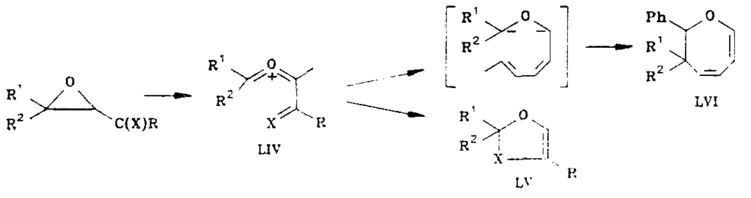
According to the Huisgen hypothesis, disrotatory opening of the oxirane ring occurs along with conrotatory opening. Quantum-chemical calculations, however, explain these "violations" by means of facile isomerization of the carbonyl ylid that occurs during rotation about the simple C—O bond [90, 96].

In the case of bicyclic oxiranes disrotatory opening of the ring is predetermined by the geometry [2, 82, 97, 98].

Ylid LI formed in the reaction of diazomalonic ester L with benzaldehyde undergoes cyclization via two pathways to give oxirane LII and 1,3-dioxolane LIII [99, 100].



When oxiranes that have a vinyl or carbonyl group are heated, the resulting ylids LIV undergo disrotatory closing to give five-membered heterocycles LV [92, 101-106].



X=CHAlk, =CH—CH=CHPh, O; R, R^1, R^2=H, Ph

If the starting compound contains a butadienyl substituent, a product of eight-electron cyclization — oxepine LVI — is formed along with vinylfuran LV [105, 106]. The conversion of vinylspirooxiranes to condensed dihydrofurans is a variant of these syntheses [107].

In contrast to the thermal opening of oxiranes, the photochemical opening of oxiranes to give carbonyl ylids proceeds via a disrotatory mechanism [108-117]. Competition between cleavage of the C—C and C—O bonds is observed in the thermal and photochemical transformations of oxiranes. In the case of condensed oxiranes cleavage of the C—O bond predominates in the thermal process, whereas opening of the C—C bond predominates in photolysis [97, 118].

Reactions involving opening of the ring of the oxirane cation radical that are exothermic and require a low energy of activation have been described [119-124].

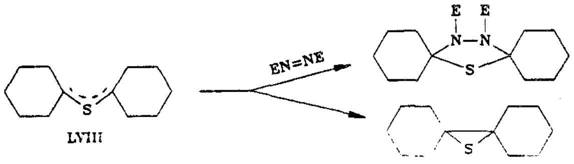
As in the case of oxiranes, reversible opening to give thiocarbonyl ylids (TCI) might be expected for thiiranes.

Electron-acceptor substituents should stabilize the open structure. However, there is no rigorous evidence for opening of the thiirane ring to give TCI, despite the existence of stable TCI [125, 126]. It has been shown that the cyclization of TCI proceeds via a conrotatory mechanism and that stereoselectivity is retained even in the case of considerable steric hindrance [2].

Thiocarbonyl ylids can be generated by the decomposition of thiadiazolines [2, 125, 127-131, the flash-vacuum pyrolysis of thiaoxolanes [125, 126, 132, 133], and the dehydrohalogenation or deprotonation of sulfides that contain active methylene protons [125], as well as, like other 1,3-dipolar particles, by electrocyclic closing of divinyl sulfide LVII [125].

LVII

Thiocarbonyl ylids have high chemical activities and undergo the most diverse reactions — they give cycloadducts with various dipolarophiles [2, 125, 127, 134-139], oxathioles [140] or thiazolines [141] as a result of 1,5-DPE, 1,3-dithietanes and 1,4-dithianes [140] on dimerization, and thioketones on reaction with acids [140]. As a rule, these processes are competitive. It has been shown by kinetic investigations that the cycloaddition of TCI LVIII in the presence of excess dimethyl azocarboxylate is faster by a factor of 35 than cyclization to a thiirane [2].



LVIII

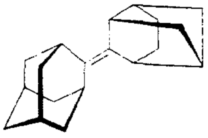
A mixture of products is usually formed as a result of the reactions. An increase in the reaction temperature, a decrease in the concentration of the dipolarophile, and the introduction of bulky substituents at both ends of the TCI lead to domination of the electrocyclic process. Thus, for example, ylids LIX are converted exclusively to thiiranes [127].

LIX

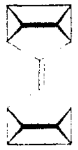
R^1, R^2, R^3, R^4 = H, *t*-Bu, Ph

Dimerization to 1,4-dithianes predominates for TCI that contain an unsubstituted methylene group [127].

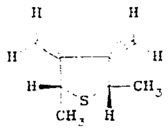
The thiiranes formed as a result of cyclization of TCI are readily converted to olefins under the influence of "thiophiles" [2, 125, 142-144]. Alkenes LX-LXII and biradical LXIII were obtained by this method.



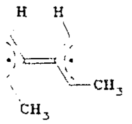
LX



LXI



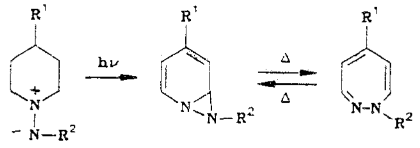
LXII



LXIII

2.2.2. Systems with Two Heteroatoms. Less study has been devoted to the electrocyclic reactions of azomethine imines and diaziridines [145-150]. The cyclization of azomethine imines LXIV to diaziridines LXV is the first step in an original method for obtaining 1,2-diazepines LXVI [148-150].

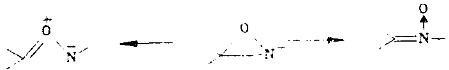
The ER of carbonyl oxides and dioxiranes [151-156], as well as thiocarbonyl oxides and thioxiranes [157-158], were recently described; investigations of these substances are hindered by the low stabilities of dioxiranes and thioxiranes.



LXIV LXV LXVI

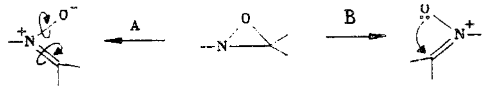
LXIV—LXVI R^1=H, CH_3; R^2=CO_2Et, Tos

Two types of ER that are accompanied by cleavage of the C=O or C=N bonds and the formation of nitrones LXVII or carbonyl imines LXVIII are realized for oxaziridine.



LXVIII LXVII

Both conrotatory opening and disrotatory opening of an oxaziridine to a nitrone are allowed [159]. One should note the special mechanism of the cyclization (or opening) of nitrones to give oxaziridines: a new σ bond is formed due to the unshared pair of the oxygen atom located in the plane of the molecule [160] (mechanism B), and rotation about the N–O bond does not occur — a heteroelectrocyclic mechanism is realized.



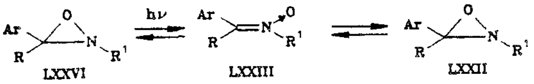
The formation of a nitrone from an oxaziridine is facilitated by the introduction of aryl substituents at the C atom [161, 162]. Oxaziridines with aryl substituents in the 2 and 3 substituents are less stable than the 2-alkyl derivatives [163]. Replacement of the phenyl groups by pentafluorophenyl groups leads to an increase in the stability of the oxaziridine ring. According to kinetic investigations a previous transition state is characteristic for the isomerization of oxaziridines to nitrones [164].

The interconversions of oxaziridines and nitrones are initiated both thermally and photochemically [2, 165-170].

LXIX LXX

A= adamantyl

In photochemical experiments the reaction pathway depends on the wavelength of the irradiating light [170]. The isomerization of cis- and trans-nitrones proceeds through oxaziridines, and, on the other hand, the photoisomerization of cis- and trans-oxaziridines LXXI and LXXII proceeds through the formation of intermediate nitrone LXXIII [2, 170].



LXXVI LXXIII LXXII

R=H, Me, Ar; R^2=Me, Pr-*i*; Bu-*i*

The photoisomerization of nitrones in chiral solvents [(+)–(S)–, (–)–(R)–2,2,2-trifluoro-1-phenylethanol] has been used for the asymmetric synthesis of oxaziridines. It was shown that the optical yield increases when there is a bulky substituent attached to the nitrogen atom and when the temperature of the reaction is decreased. Optically active oxaziridines have also been obtained from chiral nitrones when the reaction was carried out in achiral solvents [169].

2.2.3. Systems with Three Heteroatoms. Electrocyclic reactions (ER) for three-membered heterocycles with three heteroatoms remain virtually uninvestigated. They are postulated to explain the formation of oxaziridines from azoxy compounds [2], sulfones from persulfoxides [171-173], and nitro compounds from nitroso oxides [174].

Despite the large number of publications devoted to 1,3-ER, there are a number of unresolved questions in this area. Thus virtually no study has been devoted to the mechanisms of the cyclization of heteroatomic systems and the rearrangements of three-membered heterocycles, and the deviations from the predictions of the rules of the retention of orbital symmetry in reactions involving opening of the rings of oxirane and aziridine derivatives are not completely understood. The solution of these problems will lead to a deeper understanding of the scope and synthetic possibilities of ER.

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