1,4-ELECTROCYCLIC REACTIONS IN THE CHEMISTRY OF FOUR-MEMBERED CARBOCYCLIC AND HETEROCYCLIC COMPOUNDS (REVIEW)

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The electrocyclic reactions of four-atom compounds are examined. The diversity of the mechanisms of cyclizations and the synthetic utilization of 1,4-electrocyclizations of derivatives and heteroanalogs of butadiene is demonstrated. Special attention was directed to the transformation of the heterocyclic compounds.

1,4-Electrocyclic reactions include processes involving four-atom systems and proceed with the participation of 4π electrons. Like other pericyclic processes, they are characterized by a high degree of stereoselectivity and for this reason they have found extensive application in organic synthesis to obtain diverse cyclic compounds. These reactions are of special value in the chemistry of heterocycles. On the one hand, theoretical studies in this area have shed light on the principles involved in the occurrence of diverse rearrangements of heterocyclic reaction; on the other hand, the heterocycles themselves are unique models for the realization of previously unknown mechanisms of organic reactions. A voluminous amount of literature, including reviews [1, 2] and a monograph [3], has been devoted to 1,4-electrocyclic reactions. However, the reviews have been devoted to limited problems, and the monograph includes data up to 1980. Moreover, new enormous advances have been published in the last decade in this field. Thus, as a result of a set of experimental and theoretical studies, the reasons that determine the selectivity of one of the pathways of the rotation of methylene groups in the realization of a conrotatory process in the thermal opening of the ring of cyclobutenes have been discovered, a new term that characterizes this process — *torquoselectivity* — has been coined, a deviation from the predicted (by the rules) retention of the orbital symmetry of the pathway of the photochemical opening of cyclobutenes has been observed, *ab initio* calculations of the highest level for processes involving opening of cyclobutenes and their heteroanalogs have been published and have shown that the true transition state corresponds to both conrotatory and forbidden disrotatory pathways, and the possibility of the realization of a special mechanism of cyclization of heteroanalogs of butadiene in which a new σ bond is formed not through the π system but rather via the unshared electron pair of heteroatoms, and so forth. There is no doubt whatsoever that the great achievement in this regard is the synthesis of Dewar silabenzene, accomplished at 10 K.

The present review is a continuation of research previously undertaken [4] dealing with the most recent advances in this field and includes data on 1,4-electrocyclic reactions, essentially in the last 10 years.

1. STEREOCHEMICAL FEATURES OF THE INTERCONVERSIONS OF CYCLOBUTENE AND BUTADIENE DERIVATIVES

In accordance with the rules of retention of orbital symmetry [5], the thermal opening of cyclobutene rings to give butadienes is realized via a conrotatory process. The energy of activation of this process is 32.5 kcal/mole; this, for example, according to various estimates, is 7-15 kcal/mole lower than for the disrotatory variation of this reaction [3]. The disrotatory process is allowed for the corresponding photochemical processes [5].

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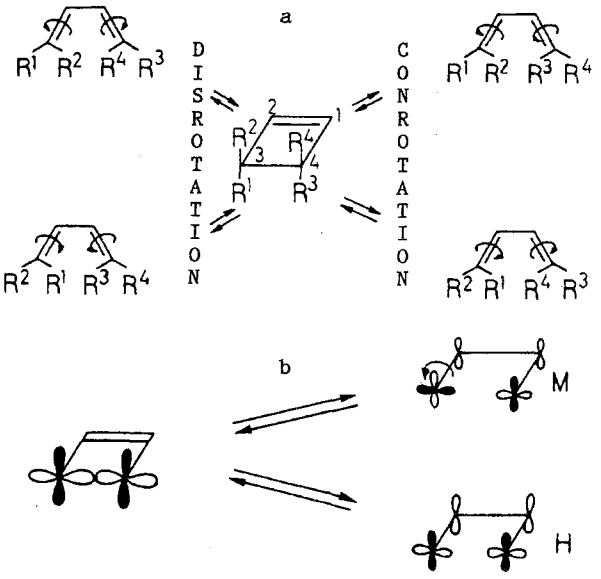


Fig. 1. Stereochemistry of the interconversions of cyclobutenes and butadienes (a) and their heteroanalogs (b).

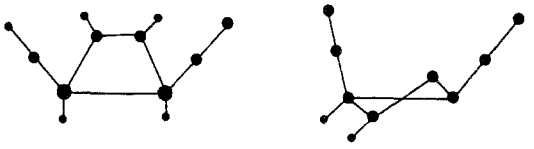


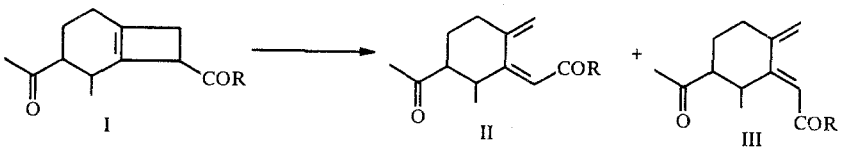
Fig. 2. Structures of the transition states for disrotatory (a) and conrotatory (b) opening of the *cis*-3,4-dicyanocyclobutene ring.

2. THERMAL REACTIONS

2.1. Allowed Processes

In connection with the predictions of the rules of retention of orbital symmetry [5] and quantum-chemical calculations [6] the thermolysis of cyclobutene derivatives leads to products of conrotatory ring opening. The selectivity of the process there, on the whole, is determined by the selectivity of the pathway of the rotation of the methylene groups, which, in its turn, depends on the volume of the substituents in the ring 3 and 4 positions [3].

In [7] it was shown that exclusively Z isomer II is formed when I, which contain a formyl group, are heated. Replacement of the formyl group by a bulkier group — an ethoxycarbonyl group — leads to a mixture of Z and E isomers II and III.

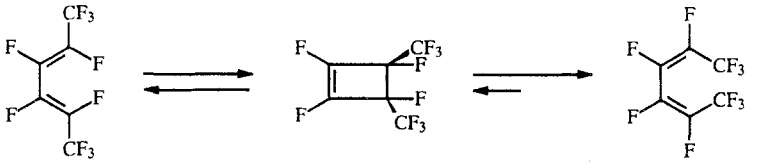


a R = H, b R = Et

It remains unclear why the bulkier (than the hydrogen atom) formyl group rotates inwardly in the conversion of cyclobutene Ia to give butadiene IIa.

Curry and Stevens have shown that rotation of the less bulky methyl group outwardly also predominates in the thermolysis of 3-ethyl-3-methylcyclobutene [8].

In an investigation of the thermal opening of the ring of polyfluorinated cyclobutenes IV Dolbier and Koroniak showed that the formation of product V with a rotated fluorine atom outwardly and a CF_3 group inwardly is preferable kinetically by 21.5 kcal/mole to the formation of diene VI [12].

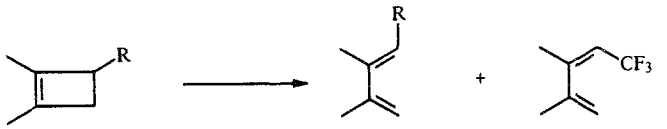


VI IV V

A thorough investigation of the opening of the rings of 3-fluoro- (VIIa), 3,3-difluoro- (VIIb), and 3-trifluoromethylcyclobutene (VIII) showed that individual dienes IX are formed in the reactions of VII, while opening of cyclobutene VIIIa leads to a mixture of E- and Z-isomeric dienes Xa and XIa [10].

VII IX

a R = H, b R = F



VIII X XI

a R = CF_3, b R = F

The rotation of the fluorine atom inwardly proceeds with an energy of activation that is 10.2 kcal/mole greater, while rotation outwardly proceeds with an energy of activation that is 3.6 kcal/mole lower than for unsubstituted cyclobutene [10].

It is interesting to compare the data on the opening of the rings of VIIIa and VIIIb. In the latter case individual E-diene Xb is formed. Since the trifluoromethyl group is bulkier than the methyl group, the fact of the formation of Z-diene XIa, although in smaller amounts, constitutes evidence that the electronic properties of the substituents affect ring opening of cyclobutenes.

As a result of kinetic studies, it was demonstrated [11, 12] that the preferableness of rotation of a substituent outwardly in the case of opening of 3-R-cyclobutenes varies in the order OR > F > Cl > Me. As Moore and coworkers have noted [1], the observed tendency with regards to the preferableness of rotation of electronic groups outwardly that is characteristic for opening of cyclobutenes is also observed in the opening of cyclobutenones: the percentage of the isomer with a substituent rotated outwardly increases as the volume and π-electron-donor properties of the substituents increase.

In 1987 Houk introduced the new term *torquoselectivity* (selectivity of the rotation pathway), which symbolizes the primary occurrence of a reaction via one of the two possible conrotatory (for thermal opening of the cyclobutene ring) pathways [13-15].

It is evident that one may also speak of the selectivity of the rotation pathway in the case of the realization of two disrotatory pathways.

Whereas the effect of the bulk of the substituent on the ratio of the various forms of conrotation is quite simply explained — the developing steric hindrance promotes that pathway which leads to the rotation of the substituent outwardly — the effect of electronic factors was not immediately comprehensible.

TABLE 1. Energies of Activation of Opening of the Rings of XXIV

Side-ring size	Configuration	E, kcal/mole	Type of opening
6	cis	41,6	Dis.
6	trans	29,6	Con.
7	cis	45,0	Dis.
7	trans	27,2	Con.

As a result of the theoretical analysis performed and thorough quantum-chemical calculations [13, 14], it was shown that the preferableness of rotation of the electronic substituents attached to the C_3 and C_4 atoms outwardly is caused by the increased (in the process) stabilizing two-electron interaction in the substituent with the C_3C_4 σ orbital and the decrease in the four-electron interaction between this donor and the C_3C_4 σ^* orbital. The same factors promote rotation of the electron-acceptor substituent inwardly.

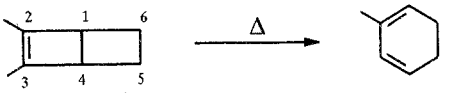
A significantly smaller amount of research has been devoted to studies of the direct cyclization of butadienes [12, 16-18]. This is evidently explained by the fact that the reverse reaction (opening of the cyclobutene rings) is energically more favorable, with several exceptions. Data on the energies of activation of the conrotatory opening of the ring of cyclobutenes were presented in [8-10, 12, 18-20], while data on the energies of activation in related instances for the cyclization of butadienes were presented in [8, 9, 11, 12].

2.2. Forbidden Processes

The conrotatory pathway of opening of the cyclobutene ring, which is allowed by the symmetry rules [5], is unfavorable because of the steric factors for bicyclic cyclobutenes of the *cis* [n.2.0] type. The transformations of these compounds therefore have a number of idiosyncrasies as compared with monocyclic cyclobutenes. With several exceptions, three principal mechanisms can be envisioned: 1) conrotatory opening to give an unstable product with its rapid conversion to a stable product with *cis,cis*-double bonds; 2) forbidden, disrotatory, concerted ring opening to give a *cis,cis*-diene; 3) a stepwise process through a biradical intermediate stabilized by allyl resonance.

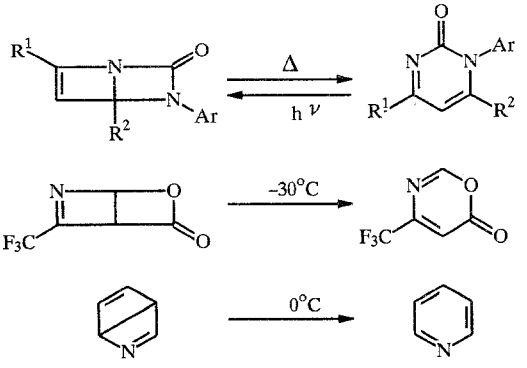
As demonstrated in Marvell's monograph [3], the realization of these mechanisms depends on *n*. Kinetic [21, 22] and thermal [23] data and the results of calculations carried out by the MINDO/3 method [24] provide evidence for the realization, for the opening of bicyclo[2.1.0]pent-2-enes, of a radical pathway rather than a forbidden disrotatory pathway.

The literature contains numerous examples of electrocyclic reactions involving opening of the ring of bicyclo[2.2.0]hex-2-enes XX, and thorough kinetic studies have been made only for several representatives of this series [3].



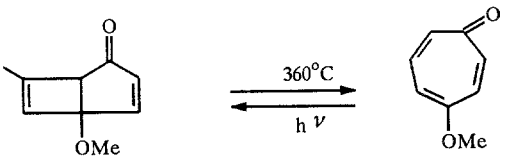
XII XIII

It was found that replacement of the methylene groups in the 5 and 6 positions carbon—carbon double bonds [25] and the introduction of a diethylamino group at the bridge carbon atom significantly accelerate ring opening. The introduction of heteroatoms into various positions of XII expands the range of application of this reaction. It was shown that the opening of such heterocyclic compounds is accomplished readily and proceeds under mild conditions [3, 26].



Kinetic studies of the transformations of Dewar benzene to benzene and a comparison with the data for bicyclo[2.2.0]hexenes [26] made it possible to conclude that the introduction of a double bond into bicyclohexene molecules significantly increases the rate of ring opening. It was also established that the introduction of substituents with electron-acceptor properties at the bridge carbon atom of Dewar benzene and the simultaneous introduction of acceptor and donor substituents at the bridge carbon atoms lead to a decrease in the energies of activation of their isomerization to benzene derivatives [3, 27-29].

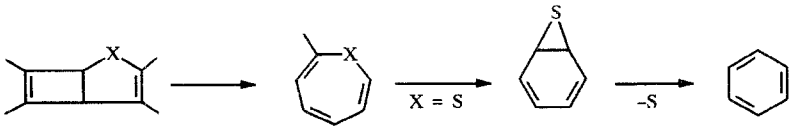
The thermal opening of the ring of bicyclo[3.2.0]hept-6-ene XIV was observed by Chapman and Pasto in 1960 [30]. It is interesting to note that the reverse process occurs when XV are irradiated with UV light [3].



XIV XV

Criegee and coworkers [31] demonstrated that the introduction of a benzene ring and a carbonyl group at the bridge positions and the placement of a double bond in the five-membered ring increase the rate of ring opening. The most pronounced effect is observed in the case of the simultaneous introduction of electron-donor and electron-acceptor substituents [32].

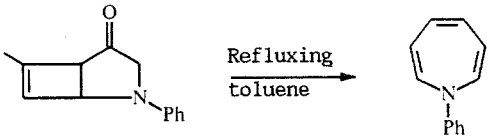
An unusually marked effect is observed when various heteroatoms are introduced into five-membered ring [3, 33-36].



XVI XVII

X = O, S, NH, NAlk

Thus the energy of activation for opening of the cyclobutene ring for XVIII is only 72.4 kJ/mole [36].

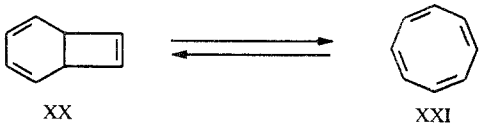


XVIII XIX

It has been noted that the use of metal salts leads to a significant lowering of the temperature of this reaction [37, 38]; this is apparently associated with elimination of the forbiddance for a disrotatory pathway of opening of the cyclobutene ring [5].

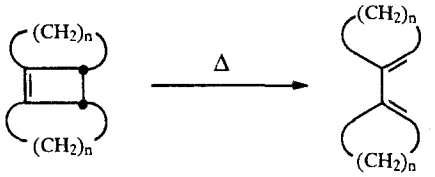
In the thermal opening of 7-bicyclo[4.2.0]octenes steric interactions in the formation of the *cis,trans*-cyclooctadiene are not as strong as in the case of smaller rings, and the permitted conrotatory pathway is therefore sometimes realized [3, 39, 40].

It has been shown that both the opening of cyclobutenes XX and the cyclization of the resulting octatetraenes XXI are realized via a disrotatory pathway. This reaction can be interpreted as opening of the cyclobutene and cyclohexadiene rings, for which the disrotatory pathway is permitted [5].



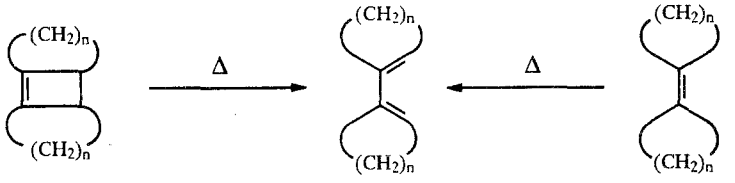
XX XXI

It has been noted that conrotatory ring opening is inhibited in the thermal opening of cyclobutenes XXII if both rings contain less than eight atoms [3].



XXII XXIII

In terms of a comparison of the rates of disrotatory and conrotatory ring opening, the data obtained by Criegee and Reinhardt [41] in a study of the reactions of XXIV-XXVI are interesting.



XXIV XXV XXVI

It is apparent from Table 1 that the conrotatory process proceeds with a lower energy of activation.

Theoretical studies to ascertain the reasons for the different effects of electronic factors of the substituents on the rates of the conrotatory and disrotatory opening of the cyclobutene ring have been undertaken [42, 43].

Houk and coworkers, on the basis of calculations of the transition states of conrotatory and disrotatory processes carried out using the restricted and unrestricted Hartree—Fock method in the 3-21-G basis set, have shown that the observed experimental data are explained by the idiosyncrasies of the structures of the transition states of the disrotatory and conrotatory processes (Fig. 2) [43]. They demonstrated that more pronounced overlapping of the components of the atomic orbitals of the substituents and the ring is realized in the disrotatory pathway, in which the distortion of the carbon skeleton is smaller than in the case of the conrotatory process. The more pronounced effect of electron-acceptor substituents on the disrotatory process is explained by the fact that they appreciably decrease the energy of the highest occupied molecular orbital (HOMO), which is situated higher in the transition state for the disrotatory process than for the conrotatory process.

It is interesting to note that Houk and coworkers were able for the first time to localize the true transition state for the disrotatory opening of cyclobutenes in the case of 3,4-dicyanocyclobutene [43].

2.3. Photochemical Transformations of Cyclobutene and Butadiene

Just as in the reverse process, reactions involving opening of cyclobutenes under the influence of UV light, in accordance with the rules of retention of orbital symmetry [5], semi-empirical data [45], and *ab initio* calculations [46], should be realized via a disrotatory process. However, the results of the calculations provide evidence that the process itself is more complex than simple disrotatory ring opening and includes transition from the ground state to the first excited state ($S_0 \rightarrow -S_1$), followed by a nonadiabatic transition to the potential-energy surface of the second excited state (S_2) and, finally, nonadiabatic transition to the ground state, which corresponds to a disrotatory pathway [44-46].

It should be noted that the overwhelming number of experimental studies involve the photochemical investigation of the opening of bicyclic compounds of the *cis*[n.0.2] type, the disrotatory mechanism of which is predetermined by the geometry [9, 47-51]. There are numerous examples of the photocyclization of dienes that enter into the composition of heterocycles [52-54]. It is interesting to note that the pathways of the first two reaction depend on the wavelength of the irradiating light; irradi-

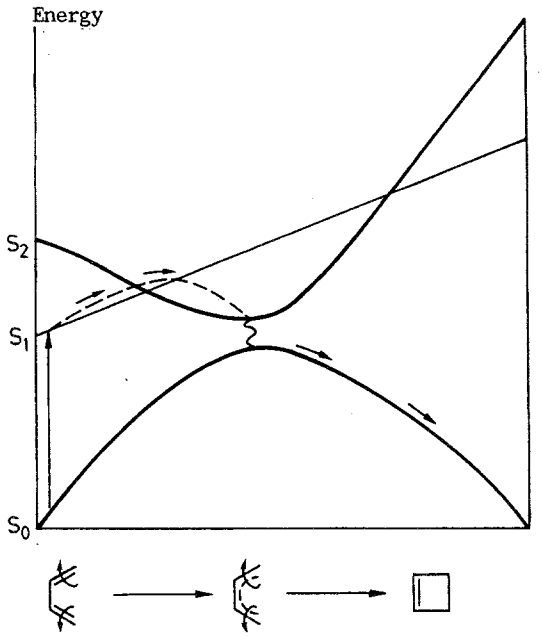
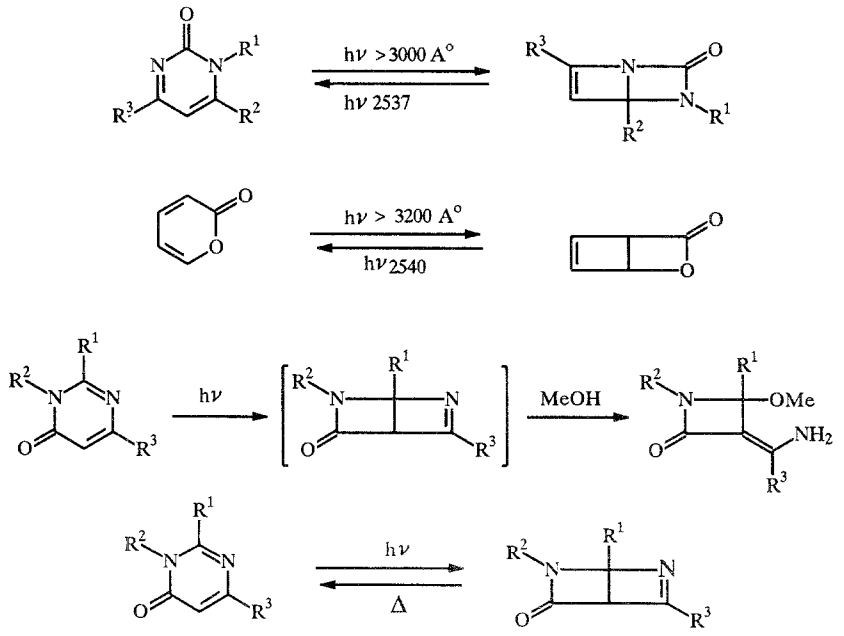


Fig. 3. Mechanism of the photocyclization of butadiene to give cyclobutene.

ation with longer-wave light leads to cyclization of the heterodiene, while shorter-wave light leads to opening of the bicyclic product.



A review [55] and a monograph [56] have been devoted to this topic. All of the data presented constitute an experimental confirmation of the theoretical conclusions. Moreover, experiments carried out on monocyclic cyclobutenes [57] and bicyclic unstrained molecules [58] using irradiating light with λ 180-200 nm have shown partial deviation from predictions made in accordance with the rules of retention of orbital symmetry. The literature data on the photochemistry of monocyclic cyclobutenes are correlated in [57], and an explanation of the reasons for the realization of a forbidden mechanism is given.

As pointed out by Kikuchi [59, 60] the participation of the unshared electron pair of the heteroatoms is possible in the photocyclization of 1-heterobutadienes. The closeness of energy surface of the electrocyclic reaction of cyclobutene of the first

excited state to the energy surface of the disrotatory pathway in the ground state, which is forbidden by the rules of retention of orbital symmetry, is noted [57, 58].

3. THERMAL REACTIONS OF HETEROANALOGS OF BUTADIENE AND CYCLOBUTENE

The interconversions of heteroanalogs of butadiene and cyclobutene are of interest in a theoretical respect. The introduction of heteroatoms markedly "perturbs" the molecular orbitals and disrupts their symmetry. The existence of vacant orbitals and unshared electron pairs leads to the possibility that the reaction will proceed via mechanisms that differ from electrocyclic mechanisms in accordance with the definition of the classics [5]. Moreover, Neiman has shown that the behavior of 2-aza analogs of butadiene in electrocyclic reactions does not differ in any respect from the cyclization of butadiene [61]; the thermal reaction is realized via a conrotatory pathway, while the photochemical process is realized via a disrotatory pathway, and the introduction of heteroatoms, although it does alter, does not disrupt the symmetry of the orbitals. Snyder has shown that, in contrast to 2-aza analogs, the behavior of 1-heterobutadienes has a number of idiosyncrasies [62]. Thus the conrotatory pathway of the cyclization of 1-azabutadiene includes correlation of the π_a and $\sigma_{C\text{-}C}$ orbitals, while the disrotatory pathway includes correlation of the π_a and $\pi_{C\text{-}C}$ orbitals. The same is valid for 1-oxa and 1-thia analogs. For these systems, just as for butadiene, the conrotatory cyclization pathway is permitted, while the disrotatory cyclization pathway is forbidden. When the methylene system is replaced by an onium center (O^+, S^+, RN^+), we obtain systems for which, as a consequence of disruption of the symmetry, both mechanisms are permitted (Table 2). Snyder explains the idiosyncrasies of the systems in an examination of the shift of the node in the HOMO during conversion of the reactants to the reaction products [62].

The introduction into the terminal positions of two heteroatoms leads to systems for which the cyclization process is forbidden in the ground state via both disrotatory and conrotatory pathways, since the ground electron state of the diene correlates with the doubly excited electron state of the cyclic product [63] (Fig. 4).

Just as from 6π-electron systems, from the heteroanalogs of cyclobutene that contain two heteroatoms in the ring 3 and 4 positions one might have expected the manifestation of aromatic properties, particularly increased stability. However, in [64] it was shown that these compounds are not aromatic because of the antibonding character of the HOMO between the heteroatoms and the pronounced difference in the electronegativities of the carbon atoms and the heteroatoms.

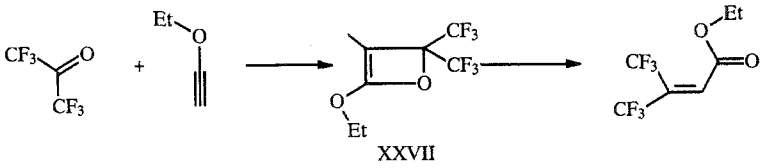
Kikuchi points out the idiosyncrasies of processes involving the photochemical cyclization of heteroatomic conjugated compounds [60]. Nguen and coworkers have shown that the cyclization of imidoyl- and formylketenes, in contrast to the vinyl derivatives, is realized without rotation relative to the terminal bonds and that a new σ bond is formed through the unshared electron pair rather than through the π system [65]. To reflect the specific characteristics of cyclizations of this sort we have proposed the term "heteroelectrocyclic reactions" [4]. In order to consider this reaction to be an electrocyclic process one must significantly expand the classic definition of an electrocyclic reaction as compared with its classics [5].

It has been demonstrated by both semiempirical methods [66] and *ab initio* calculations [3], including the highest level [67], that introduction of heteroatoms into the 2 position leads to a significant decrease in the energy required to open the ring.

All of the subsequent material on the reactions of heteroanalogs of cyclobutene is set forth in two subdivisions. In the first subdivision we present data on compounds that contain one heteroatom, while in the second we present data on compounds that contain two or more heteroatoms.

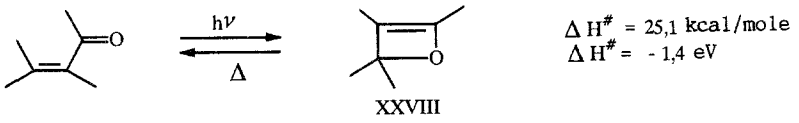
3.1. Electrocyclic Reactions of Systems with One Heteroatom

The first representative of heteroanalogs of cyclobutene is oxytene XXVII, which was isolated and identified in the cycloaddition of ethoxyacetylene to hexafluoroacetone [68].



XXVII

The oxytene ring opens when the compound is heated. Friedrich and Schuster [69] isolated a compound and conducted kinetic studies of the opening of the ring of 1,2,3,3-tetramethyloxytene XXVIII. They showed that this reaction proceeds 10 times faster than opening of *cis*-1,2,3,4-tetramethylcyclobutene [3, 69].



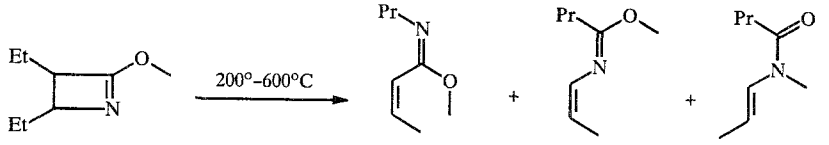
XXVIII

Calculations *ab initio* of the highest level [67] made it possible to estimate the energy of activation of the opening of the oxytene as being 26 kcal/mole, which is in good agreement with the experimental data [69].

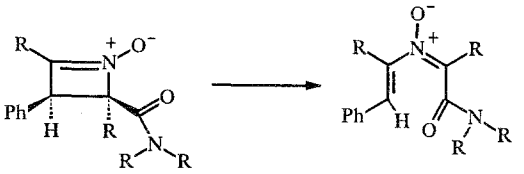
There are two isomeric azacyclobutanes — 1-azacyclobut-1-ene (1-azetine) and 1-azacyclobut-2-ene (2-azetine). Both rings can undergo ring opening [3].

Calculations by the 1CNDO/2 and 1HMO methods predict that the opening of 1-azetine, like that of cyclobutene itself, should occur via a conrotatory pathway in the ground state and via a disrotatory pathway in the first excited state [62].

Simple 1-azetines are surprisingly stable substances. The introduction of an ethoxy group leads to a decrease in the stability of the ring:

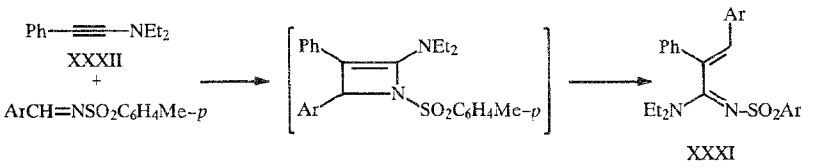


1-Azetine N-oxides XXIX are converted to nitrones XXX when they are heated [70]. Penninings and Reinhoudt [70] showed that the ring opening is a conrotatory process.



XXIX XXX

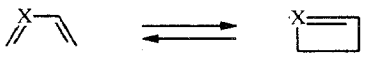
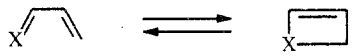
Not as much is known about the thermal opening of the ring of 2-azetines. They polymerize when they are heated. It is assumed that the opening of 2-azetines is one of the steps in the synthesis of dienes XXXI from ynamines XXXII [3].

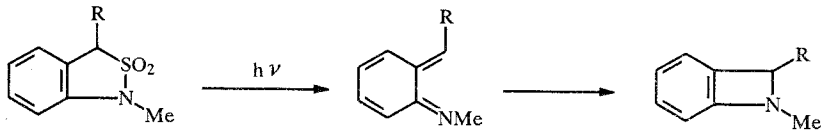


XXXI

On the other hand, the azadienes XXXIV formed in the photolysis of sultams XXXIII are converted to benzazetidines XXXV via a 1,4-electrocyclic reaction [71].

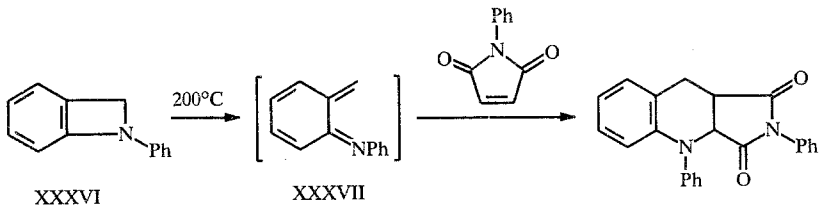
TABLE 2. Effect of the Introduction of Heteroatoms on the Interconversion of Butadiene and Cyclobutene

X	Permitted process	
	photochemical	thermal
		
CH –	Disrotatory	Conrotatory
N	Disrotatory	Conrotatory
NH	Disrotatory	Conrotatory
		
N	Disrotatory	Conrotatory
O	Disrotatory	Conrotatory
S	Disrotatory	Conrotatory
NH	—	Con. and dis.
OH	—	Con. and dis.
SH	—	Con. and dis.
O, S, NR	—	Both forbidden



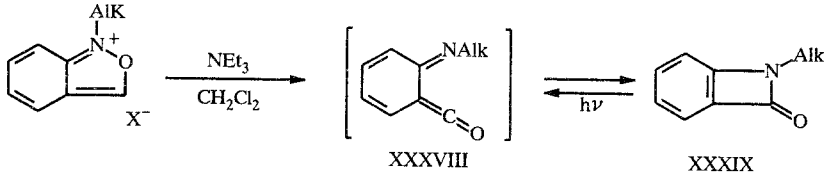
XXXIII XXXIV XXXV

It has been shown that N-phenylbenzazetine XXXVI undergoes ring opening when it is heated [72]. The 1-azabutadiene XXXVII formed in this reaction can be captured by active dienophiles [72].



XXXVI XXXVII

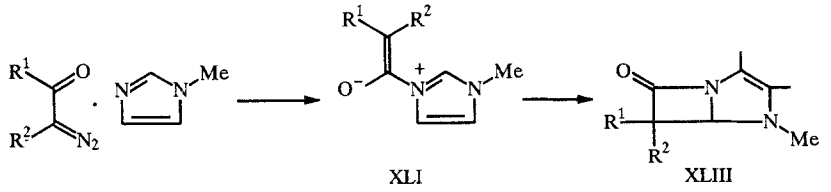
Olofson and coworkers have thoroughly demonstrated the possibility of the cyclization of imidoylketenes XXXVIII to give lactams XXXIX [73-75]:



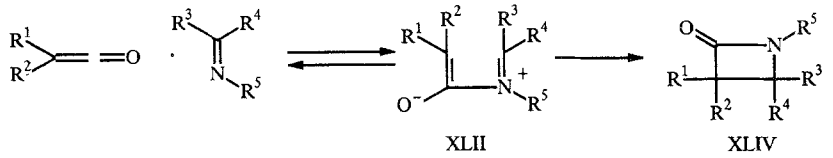
XXXVIII XXXIX

They have shown that an equilibrium that is shifted to favor XXXVIII under the influence of UV light exists between these substances.

Formally, the cyclization of azomethylylids XLI and XLII to give lactams XLIII and XLIV can also be classified as electrocyclic reactions [76, 77].

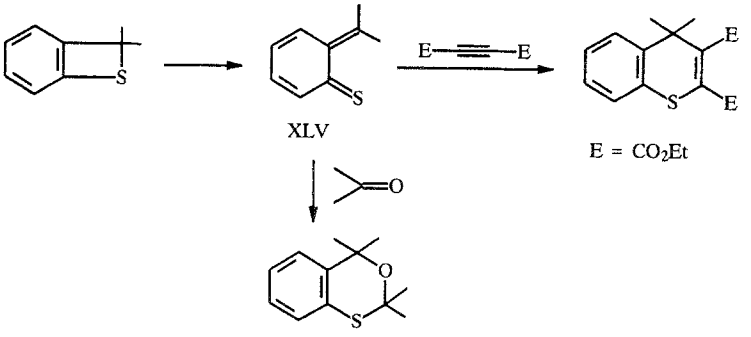


XLI XLIII



XLII XLIV

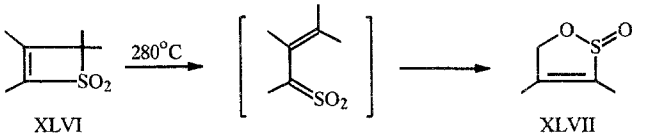
3-Thiacyclobutenes (thietes) are stable at low temperatures and readily undergo polymerization when they are heated [3]. The electrocyclic opening of benzothietes is postulated to explain the formation of thiaanthrenes in the photochemical decomposition of 1,2,3-benzothiadiazoles [78]. The products of opening of the thietes, viz., 1-thiabutadienes XLV, can be identified via capture by active dienophiles [79, 80].



XLV

E = CO_2Et

Thiete 1,1-dioxide XLVI is stable but is converted to sulfonate XLVII under certain conditions [3]:



XLVI XLVII

The first step in this process is a retro-1,4-electrocyclic reaction. The isomerization of the selenium analog (XLVIII) of benzocyclobutene to give 1-selenobutadiene XLIX was described in [81].

XLVIII XLIX

The conversion of silene L to silylene LI is one of the examples that illustrate the occurrence of electrocylic reactions in the silacyclobutene series [82].

L LI

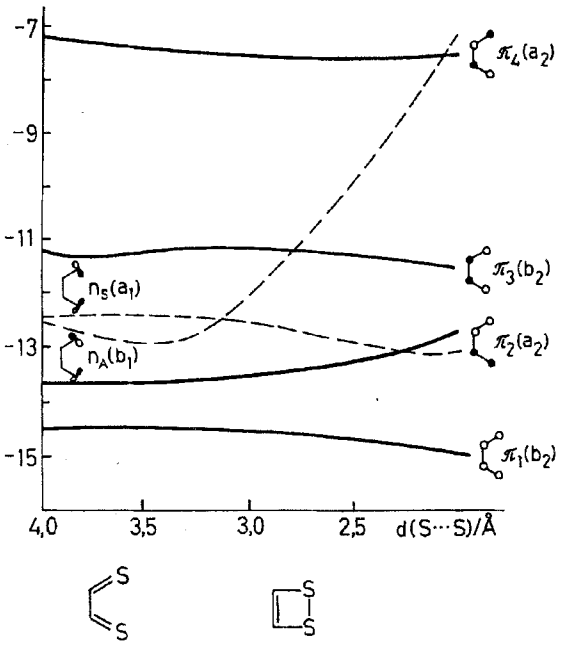
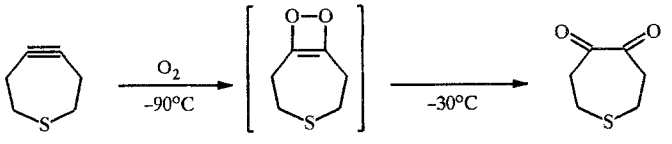


Fig. 4. Correlation diagram of the MO of 1,4-dithiabutadiene and dithiete. The occupied $n_s(a_1)$ orbital of the starting compound correlates with the orbital of the final compound. The process is forbidden [63].

According to *ab initio* calculations, the opening of the ring of monophosphacyclobutenes should be realized via a conrotatory pathway [83].

3.2. Reactions of Systems with Two or More Heteroatoms

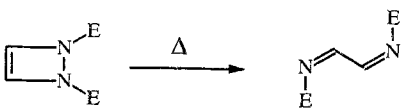
The introduction of yet another oxygen atom into the oxytene molecule leads to a decrease in the energy of activation of ring opening to 10 kcal/mole [67]. Despite the extremely low stability of dioxytene LII, Turro and coworkers were able to experimentally determine the energy of activation of opening of this compound [84].



LII

E_a = 18 kcal/mole

Only one example of the opening of the 3,4-diazocyclobutene ring has been published [85].

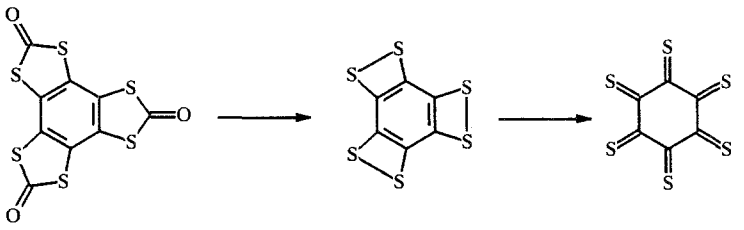


On the other hand, the opening of dithietes LIV has been presented in numerous publications [3, 63, 66, 86-92].

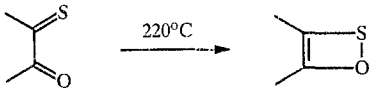
LIV LV

Thus dithietes LIV undergo thermal ring opening to give unstable intermediates, viz., α-dithiones LV, which can be dimerized and also react with alkenes and alkynes [3]. Kinetic studies of this isomerization have been conducted [92]. It has been shown by means of photoelectronic spectroscopy that dithietes LIV have higher stabilities than α-dithiones LV [87, 90].

It should be especially noted that was able to be generated and identified under the conditions of neutralization reionization mass spectrometry [91].

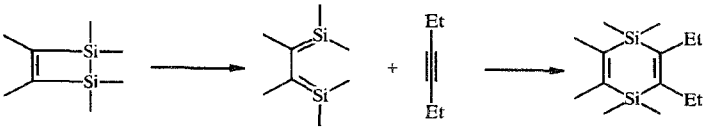


In contrast to dithietes, oxathietes are extremely unstable. Except for one publication [93], experimental data on the cyclization of thia-4-oxabutadiene to give oxathietes are not available. The results of calculations by the MNDO method and photoelectronic spectroscopy explain this phenomenon by the absence of overlapping of the orbitals of the C=S and C=O groups in the LVI molecule [94].



LVI

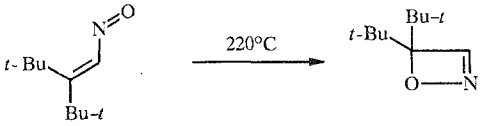
Data on the opening of 3,4-disilacyclobutenes are available. The intermediate 1,4-disilabutadienes LVII are unstable but can be captured by dienophiles [3].



LVII

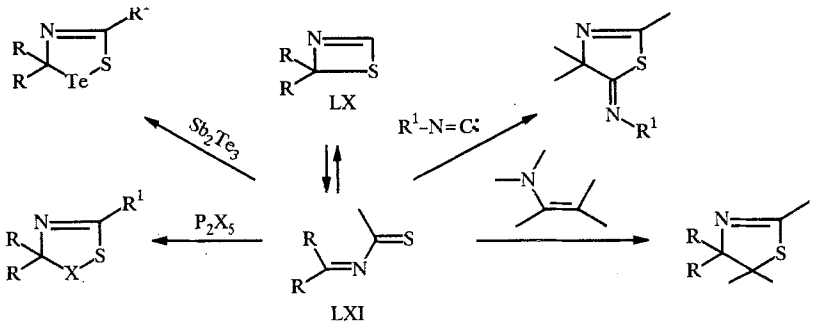
Cyclobutenes that have two different heteroatoms are intermediates in various reactions [3, 93-99]. They have stability as a consequence of electron repulsion between the unshared pairs.

Monomeric nitroso compounds LVIII are stable at room temperature but are converted to the more stable oxazetines LIX in 54% yield when they are heated [100].



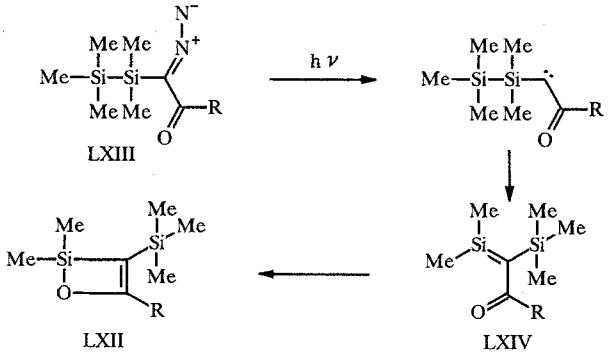
LVIII LIX

1,3-Thiazetenes LX, stabilized by trifluoromethyl groups, exist in equilibrium with open isomers LXI, which can be captured by various dienophiles.



X = S, Se; R = CF_3; R^1 = Alk, Ar

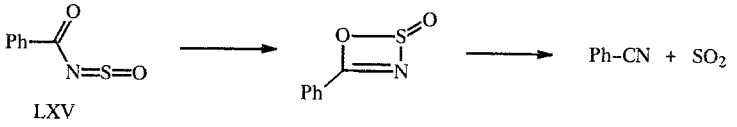
Stable silaoxytenes LXII were obtained in the decomposition of silicon-containing diazo compounds LXIII [97, 98]:



This process evidently includes cyclization of 1-oxa-4-silabutadienes LXIV. The structures of LXII were confirmed by the results of x-ray diffraction analysis for R = adamantyl [97, 98].

There are publications in which the electrocyclic reactions of heteroanalogs of cyclobutene that contain O—S [93, 99] and N—P [101] bonds are described.

A cyclobutene that contains three heteroatoms is possible as an intermediate in the thermal decomposition of LXV [102].



3.3. Electrocyclic Reactions of Heteroanalogs of Dewar Benzene

The 1,4-electrocyclic reactions of heteroanalogs of Dewar benzene are of great interest from the point of view of the investigation of the chemical properties of heterocyclic compounds. Reactions of this sort are most abundant in series of six-membered nitrogen-containing heterocycles [3, 49-52, 54, 103-108]. Data on other heterocycles are also available [51]. Thus, for example, a Dewar isomer for silabenzene was detected at 10 K in an argon matrix [109].

Reactions of this type were the subject of several reviews [51, 55] and therefore are not examined here.

CONCLUSION

In conclusion, we would like to note some trends in the development of research devoted to 1,4-electrocyclic reactions.

Progress in this area will evidently involve the elucidation of the fine mechanisms of the interconversions of butadiene and cyclobutene derivatives. One should expect vigorous development in research on the reactions of heteroanalogs of these compounds that take place under conditions that differ significantly from the standard conditions — under the influence of metal ion, UV light at various wavelengths, ultrasound, electron impact, and other strong forces.

The stereochemical idiosyncrasies of 1,4-electrocyclic reactions have been thoroughly studied, and one should therefore expect further development, on the basis of them, of synthetic methods for obtaining complex organic compounds, vitamins, alkaloids, steroids, etc.

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