4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE IN ORGANIC SYNTHESIS (REVIEW)

I. K. Korobitsyna, A. V. Khalikova,
L. L. Rodina, and N. P. Shusherina

UDC 547.792

The principal trends in the investigation of 4-phenyl-1,2,4-triazoline-3,5-dione are described.

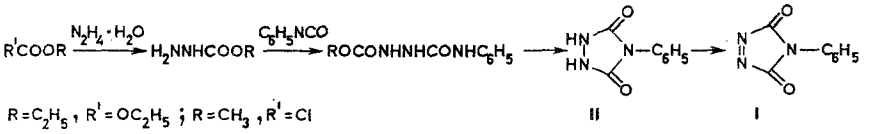
4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) has become one of the most important reagents of organic synthesis in the last decade. Many previously difficult-to-obtain classes of organic substances, including strained polycyclic and heterocyclic compounds, have been obtained by means of this compound. It is difficult to overrate the significance of phenyltriazolinedione, and the best evidence of the promise its future utilization offers is the fact that it is currently being produced on an industrial scale [1].

Data on the principal trends in the investigation of this compound are systematized in the present paper.

Preparation and Some Properties of 4-Phenyl-1,2,4-triazoline-3,5-dione

There is only one method for the preparation of 4-phenyl-1,2,4-triazoline-3,5-dione (I), viz., oxidation of 4-phenylurazole (II) with various oxidizing agents; thus the accessibility of triazolinedione I is determined, on the one hand, by the ease of preparation of 4-phenylurazole, and, on the other, by the selection of a suitable oxidizing agent.

No difficulties are encountered in the synthesis of 4-phenylurazole: It is obtained in good yields (80-90%) from diethyl carbonate [2] or methyl chlorocarbonate [3]:



It is more difficult to select a good oxidizing agent. Triazolidinedione I was evidently obtained for the first time by Thiele and Strange [4] in 1894 by oxidation of phenylurazole with lead dioxide in sulfuric acid. However, only the formation of a very small amount of a bright-red substance, which was not identified, was established in their research.

Stolle [5] obtained triazolinedione I in the crystalline state in 1912 by oxidation of the disilver salt of phenylurazole with an ether solution of iodine. The yield of the triazolinedione was also low under these conditions, but Stolle was able to study its thermal stability and sensitivity to moisture, acids, and alkalis. Fifty years later, Cookson and coworkers [6] obtained I in 86% yield by oxidation of 4-phenylurazole with tert-butyl hypochlorite in acetone at low temperatures. In the opinion of Strickler and Pirkle [7], all of the above-mentioned oxidizing agents used for the synthesis of triazolinedione I give side products that either decompose the dione or are difficult to extract from the reaction mixture – they feel that nitrogen tetroxide, which is convenient to use in laboratory work and gives pure 4-phenyl-1,2,4-triazoline-3,5-dione in almost quantitative yield, is the best oxidizing agent. In addition, concentrated nitric acid [8], bromine [9], and N-bromosuccinimide (NBS) [10] have been used as oxidizing agents for phenylurazole.

Gillis and Hagarty [2] oxidized 4-phenylurazole with lead tetraacetate and, without isolating I, immediately subjected it to diene synthesis. Compound I was also obtained in situ with dimethyl sulfoxide (DMSO) [11] or phenylselenic acid anhydride [12] as the oxidizing agent.

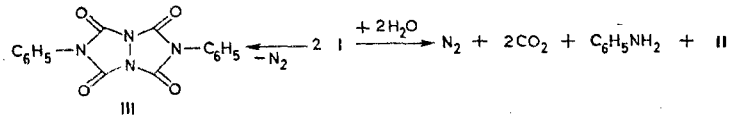
A. A. Zhdanov Leningrad State University, Leningrad 199164. M. V. Lomonosov Moscow State University, Moscow 117239. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 147-169, February, 1983. Original article submitted February 9, 1982.

The method of synthesis presented above is also suitable for the preparation of 4-alkyl- and 4-aryl-1,2,4-triazoline-3,5-diones, but in this case the corresponding alkyl and aryl isocyanates are used in place of phenyl isocyanate. It should, however, be noted that N-substituted analogs of 4-phenyl-1,2,4-triazoline-3,5-dione are harder to obtain, and considerably less study has therefore been devoted to them than to phenyltriazolinedione I [2, 13-15].

Freshly sublimed triazolinedione I is obtained in the form of crimson acicular crystals that are quite soluble in many organic solvents (ether, chloroform, ethyl acetate, etc.) and melt with decomposition at 165-175°C [13].

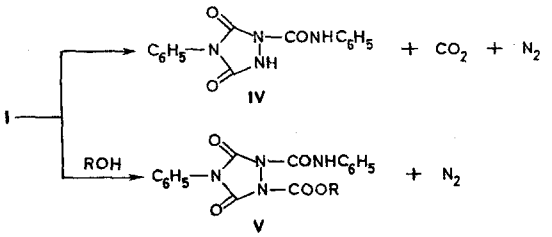
Two intense bands in the region of the stretching vibrations of carbonyl groups are present in the IR spectrum of I at 1780 and 1760 cm^{-1} [6]. The UV spectrum of a solution of I in dioxane is characterized by absorption maxima at 530 (ε 170) and 220 nm (ε 9530) [9]. The absorption band with λ_{max} 530 nm corresponds to an $n \rightarrow \pi^*$ transition of the electrons of the N=N bond, which is responsible for the color of the compound in the visible region of the spectrum; the band of a $\pi \rightarrow \pi^*$ transition shows up in the shorter-wave region. (An intense $\pi \rightarrow \pi^*$ band, which is characteristic for extended conjugation systems [16], is observed at 220-270 nm when a double bond that is conjugated with the azo group is present.) The PMR spectrum [13] contains a singlet of aromatic protons at 7.48 ppm (in $CDCl_3$).

Under the influence of water, triazolinedione I is readily converted to urazole II, and it should therefore be stored without access to moisture and must be sublimed prior to use in the reaction [5]. However, it should be borne in mind that the sublimation of I entails significant losses, since some of it is converted to bisimide III [5]:



III

The conversion of triazolinedione I to 4-phenylurazole-1-carbanilide (IV) (in acetonitrile with added aqueous pyridine) [17] and to V by the action of alcohols [18, 19] evidently takes place through a step involving bisimide III:



IV

V

4-Phenyl-1,2,4-triazoline-3,5-dione in the Diene Synthesis

Of all of the chemical transformations of I, its use in the diene synthesis has been investigated in greatest detail: Triazolinedione I is one of the most active dienophiles due to the fixed cis configuration of this compound and the presence of two strong electron-acceptor groups attached to the N=N bond. It is widely used for the construction of the most diverse (including highly condensed) nitrogen-containing heterocycles: Thus, for example, a number of previously unknown derivatives of pyridazine, tetrazine, and azacinnoline, as well as certain carcass structures, have been obtained on the basis of I. The extensive use of phenyltriazolinedione I as a dienophile is due to a considerable degree to the fact that the reactions involved in the diene synthesis with phenyltriazolinedione are generally carried out under mild conditions at temperatures that do not exceed room temperature.

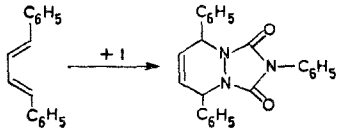
A comparison of the rate constants of the reactions of triazolinedione I and tetracyanoethylene with various dienes [9] shows that in many cases, such as in the reaction with 4,5-diphenyl-1,3-butadiene or chloroprene, the triazolinedione I is a considerably more active dienophile than tetracyanoethylene, which is the strongest dienophile in the hydrocarbon dienophile series.

The great effect of the character of the solvent on the change in the enthalpy of activation was demonstrated on the basis of a kinetic study of solvation effects in the reaction of triazolinedione I with anthracene. The results of a study of the kinetics and a determination of the activation parameters of the Diels–Alder reaction for series of 4-substituted

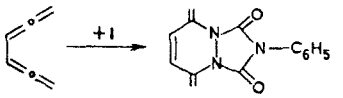
1,2,4-triazoline-3,5-diones with diphenylbutadiene, anthracene, hexachlorocyclopentadiene, and bicyclo[2.2.1]heptadiene are in better agreement with the concept of the frontal-orbital model of the Diels—Alder reaction than with the standard approach from the position of linear free energies [13]. The order of the change in the reactivities of 4-substituted 1,2,4-triazoline-3,5-diones is not in complete agreement with the order predicted on the basis of the electronic effect of the substituent but depends on the polarity of the solvent and the structure of the diene used.

However, as has been demonstrated in a number of cases [21, 22], one should assume that the reaction of triazolinedione I with various dienes implies the primary formation of a 1,4-diol, which is also characteristic for other strongly polarized dienophiles [23]. Of course, one cannot exclude the possibility that such transformations of triazolinedione I proceed through intermediate diradicals [24].

In most cases conjugated acyclic dienes react smoothly with triazolinedione I via a mechanism of the diene synthesis type [2, 25].



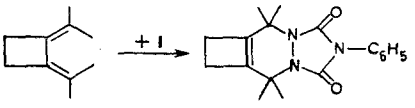
Conjugated bisallenes also undergo the diene synthesis with I very readily [1, 26].



A monoallene (2,4-dimethyl-2,3-pentadiene) also reacts via a mechanism of the 1,4-cycloaddition type, inasmuch as it initially undergoes isomerization to 2,4-dimethyl-1,3-pentadiene, which then gives a Diels—Alder adduct [27].

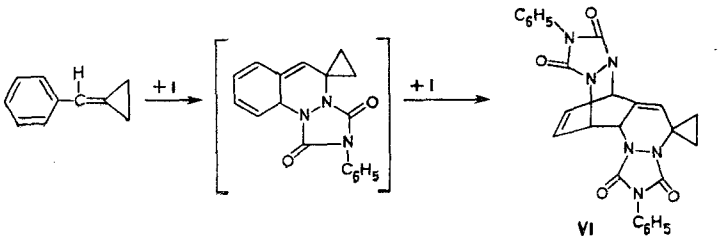
The reaction with triazolinedione I can be successfully used for the identification of isomeric dienes by the production of crystalline adducts [28].

Compounds with exocyclic double bonds react readily with phenyltriazolinedione I via a mechanism of the Diels—Alder type [29]:



Treatment of cisoid and transoid dienes that contain a diosphenol grouping (each separately and in the case of a mixture of them) with a solution of triazolinedione I in chloroform leads to the same stable adduct in good yields [30].

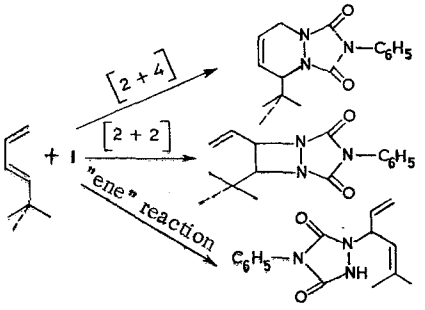
Benzylidenecyclopropane, in which the exocyclic double bond is conjugated with the aromatic ring, is capable of adding two molecules of triazolinedione I successively to give bisadduct VI [31]:



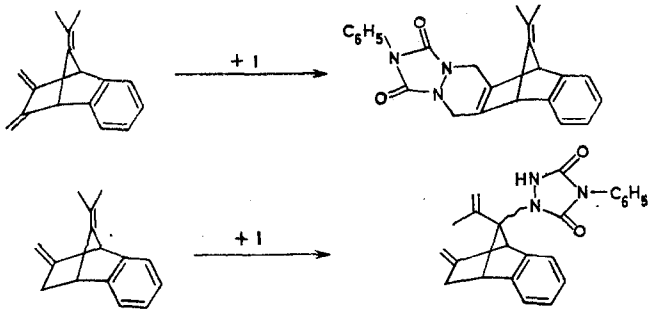
A vinyl group conjugated with an endocyclic double bond forms a system that also readily reacts with unsubstituted triazolinedione to give Diels—Alder adducts. Several triazasteroids have been obtained by this method [32]. Compounds that have a vinyl group attached to an aromatic ring react with triazolinedione I at —77°C to give the normal 1,4-cycloaddition products [33, 34].

The triple bond of 5-ethynyl-1,3-cyclohexadiene is not involved in the reaction with I [35].

It should, however, be noted that the presence of a conjugated diene system in the starting molecule does not exclude the formation of products other than the classical Diels–Alder adducts in the reaction with triazolinedione. Thus [2+2] cycloaddition to form diazetidines and "ene" reactions can be observed even in the case of rather simple dienes [36, 37]:

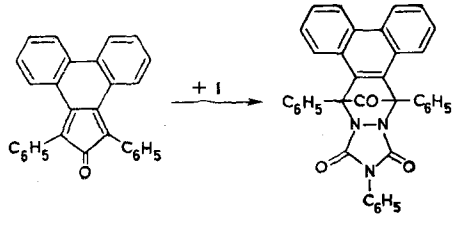


Interesting results were recently obtained in a study of the reaction of I with 2,3-dimethylene- and 3-methylene-7-isopropylidenebenzonorbornenes [38]. A [4+2] cycloadduct was isolated in quantitative yield in the first case, whereas a mixture of stereoisomeric "ene" adducts (syn and anti in a ratio of 16:9) was isolated in the second case:



The reaction of triazolinedione I with cyclopentadiene and its diverse derivatives has been investigated extensively [2, 6, 39-43]. For example, cyclopentadiene itself gives a 1,4-cycloaddition adduct in high yield at −78 [6] or 0-5°C [2]. Tetraphenylcyclopentadiene [8], polychlorocyclopentadienone acetals [39], hexachlorocyclopentadiene [9], dicyclopentadienylmercury [41], and other substituted cyclopentadienes [42, 43] also react readily with it to give 1,4 adducts. A 5,5-dialkoxycyclopentadiene, which undergoes dimerization at a high rate during its preparation from the corresponding dibromide, can be readily "trapped" in the form of a 1,4-adduct with triazolinedione I. The reaction proceeds quantitatively, and titration of a benzene solution of the reaction mixture with the triazolinedione is used to determine the yield of the dialkoxycyclopentadiene [40].

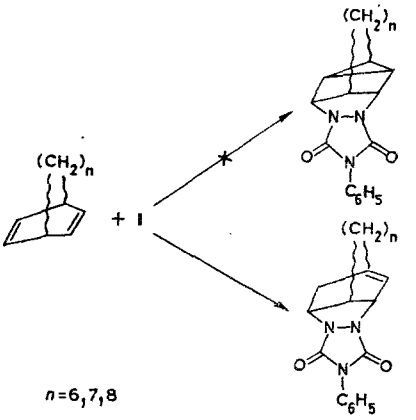
Polycyclic condensed systems that contain a cyclopentadiene ring also react with I to give 1,4-cycloadducts [8, 42-44]. Thus phencyclone reacts with I to give VII:



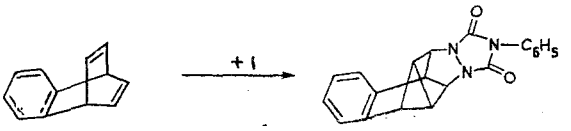
VII

Cyclohexadiene (at 0-5°C) [2] and substituted and condensed cyclohexadienes [45-48] react similarly with triazolinedione I. The high rates of the reaction of dienophile I with condensed diene systems make it possible to also trap unstable cyclohexadiene compounds in the form of stable adducts [49, 50]. 1,4 Adducts with triazolinedione, which readily undergo retrodiene fragmentation, have found application for the protection of the cyclohexadiene fragment in several natural compounds (for example, in vitamin D) [51, 52].

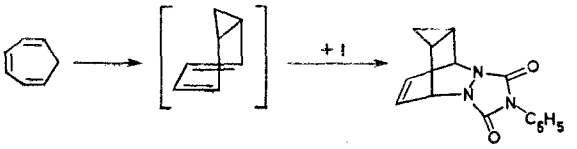
In the reaction of triazolinedione I with strained bridged 1,4-cyclohexadienes one should have expected that the process would proceed as a normal Diels–Alder homoreaction with the formation of three new σ bonds and the development of two new rings. Gassman and Hoye [24], in conformity with the results of a kinetic study, explain the anomalous cycloaddition of triazolinedione I with retention of one π bond and its migration to the bridgehead by means of the intermediate formation of diradicals or by means of a concerted mechanism:



At the same time, it has been shown that benzobarrelene and triazolinedione I give an adduct of the Diels–Alder homoreaction in quantitative yield [21]:



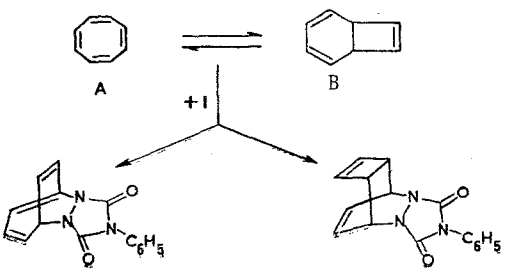
Seven-membered conjugated polyenes react readily with triazolinedione I; thus cycloheptatriene reacts in the form of a valence isomer and forms a 1,4-cycloadduct [6, 53, 64].



3,5-Cycloheptadienone reacts with I to give a 1,4-adduct in good yield [54, 55].

Tropone and tropolone react differently with triazolinedione I. While the former gives a 1,4-cycloadduct, tropolone forms a substitutive addition product [56].

A great deal of research has been devoted to the study of the reaction of triazolinedione I with cyclooctatetraene and its derivatives [57-64] in connection with the problem of the valence tautomerism of this cyclic tetraene. According to the data in [57], 1,4-adducts of both tautomers (A and B) are formed in approximately equal amounts (22% each) at room temperature in benzene or acetone:

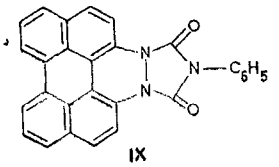


1,3-Di-tert-butylcyclooctatetraene [63] reacts with triazoli-edione I in refluxing ethyl acetate to give a cycloadduct (VIII) only of tautomer B; the tert-butyl groups in the cycloadduct are located in the cyclobutene ring.

A method for the preparation of enantiomeric olefins on the basis of the reaction of substituted cyclooctatetraenes [65, 66] and optically active (–)-4-endo-bornyl-1,2,4-triazolinedione, which was obtained from endo-bornylamine hydrochloride via the conventional scheme [14].

Cyclononatetraene and its chloro derivative readily form 1,4-adducts with triazolinedione I [67, 68].

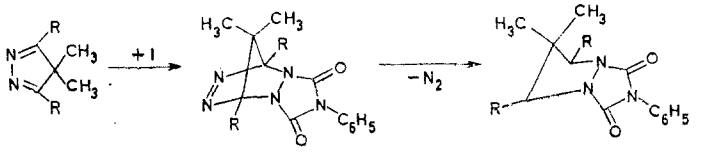
Like other dienophiles, triazolinedione I adds to anthracene in the 9 and 10 positions [6, 9, 13]. Thermally stable phenylimide IX was isolated as a result of the reaction of triazolinedione, which was obtained in situ by oxidation of urazole with lead tetraacetate, with perylene [69], i.e., in this case the resulting adduct undergoes aromatization during the reaction.



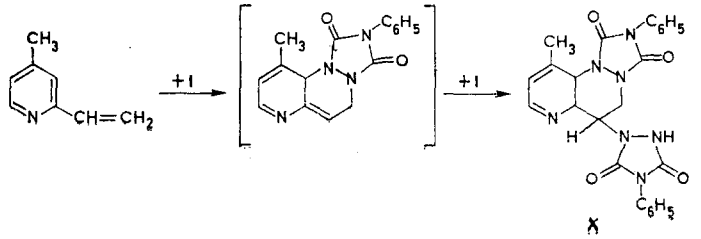
IX

Various carcass structures have been obtained on the basis of triazolinedione I and propellanes with various structures [70-77]. Propellanes that contain two pairs of conjugated diene fragments form bisadducts [77, 89].

Compound I also reacts via a 1,4-cycloaddition pathway with numerous heterodienes [78-80] such as diazepine [56], oxazepine [81], 1,3-dioxepine [82], vinylpyridines [83, 84], pyridone and pyrone derivatives [85, 86], and isopyrazoles [87, 88]. One of the first examples of the reaction of triazolinedione I with nitrogen-containing heterocycles is presented in the following scheme [87]:

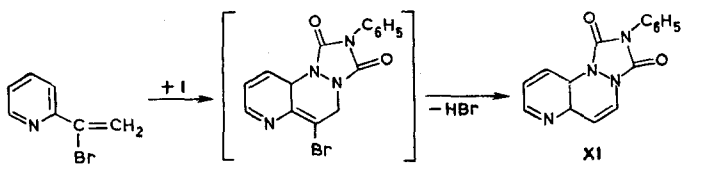


Kost, Terent'ev, and Kartsev [83] have shown that vinylpyridine reacts with triazolinedione I to give a bisadduct; one molecule of the diene adds via the scheme of the diene synthesis, while a second molecule adds via a mechanism of the substitutive addition type. The previously unknown 5-azacinnolines X are formed as a result of these two successive reactions:



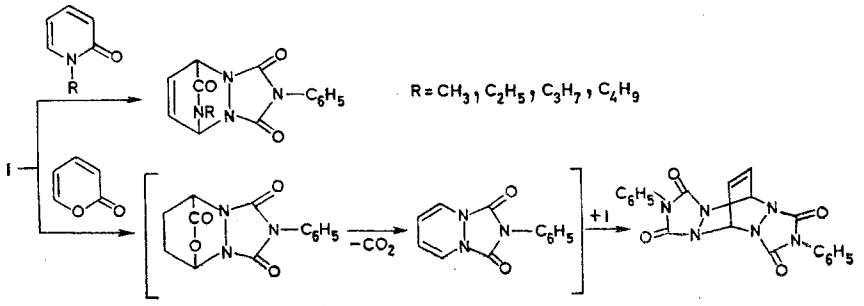
X

Monoadduct XI was isolated in the reaction with α-bromovinylpyridine [84]:



XI

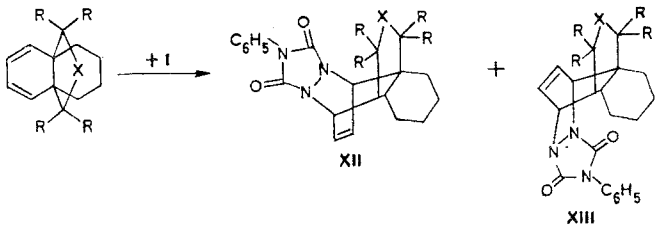
It has been demonstrated in a significant number of cases that 1-alkyl-2-pyridones [85] react in the cold with I to give [4+2] cycloadducts (in 79-87% yields) that are tetrahydropyridazine derivatives with an endo-azocarbonyl bridge. At the same time, 2-pyrone [86] reacts with the same dienophile to give a tetrazine derivative (in 85% yield) via a scheme involving double diene synthesis.



Various natural compounds, viz., cholestadiene [90], ergosterol [91-93], androstatriene [94], vitamin D_3 metabolites [92, 95], and levopimaric acid [96], have also been subjected to reaction with the triazolinedione. The ease of retrodiene decomposition for adducts with I when they are heated or in the case of acidic catalysis has been used to protect conjugated double bonds in steroids and also for their purification and separation [91, 95].

Endo, exo stereoisomerism has not been observed for 1,4-cycloadducts of triazolinedione I with cyclic and heterocyclic dienes; this is explained by the planar character of the hydrazine nitrogen atoms in the urazole fragment of the cycloadducts. This fact is confirmed by the absence of the temperature dependence in the PMR spectra of the adducts with triazolinedione I that is usually observed in inversion processes [78, 87, 97].

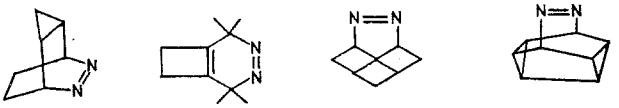
However, plane-symmetrical dienes (propellanes, for example) form two stereoisomers in reactions with I as a consequence of attack by the dienophile from "above" or "below," which is determined by the structure of the starting diene.



XII XIII

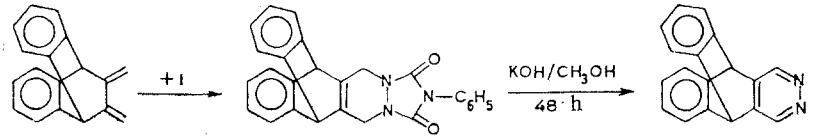
Thus when R = R = 0 and X = NH, the dienophile adds only from the sterically most hindered side (from "above") to give adduct XII as a consequence of additional stabilization of the transition state due to secondary orbital interaction of the CO_{π}^{*} orbitals of the diene with the vacant orbitals of the nitrogen atoms [72-74], whereas when R = R = H, in which case such stabilization is impossible, the dienophile adds primarily from "above" to give isomer XIII.

The most important trend in the utilization of adducts based on triazolinedione I is the preparation from them of carcass and strained polycyclic systems [30, 54, 64, 89, 98]:



In contrast to the adducts with azodicarboxylic acid ester, the cycloadducts with triazolinedione I are hydrolyzed with difficulty [8] (by prolonged heating at elevated temperatures). At the same time, they undergo retrodiene decomposition at room temperature. Thermally stable hydrogenated adducts are therefore used more often for hydrolysis [46, 58, 90].

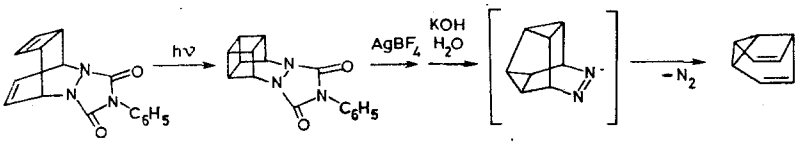
It is interesting that the adducts of triazolinedione I with a diene that has a fixed s-cis configuration of the conjugated bonds was found to be resistant to retrodiene decomposition, and its hydrolysis led immediately to 2,3-diazatriptycene (in 60% yield without an oxidizing agent) [99, 100].



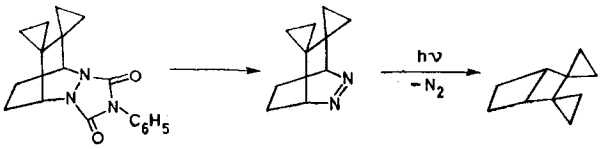
It was very recently observed that the most effective method for the conversion of urazoles to azoalkanes is hydrazinolysis [101].

The further development of mild and selective methods for the hydrolysis of urazoles would expand the range of their application significantly. The hydrolysis of the imide group in 1,4 cycloadducts with the sulfur analog of triazolinedione I proceeds readily; however, the sulfur analog is unstable at room temperature [54].

The azo compounds obtained by the method described above are labile and readily split out a molecule of nitrogen to give the corresponding hydrocarbons upon heating or photolysis; this process may also take place spontaneously. Thus, for example, semibulvalene was synthesized from the adduct of triazolinedione I and cyclooctatetraene without isolation of the intermediately formed azo compound [59].

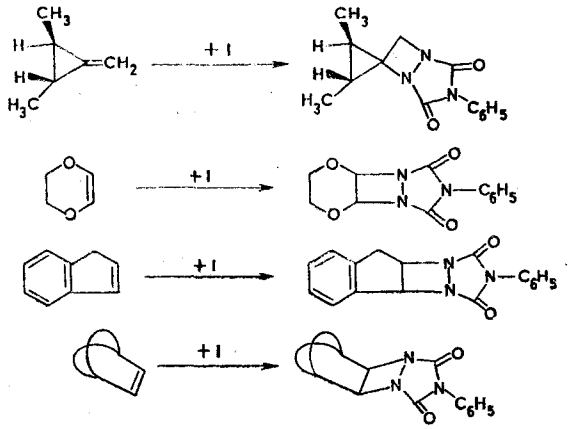


A stained bicyclo[2.2.0]hexane was obtained by photochemical decomposition of an azoalkane [46].

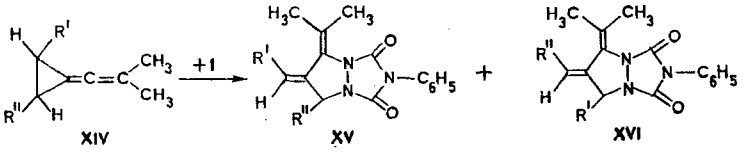


Other Cycloaddition Reactions of 4-Phenyl-1,2,4-triazoline-3,5-dione

In addition to the diene synthesis, [2+2]-cycloddition reactions are characteristic for phenyltriazolinedione I. 1,2-Cycloadducts of I with methylenecyclopropane [102], dehydro-1,4-dioxane, indene [36], and other compounds [103, 104] have been described. Norbornenes react with triazolinedione I via a [2+2]-cycloaddition scheme [37].



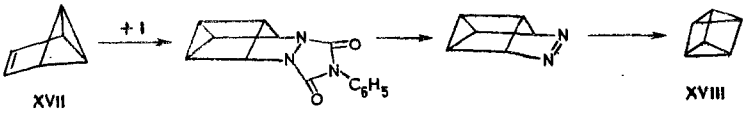
Triazolinedione I reacts with strained alkenyldienecyclopropanes XIV via the same pathway [104, 105] to give urazoles XV and XVI:



XIV XV XVI

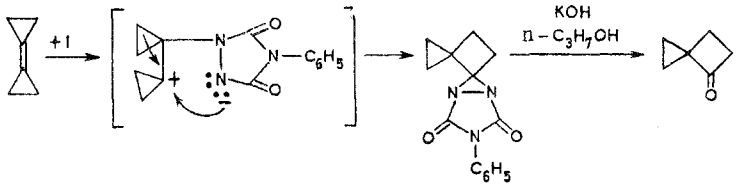
$R' = C_6H_5$, $R'' = H, CH_3$

The addition of triazolinedione I to the double bond of benzovalene (XVII) is accompanied by rearrangement of the carbon sleketon; prismane XVIII was obtained by subsequent elimination of the imide fragment [106]:

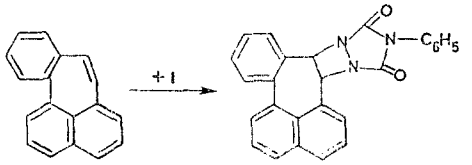


XVII XVIII

Triazolinedione I adds readily at 0°C to bicyclopropylidene to give a single product, viz., a diaziridine derivative, in 83% yield [107]. Cyclization of the intermediate zwitterion evidently occurs simultaneously with expansion of the three-membered ring in this case. As in the preceding case, the entire urazole grouping is split out during alkaline hydrolysis.

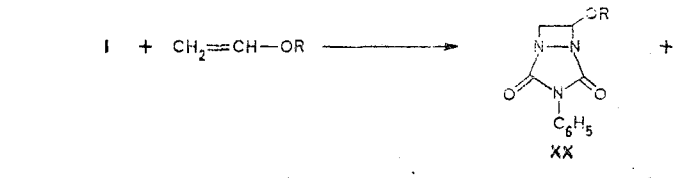


The character of the cycloaddition products formed from 1-vinylnaphthalenes is determined by the orientation of the vinyl groups. The products of the reaction of XIX with triazolinedione I is a [2+2] cycloadduct [33]:



XIX

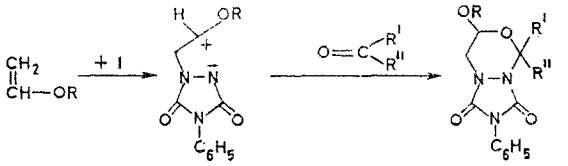
The reactions of I with vinyl ethers and esters have been studied [108-111]. Triazolinedione reacts with vinyl ethers [108] to give 1,2 cycloadducts XX and mixtures of copolymers XXI and XXII:



XX

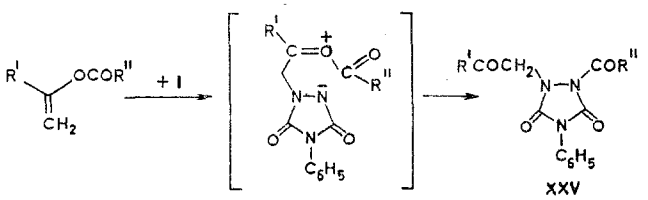
XXI XXII

It has been shown [111] that 1,4-dipoles XXIII are formed intermediately in the case of attack at the nitrogen atom of triazolinedione I. If the reaction is carried out in solutions of ketones, XXIV with a tetrahydro-1,3,4-oxadiazine ring are obtained:



XXIII XXIV

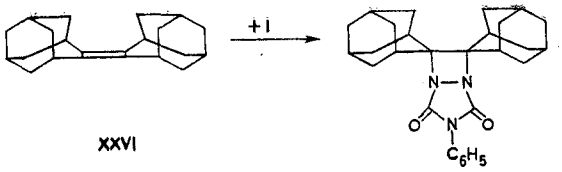
The reaction of I with vinyl esters also leads to the development of 1,4-dipoles, which however, undergo further intramolecular rearrangement to give substituted urazoles XXV [109]:



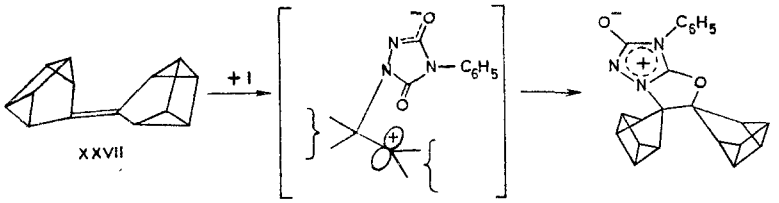
XXV

The formation of a diazetidine was observed as a result of [2+2] cycloaddition of triazolinedione I at room temperature to adamantylideneadamantane (XXVI). Reversion is observed

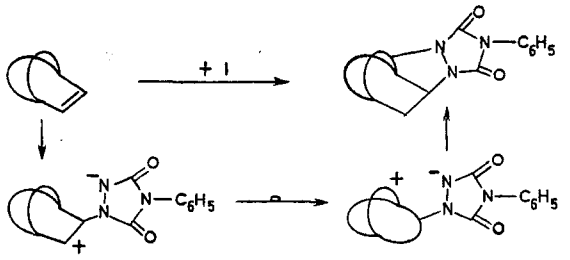
when the adduct is heated in chloroform containing tetraethylmethylethylene — the starting olefin and triazolinedione I are isolated [104].



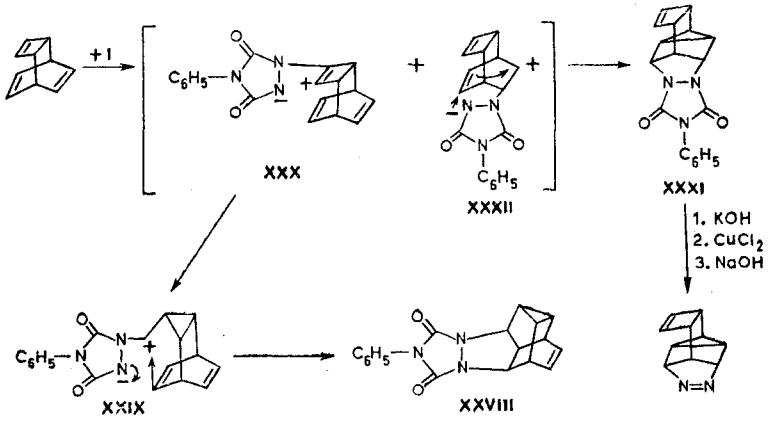
In the case of biquadricyclanylidene XXVII addition of triazolinedione I to the central double bond leads to the formation of an unstable monoadduct (according to data from the mass spectrum), which evidently has a triazoliaolate structure [112]:



The anomalous cycloaddition of triazolinedione I to strained bi- and polycyclic olefins has been observed [21, 22, 54]. Adam and co-workers feel that the mechanism of the formation of the substituted urazoles obtained in these reactions involves the intermediate development of 1,4 dipoles and their rearrangement:

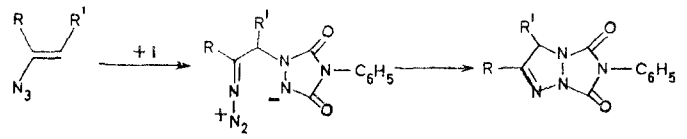


An example of the ambiguous behavior of triazolinedione I is its reaction with the so-called Nenitzescu hydrocarbon (tricyclo[4.2.2.$0^{2,5}$]-deca-3,7,9-triene) [113]. The principal product of this reaction is XXVIII, the formation of which is explained by ring closure to give cyclopropylcarbinyl cation XXIX, which is formed by skeletal rearrangement of primary 1,4 dipole XXX.

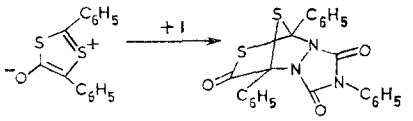


A side product of the reaction is XXXI, the development of which can be explained either by rearrangement of intermediate zwitterion XXXII or by concerted homodiene cycloaddition.

According to the data in [114], the reaction of triazolinedione I with vinyl azides proceeds via a mechanism of the [3+2]-cycloaddition type and leads to condensed cyclic systems that contain 1,2,3- and 1,2,4-triazoline rings.



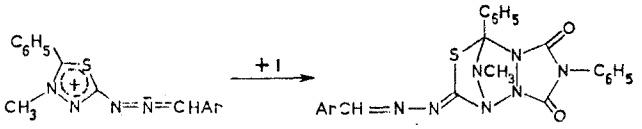
Triazoline I reacts with 2,5-diphenyl-1,3-dithiolia-4-olate via the same scheme. Tricyclic product XXXIII is obtained in 90% yield at 40-50°C [115].



XXXIII

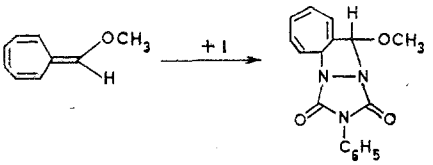
Let us note that only active dipolarophiles undergo this reaction with 1,3-dipolar compounds (dimethyl azodicarboxylate reacts in the same way as triazolinedione I).

Mesoionic 1,3,4-thiadiazolinina-2-benzylidenehydrazinide does not give stable products upon reaction with 1,3 dipoles. On the other hand, acting as a 1,3 dipole, it forms orange adduct XXXIV with triazolinedione I [116]:



XXXIV

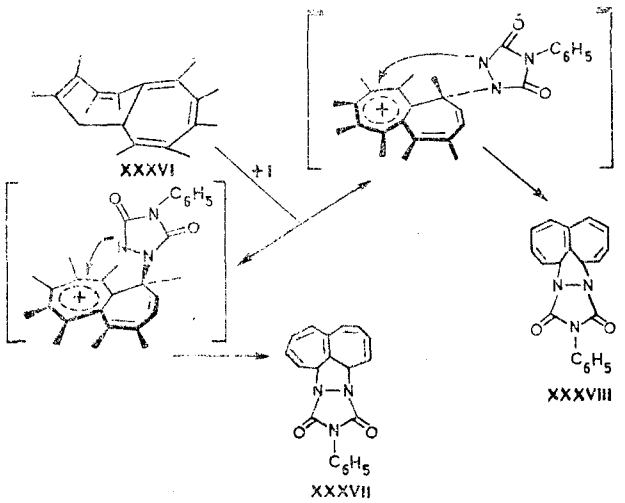
[3+2] Cycloaddition also occurs in the reaction of triazolinedione I and 8-methoxyheptafulvene, which leads to urazole XXXV [117]:



XXXV

Interesting examples of [3+2] cycloaddition are presented in [102, 118].

The reaction of triazolinedione I with heptalene XXXVI is not a concerted process, since a mixture of epimers XXXVII and XXXVIII is obtained [54]:

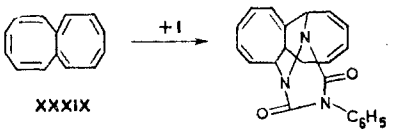


XXXVI

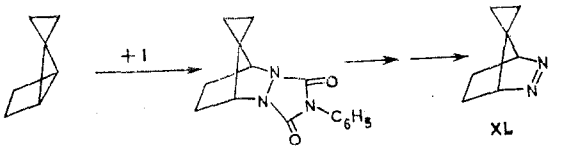
XXXVII

XXXVIII

Vogel and co-workers [119] explain the result of the reaction of triazolinedione I with octalene XXXIX by means of permitted (in the ground state) concerted [8+2] cycloaddition:

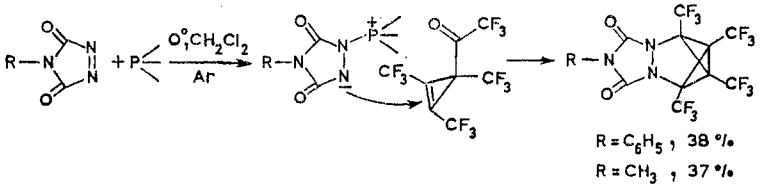


A peculiar transformation, which probably proceeds via a radical mechanism, occurs in the action of I on bicyclo[2.1.0]pentane-5-spirocyclopropane; azoalkane XL was obtained after saponification, decarboxylation, and oxidation of the resulting adduct [120]:



An unsaturated hydrocarbon with a strained 1,2 bond undergoes cycloaddition in this case.

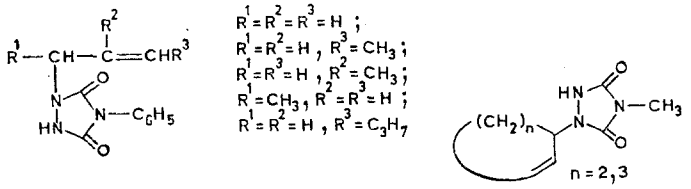
It should be mentioned that unique heterocyclic systems are formed from tris(trifluoromethyl)cyclopropenyl trifluoromethyl ketone and triazolinediones in the presence of triphenylphosphine [121]:



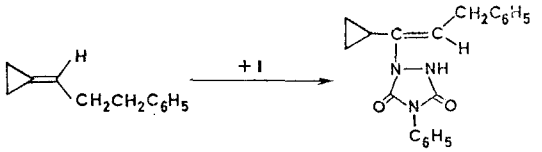
Preparation of 1(2)-Substituted 4-Phenylurazoles from 4-Phenyl-1,2,4-triazoline-3,5-dione

The accumulated experimental data show that the most characteristic transformation of traizolinedione I is its reaction with unsaturated systems. This reaction proceeds via a mechanism of the type involving cycloaddition to "electron-deficient" compounds [107], whereas the so-called "ene" reaction [122] or substitutive addition occurs in the case of "electron-rich" olefins. The formation of 1(2)-substituted 4-phenylurazoles with migration of the multiple bonds in the starting olefin in the case of the "ene" reaction or without migration of the multiple bonds in the case of substitutive addition occurs in both cases.

Products of the "ene" type have been isolated both in the acyclic [123, 124] and in the cylic [125] series.



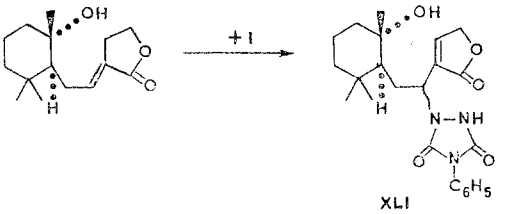
An "ene" adduct was obtained from phenyltriazolinedione I for the first time in the case of a cyclopropylidene derivative [31]:



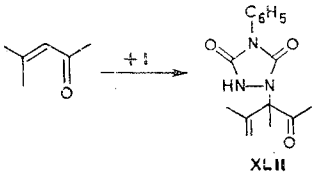
In [31] it was established that 4-methyltriazolinedione is at least 30,000 times more reactive in the reaction with cyclohexene than diethyl azodicarboxylate.

4-Phenyl-1,2,4-triazoline-3,5-dione (I) reacts with α,β-unsaturated ketones, esters, and lactones to give ene adducts. These reactions give the products in 65-94% yields and proceed regio- or stereoselectively. Ene substrates that are capable of assuming an s-cis conformation display considerably higher reactivities. As a result of these reactions, which proceed

with migration of the multiple bond, α,β-unsaturated XLI are formed [122], while pulegone and mesityl oxide give β,γ-unsaturated carbonyl compounds XLII [126].



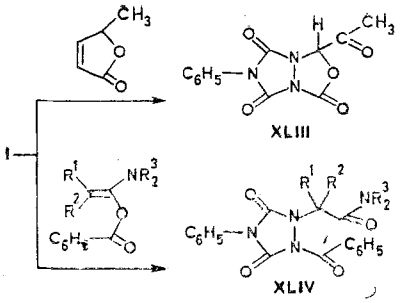
XLI



XLII

The reaction with organometallic alkenes [127], allylsilanes [128], condensed alkenes [129], and allylidenedithiane [130] also proceeds with migration of the multiple bond.

Triazolinedione I reacts with α-angelica lactones and 1-acyloxy enamines to give products of the "ene" type (XLIII and XLIV), in which the "acyl" group is transformed [131, 132]:



XLIII

XLIV

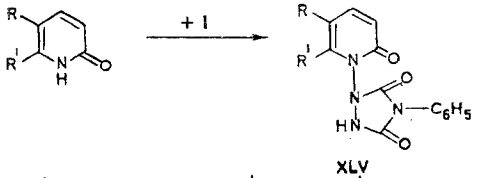
The sulfur analog undergoes a similar transformation [131].

Detailed studies of the mechanism [123-125] of the reaction of triazolinedione I with a series of olefins and α,β-unsaturated carbonyl compounds and the solution of the problems of the regio- and stereoselectivity of these reactions make it possible to regard them as concerted processes [122]. However, in individual cases one also cannot exclude the intermediate formation of zwitterions, which is confirmed, for example, by data from a kinetic study of the reaction of triazolinedione I with β-dicarbonyl compounds [133].

It should be emphasized that "ene" reactions sometimes accompany 1,4- or 1,2-cycloaddition processes and that they prevail if the cycloaddition processes are sterically hindered [39, 110, 134].

Substitutive addition generally takes place with compounds that contain a labile hydrogen atom; in the case of unsaturated compounds this atom is located in a position that excludes the possibility of migration of the multiple bonds in the starting molecule. The reactions of triazolinedione I with alcohols [18] and amines [84] can also be classified as examples of substitutive addition. However, tropolone reacts with I to give a product of substitutive addition in the carbocycle rather than at the hydroxy group [56].

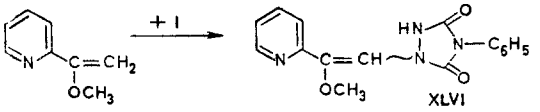
In contrast to 1-alkyl-2-pyridones, which react with triazolinedione I via the scheme of the diene synthesis [85, 86], N-unsubstituted 2-pyridones react with phenyltriazolinedione I to give substitutive addition products XLV in high yields [135]:



XLV

R=R'=H ; R=R'=CH$_3$; R=H, R'=C$_6$H$_5$; R–R'=(CH$_2$)$_4$

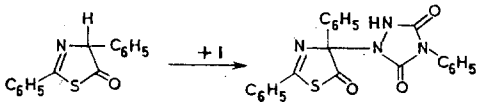
In contrast to α-bromovinylpyridine, α-methoxyvinylpyridine reacts faster with triazolinedione I and gives substitutive addition product XLVI [84]:



XLVI

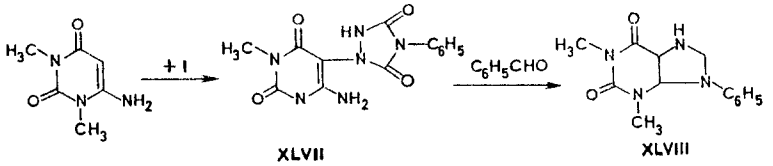
Activation of the pseudodiene system of vinylpyridines by the introduction of electron-donor substituents leads to a pronounced change in the specificity of their reaction with azadienophiles to favor substitutive addition processes and to suppression of their strictly diene properties.

4-Phenylthiazolone, which contains a labile hydrogen atom, gives a substitutive addition product [136]:



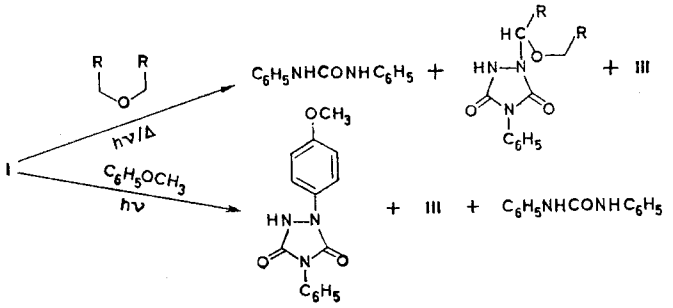
A transformation of the same character occurs with uracils [137].

The reaction of triazolinedione I with 6-aminopyrimidines constitutes the basis of a new method for the synthesis of purines [138]. The addition of triazolinedione I in the 5 position of the pyrimidine ring leads, via the scheme of the Michael condensation, to adducts XLVII in quantitative yields; upon reaction with aromatic aldehydes adducts XLVII are converted to theophylline derivatives XLVIII.

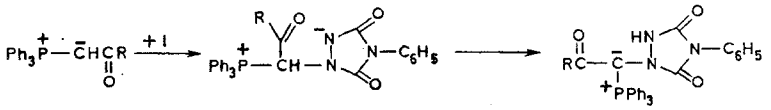


XLVII XLVIII

Triazolinedione I forms 1(2)-substituted 4-phenylurazoles with various ethers [17]. Thus the corresponding substituted urazoles, which are formed as a consequence of migration of the α-hydrogen atom of the ethers to the nitrogen–nitrogen double bond, were obtained when triazolinedione I was heated with tetrahydrofuran, dioxane, and diethyl ether. These reactions can also take place under the influence of light.

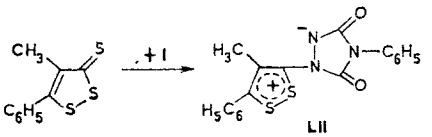


Ylid XLIX reacts with triazolinedione I to give L, in which the hydrogen atom undergoes migration to give product LI [96]:



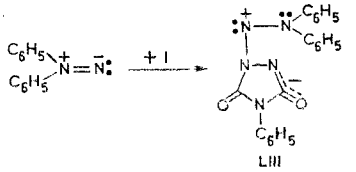
XLIX L LI

Compound LII, which has zwitterion character, was obtained in the reaction of triazolinedione I with 4- and 5-aryl-1,2-dithiole-3-thiones [139, 140].



LII

The reaction of triazolinedione I with an amino nitrene, which leads to the formation of aminoazimine LIII, is similar to this process [141-144]:

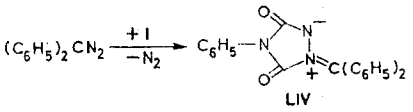


LIII

Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with Aliphatic Diazo Compounds

While the reactions of aliphatic diazo compounds with compounds that contain an activated N=N bond in an open chain (for example, with azodicarboxylic acid esters or with azodibenzoyl) have been studied quite thoroughly and in a number of cases have been used for the synthesis of heterocycles such as 1,2,4-oxadiazolines [145], data on the reaction of triazolinedione I with aliphatic diazo compounds are extremely scanty and to a certain degree contradictory.

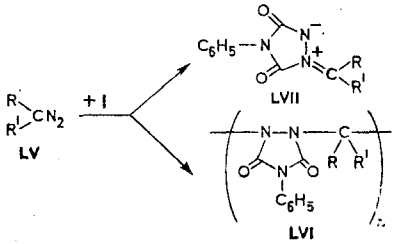
The reactions of triazolinedione I with aliphatic diazo compounds were investigated for the first time in 1965 by Bettinetii and Capretti, who showed that diphenyldiazomethane forms dipolar azomethineimine LIV upon reaction with triazolinedione I in ether solution at low temperatures [146]:



LIV

The reaction with diazofluorene proceeded similarly [147]. However, oligomers with average molecular masses of 950 to 1850 were obtained with diazomethane and diazoacetic ester [147]. A diaziridine structure was later assigned to the product of the reaction of triazolinedione I with idazoacetic ester [148]. The latter study [148] has been cited repeatedly in various papers, and the opinion that this is either a unique example of 1,1 cycloaddition of carbethoxycarbene to the N=N bond to give a diaziridine ring or an example of 1,3 cycloaddition of the diazo ester to the N=N bond with subsequent elimination of nitrogen has taken root in the literature.

A systematic study of the reactions of triazolinedione I with aliphatic diazo compounds with various structures showed that triazolinedione I reacts rapidly in the cold (with nitrogen evolution) with virtually any diazo compounds; however, the character of the products depends on the structure of the diazo compound — the simplest diazoalkanes, viz., α-diazo carbonyl compounds LV, form oligomers LVI with degrees of polymerization ranging from two to six in all cases [149]:



LV LVII LVI

The data presented above refute the diaziridine structure of the products of the reaction of triazolinedione I with ethyl diazoacetate [148]: The isolated substance had the same constants as those indicated in [148], but, according to a determination of the molecular mass, it is a trimer.

The reaction of triazolinedione I with diaryldiazomethanes or with an aryldiazomethane, that has a strong electron-acceptor substituent proceeds via a different pathway: In the case

of large amounts of diazo compounds LV it has been shown that they form azomethineimines LVII [150].

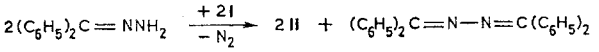
Azomethineimines LVII are brightly colored (from yellow to dark-violet) extremely reactive dipolar compounds that can be successfully used for the construction of various complex heterocyclic systems. Thus, for example, they can be used as 1,3 dipoles in reactions involving 1,3 cycloadditions to various dipolarophiles, viz., ethyl acrylate, dimethyl fumarate, dimethyl maleate, dimethyl acetylenedicarboxylate, and norbornene.

Similar dipolar systems, also based on aryldiazomethanes and triazolinedione I, were obtained by Regitz and co-workers [151]. In the opinion of these authors, unstable azomethineimines, which can be detected only in the form of derivatives with ethanol, are obtained in the case of α-diazo carbonyl compounds and alkyl-substituted and certain aryl-substituted diazo compounds. At the same time, when a diene fragment is present in the starting diazo compound, the reaction with triazolinedione I proceeds via a mechanism of the 1,4 cycloaddition type, in which the diene system turns out to be more active than the diazo group.

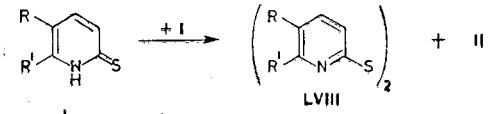
4-Phenyl-1,2,4-triazoline-3,5-dione as an Oxidizing Agent

According to the data in [152], triazolinedione I is capable of oxidizing alcohols to carbonyl compounds. However, it was later shown [18, 19] that only reactive alcohols of the alkylarylmethanol type are oxidized via this pathway.

Triazolinedione I, acting as an oxidizing agent, converts benzophenone hydrazone to its azine [153]:



The oxidizing properties of triazolinedione I are also manifested in reactions with N-unsubstituted 2-thiopyridones, which do not give Diels–Alder adducts or substitutive addition products with triazolinedione I but are converted to the corresponding disulfides LVIII [154]:

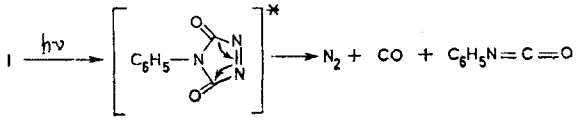


LVIII

R = R' = H ; R-R' = $(CH_2)_4$

Photolytic and Thermal Transformations of 4-Phenyl-1,2,4-triazoline-3,5-dione

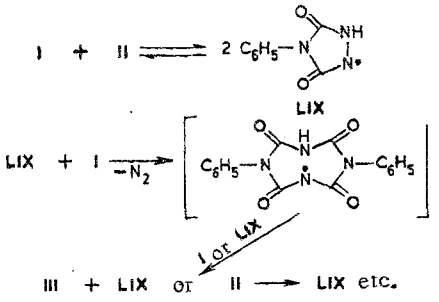
When triazolinedione I is irradiated with UV light in acetonitrile, methylene chloride, or benzene (Pyrex, λ_{max} 313 nm), it undergoes decomposition to nitrogen, carbon monoxide, and phenyl isocyanate [17]. The quantum yields (in acetonitrile) are $F_c^{532} = 0.016 \pm 20\%$ and $F_c^{313} = 0.045 \pm 10\%$. The experimental data are in agreement with a mechanism that implies the synchronous elimination of nitrogen and carbon monoxide:



However, it has not yet been possible to draw definite conclusions regarding the character of the excited state of triazolinedione I.

As compared with many other azo carbonyl compounds, triazolinedione I is characterized by considerable stability. Thus it decomposes only at 165-175°C, and the chief decomposition product, in addition to a small amount of phenyl isocyanate, is 1,3,5,7-tetraoxo-2,6-diphenylperhydro-s-triazolo [1,2-a]-s-triazole (III). An intense resonance signal of a monoradical, to which the 4-phenylurazolyl structure (LIX) has been assigned, was observed in investigations by EPR spectroscopy in solution (anisole, dioxane, and tetrahydrofuran) even at room temperature and in the solid state at temperatures above 120°C.

Its development is explained by the presence of traces of urazole II even in freshly sublimed samples of I. The catalytic effect of even very small amounts (1.5%) of admixed urazole II on the development of III has been proved by a series of experiments [17]:



Uncontrolled fragmentation, which gives phenyl isocyanate as the principal product, occurs along with the urazole-catalyzed chain reaction when triazolinedione I is subjected to thermolysis in the solid phase at 160°C. In addition, very small amounts of III and a yellow solid, the structure of which has not yet been established, are isolated [17]. At 180°C the thermal fragmentation products predominate, and urazole-catalyzed decomposition plays a very small role.

As this review was being written, ∿50 new studies of the problem under discussion appeared. Most of them deal with cycloaddition reactions [155-164]. The results of crystallographic analysis of cycloadducts are presented in several papers [165-167]. Special cases of the reaction of triazolinedione I with bicyclobutane are of interest [168, 169]. Other studies come under the heading of the "ene" reaction and substitutive addition [170, 171]. Various conditions for the transformation of the triazolinedione ring are presented in [172-175]. A simple method for the electrolytic synthesis of triazolinedione I is described in [176]. Jones [177] describes an unusual example of the production of an azomethineimine on the basis of I and a substituted benzofuran.

LITERATURE CITED

1. G. Schön and H. Hopf, Chem., No. 1, 165 (1981).
2. B. Gillis and J. Hagarty, J. Org. Chem., 32, 330 (1967).
3. R. Cookson, S. Gupte, J. Stevens, and C. Watts, Organic Syntheses, Vol. 51 (1971), p. 121.
4. J. Thiele and O. Stange, Ann. Chem., 283, 1 (1894).
5. R. Stolle, Chem. Ber., 45, 273 (1912).
6. R. Cookson, S. Gilani, and J. Stevens, Tetrahedron Lett., No. 14, 615 (1962).
7. J. Strickler and W. Prikle, J. Org. Chem., 31, 3444 (1966).
8. W. Ried and S.-H. Lim, Ann. Chem., 129 (1973).
9. J. Sauer and B. Schroder, Chem. Ber., 100, 678 (1967).
10. H. Wamhoff and K. Wald, Org. Prep. Proced. Int., 7, 251 (1975).
11. J. Moore, R. Muth, and R. Sorace, J. Org. Chem., 39, 3799 (1974).
12. D. Barton, D. Lester, and S. Ley, Chem. Commun., No. 6, 276 (1978).
13. M. Burrage, R. Cookson, S. Gupte, and J. Stevens, J. Chem. Soc., Perkin Trans. II, No. 13, 1325 (1975).
14. J. Gardlik and L. Paquette, Tetrahedron Lett., No. 38, 3597 (1979).
15. Y. Kashman and O. Awerbouch, Tetrahedron, 31, 54 (1975).
16. O. V. Sverdlova, Electronic Spectra in Organic Chemistry [in Russian], Khimiya, Leningrad (1973), p. 118.
17. H. Wamhoff and K. Wald, Chem. Ber., 110, 1699 (1977).
18. L. Dao and D. Mackay, Chem. Commun., No. 9, 326 (1976).
19. L. Dao and D. Mackay, Can. J. Chem., 57, 2727 (1979).
20. A. I. Konovalov, I. P. Breus, I. A. Sharagin, and V. D. Kiselev, Zh. Org. Khim., 15, 361 (1979).
21. W. Adam, O. de Lucchi, and I. Erden, J. Am. Chem. Soc., 102, 4806 (1980).
22. W. Adam and O. de Lucchi, Tetrahedron Lett., No. 45, 4367 (1979).
23. T. Sasaki, S. Eguchi, M. Sugimotu, and F. Hibi, J. Org. Chem., 37, 2317 (1972).
24. P. Gassman and R. Hoye, J. Am. Chem. Soc., 103, 2496 (1981).
25. C. Davies and J. Davies, J. Chem. Soc., Perkin Trans. I, No. 22, 2390 (1976).
26. C. Boan and L. Skattebol, J. Chem. Soc., Perkin Trans. I, No. 12, 1568 (1978).
27. C. Lee and D. Taylor, J. Chem. Soc., Perkin Trans. I, No. 12, 1463 (1977).
28. M. Poutsma and P. Ibarbia, J. Am. Chem. Soc., 93, 440 (1971).
29. T. Levek and E. Kiefer, J. Am. Chem. Soc., 98, 1875 (1976).

30. S. Wratten and D. Faulkner, Tetrahedron Lett., No. 11, 961 (1978).
31. D. Pasto and A. Chen, Tetrahedron Lett., No. 30, 2995 (1972).
32. J. Castellano, M. Brana, M. Tamayo, and J. Soto, Tetrahedron Lett., No. 47, 4141 (1977).
33. R. Wildox, R. Pagni, H. Hasseneen, and G. Gabalka, J. Org. Chem., 46, 1931 (1981).
34. T. Wagner-Jauregg, Synthesis, No. 10, 769 (1980).
35. M. Christ and M. Lechner, Angew. Chem., 87, 815 (1975).
36. E. Gustorf, D. White, B. Kim, D. Hess, and J. Leitich, J. Org. Chem., 35, 1155 (1970).
37. W. Adam and O. de Lucchi, Tetrahedron Lett., No. 10, 929 (1981).
38. T. Sasaki, T. Manabe, and K. Hayakawa, Tetrahedron Lett., No. 27, 2579 (1981).
39. C. Anderson, J. Bremner, I. McCay, and R. Warrener, Tetrahedron Lett., No. 10, 1255 (1968).
40. R. Hoffman and J. Csomor, Chem. Ber., 109, 1577 (1976).
41. A. Bursics, M. Murray, and F. Stone, J. Organomet. Chem., 111, 31 (1976).
42. W. Friedrichsen, W. Schroer, and R. Schmidt, Ann. Chem., No. 5, 793 (1976).
43. T. Debaermacker, W. Schröer, and W. Friedrichsen, Ann. Chem., No. 3, 502 (1981).
44. R. Askani and J. Chesich, Chem. Ber., 106, 8 (1973).
45. T. Imagawa, N. Sueda, and M. Kawanisi, Chem. Commun., No. 6, 388 (1972).
46. D. Kaufmann and A. de Meijere, Tetrahedron Lett., No. 9, 779 (1979).
47. M. Serve and D. Jerina, J. Org. Chem., 43, 2711 (1978).
48. D. Danion, B. Arnold, and M. Regitz, Angew. Chem., Int. Ed., 20, 113 (1981).
49. D. Findlay, M. Roy, and S. McLean, Can. J. Chem., 50, 3186 (1972).
50. H. Prinzbach, H. Rabsch, and D. Hunkler, Tetrahedron Lett., No. 7, 649 (1978).
51. J. Meaetows and D. Williams, Tetrahedron Lett., No. 45, 4373 (1980).
52. M. Lindey and D. Williams, Tetrahedron Lett., No. 45, 4377 (1980).
53. J. Berson and S. Olin, J. Am. Chem. Soc., 91, 777 (1969).
54. W. Adam and O. de Lucchi, Angew. Chem., 92, 815 (1980).
55. W. Adam, I. Erden, and O. Cox, J. Org. Chem., 44, 861 (1979).
56. T. Sasaki, K. Kanematsu, and K. Hayakawa, Chem. Commun., No. 1, 80 (1970).
57. A. Evnin, R. Miller, and G. Evanega, Tetrahedron Lett., No. 56, 5863 (1968).
58. R. Warrener, E. Nunn, and M. Paddon-Row, Tetrahedron Lett., No. 27, 2355 (1976).
59. L. Paquette, J. Am. Chem. Soc., 92, 5765 (1970).
60. R. Huisgen, W. Konz, and G. Gream, J. Am. Chem. Soc., 92, 4105 (1970).
61. G. Schroder, G. Kirsch, J. Oth, R. Huisgen, W. Konz, and U. Schnegg, Chem. Ber., 104, 2405 (1971).
62. R. Askani, T. Hornykiewytsch, W. Schwertfeger, and M. Jansen, Chem. Ber., 113, 2154 (1980).
63. G. Wells, Y. Hanzawa, and L. Paquette, Angew. Chem., 91, 578 (1979).
64. R. Cookson, S. Gilani, and J. Stevens, J. Chem. Soc., C, No. 19, 1905 (1967).
65. J. Jenkins, R. Doehner, and L. Paquette, J. Am. Chem. Soc., 102, 2131 (1980).
66. L. Paquette, R. Doehner, and J. Jenkins, J. Am. Chem. Soc., 102, 1188 (1980).
67. A. Anastassiou and R. Cellura, Tetrahedron Lett., No. 12, 911 (1970).
68. A. Anastassiou and M. Yakali, Chem. Commun., No. 1, 92 (1972).
69. M. Zander, Chem. Ber., 107, 1406 (1974).
70. J. Kalo, J. Photis, L. Paquette, E. Vogel, and D. Ginsburg, Tetrahedron, 32, 1013 (1976).
71. M. Bohm and R. Gleiter, Tetrahedron, 36, 3209 (1980).
72. R. Askenazi, R. Geliter, W. Philipsborn, P. Bigler, and D. Ginsburg, Tetrahedron, 37, 127 (1981).
73. M. Korat, D. Tatarsky, and D. Ginsburg, Tetrahedron, 28, 2315 (1972).
74. C. Amith and D. Ginsburg, Tetrahedron, 30, 3415 (1974).
75. J. Kalo and D. Ginsburg, Tetrahedron, 34, 2155 (1978).
76. M. Kaffory, Acta Cryst., B37, 268 (1981).
77. M. Askenazi, R. Macfarlane, W. Vertling, H. Wamhoff, K. Wald, and D. Ginsburg, Angew. Chem., Int. Ed., 19, 933 (1980).
78. E. Knaus, F. Pasutto, and C. Giam, J. Heterocycl. Chem., 11, No. 5, 843 (1974).
79. R. Kreher and H. Herd, Tetrahedron Lett., No. 20, 1661 (1976).
80. A. Padwa and F. Nobs, Tetrahedron Lett., No. 2, 93 (1978).
81. T. Toda and T. Takase, Heterocycles, 331 (1978).
82. J. Keana and R. Morse, Tetrahedron Lett., No. 25, 2113 (1976).
83. P. B. Terent'ev, A. N. Kost, and V. G. Kartsev, Khim. Geterotsikl. Soedin., No. 5, 702 (1976).
84. P. B. Terent'ev, N. G. Kotova, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 5, 651 (1978).

85. N. P. Shusherina and M. Said, Zh. Org. Khim., 12, 2270 (1976).
86. N. P. Shusherina, M. Said, and T. Likhomanova, Zh. Org. Khim., 14, 841 (1978).
87. A. Evnin, D. Arnold, L. Karnischky, and E. Strom, J. Am. Chem. Soc., 92, 6218 (1970).
88. M. Breuninger, R. Schweisinger, B. Gallen-Kamp, K. Muller, H. Fritz, D. Hunkler, and H. Prinzbach, Chem. Ber., 113, 3161 (1980).
89. M. Korat and D. Ginsburg, Tetrahedron, 29, 2373 (1973).
90. S. Gilani and D. Triggle, J. Org. Chem., 31, 2397 (1966).
91. D. Barton, T. Shiori, and D. Widdowson, J. Chem. Soc., C, No. 10, 1969 (1971).
92. A. Garry, J. Midgley, W. Whalley, and B. Wilkins, J. Chem. Soc., Perkin Trans. I, No. 8, 809 (1977).
93. A. Solo, H. Sachdev, and S. Gilani, J. Org. Chem., 30, 769 (1965).
94. D. Aberhart and A. Hsu, J. Org. Chem., 41, 2098 (1976).
95. D. Morris, D. Williams, and A. Norris, Chem. Commun., No. 9, 424 (1981).
96. G. Mehta, Indian J. Chem., 7, 565 (1969).
97. Y. Nomura, N. Masai, and Y. Takeuchi, Chem. Commun., No. 8, 288 (1974).
98. M. Wyvratt and L. Paquette, Tetrahedron Lett., No. 28, 2433 (1974).
99. V. R. Skvarchenko and N. P. Koshkina, Zh. Org. Khim., 15, 2367 (1979).
100. N. P. Koshkina, Master's Dissertation, Moscow State University (1982).
101. W. Adam, L. Arias, and O. de Lucchi, Synthesis, No. 7, 543 (1981).
102. D. Pasto and J. Borchardt, J. Am. Chem. Soc., 96, 6944 (1974).
103. J. Berridge, J. Forrester, B. Toulger, and A. Gilbert, J. Chem. Soc., Perkin Trans. I, No. 11, 2425 (1980).
104. C. Seymour and F. Greene, J. Am. Chem. Soc., 102, 6384 (1980).
105. D. Pasto and A. Chen, J. Am. Chem. Soc., 93, 2562 (1971).
106. T. Katz and N. Acton, J. Am. Chem. Soc., 95, 2738 (1973).
107. W. Weker, I. Erden, and A. de Meijere, Angew. Chem., 92, 387 (1980).
108. G. Butler, L. Guilbault, and S. Turner, J. Pol. Sci., B, No. 2, 115 (1971).
109. K. Wagener and G. Butler, J. Org. Chem., 38, 3070 (1973).
110. K. Wagener, S. Turner, and G. Butler, J. Org. Chem., 37, 1454 (1972).
111. S. Turner, L. Guilbault, and G. Butler, J. Org. Chem., 36, 2838 (1971).
112. H. Prinzbach, K. Weidmann, S. Trah, and L. Knothe, Tetrahedron Lett., No. 27, 2541 (1981).
113. I. Erden and A. de Meijere, Tetrahedron Lett., No. 19, 1837 (1980).
114. A. Hassner, D. Tang, and J. Keogh, J. Org. Chem., 41, 2102 (1976).
115. H. Gotthardt and C. Weisshuhn, Chem. Ber., 111, 3171 (1978).
116. E. Cawkill, W. Ollis, C. Ramsden, and G. Powson, Chem. Commun., No. 12, 439 (1976).
117. A. Hasenhündl, K. Rapp, and J. Daub, Chem. Lett., No. 5, 597 (1979).
118. P. Cernuschi and C. De Micheli, Tetrahedron Lett., No. 41, 3667 (1977).
119. E. Vogel, H. Runzheimer, F. Hogrefe, B. Baasner, and J. Lex, Angew. Chem., 89, 909 (1977).
120. W. Roth and M. Martin, Tetrahedron Lett., No. 47, 4695 (1967).
121. Y. Kobayashi, T. Nakano, K. Shirahashi, A. Takeda, and I. Kumadaki, Tetrahedron Lett., No. 21, 4615 (1980).
122. T. Hoye, K. Bottorff, C. Caruso, and J. Dellaria, J. Org. Chem., 45, 4287 (1980).
123. S. Ohashi, K. Leong, K. Matyjaszenski, and G. Butler, J. Org. Chem., 45, 3467 (1980).
124. S. Ohashi and G. Butler, J. Org. Chem., 45, 3472 (1980).
125. W. Pirkle and J. Stickler, Chem. Commun., No. 15, 760 (1967).
126. J. Schiloff and N. Hunter, Tetrahedron Lett., No. 42, 3773 (1976).
127. A. Laporterie, J. Dubac, and U. Lesbre, J. Organomet. Chem., 101, 187 (1975).
128. S. Ohashi, W. Ruch, and G. Butler, J. Org. Chem., 46, 614 (1981).
129. K. Hayakawa and H. Schmid, Helv. Chim. Acta, 60, 1551 (1977).
130. S. Danishefsky, R. McKee, and K. Singh, J. Org. Chem., 41, 2934 (1976).
131. W. Bottomley, G. Boyd, and R. Monteil, J. Chem. Soc., Perkin Trans. I, No. 4, 843 (1980).
132. W. Bottomley and G. Boyd, Chem. Commun., No. 16, 790 (1980).
133. A. Grady and W. Butler, J. Org. Chem., 45, 1232 (1980).
134. J. Sasson and J. Kabovitz, J. Org. Chem., 40, 3672 (1975).
135. N. P. Shusherina and M. Said, Dokl. Akad. Nauk SSSR, 233, 606 (1977).
136. G. Barrett and R. Walker, Tetrahedron, 32, 571 (1976).
137. H. Wamhoff and K. Wald, Chem. Ber., 110, 1716 (1977).
138. F. Yoneda, S. Matsumoto, and M. Higuchi, Chem. Commun., No. 14, 551 (1974).
139. V. N. Drozd and G. S. Bogomolova, Zh. Org. Khim., 13, 2012 (1977).
140. V. N. Drozd, V. M. Fedoseev, G. S. Bogomolova, V. V. Sergeichuk, N. M. Semenenko, and A. A. Mandrugin, Zh. Org. Khim., 16, 198 (1980).
141. K. Koch and E. Fahr, Angew. Chem., 82, 636 (1970).

142. J. Weidenborner, E. Fahr, M. Richter, and K. Koch, Angew. Chem., 85, 229 (1973).
143. W. Schmitt-Sody, E. Fahr, and K. Koch, Ann. Chem., No. 10, 1509 (1979).
144. E. Fahr and D. Koch, Ann. Chem., No. 2, 219 (1980).
145. I. Korobizina and L. Rodina, Z. Chem., 20, 172 (1980).
146. G. Bettinetti and L. Capretti, Gazz. Chim. Ital., 95, 33 (1965).
147. W. Ried and S.-H. Lim. Ann. Chem., No. 7, 1141 (1973).
148. R. Izydore and I. McLean, J. Am. Chem. Soc., 97, 5611 (1975)
149. I. K. Korobitsyna, L. L. Rodina, and A. V. Lorkina, Zh. Org. Khim., 17, 2021 (1981).
150. L. L. Rodina, A. V. Lorkina, and I. K. Korobitsyna, Zh. Org. Khim., 18, 1119, 1986 (1982).
151. W. Bethauser, M. Regitz, and W. Theis, Tetrahedron Lett., No. 27, 2535 (1981).
152. R. Cookson, J. Stevens, and C. Watts, Chem. Commun., No. 20, 744 (1966).
153. R. Ahmed and J.Anselme, Tetrahedron, 28, 4939 (1972).
154. V. S. Pilipenko and N. P. Shusherina, Zh. Org. Khim., 16, 2444 (1980).
155. J. Erden and D. Kaufmann, Tetrahedron Lett., No. 3, 215 (1980).
156. D. Danion, B. Arnold, and M. Regitz, Angew. Chem., 93, 118 (1981).
157. H. Olsen, Angew. Chem., 94, 387 (1982).
158. T. Gilchrist, C. Rees, and D. Tuddenham, Chem. Commun., No. 15, 689 (1980).
159. L. Paquette and F. Klinger, J. Org. Chem., 47, 272 (1982).
160. W. Adam, O. de Lucchi, K. Peters, E.-M. Peters, and H. Schnering, J. Am. Chem. Soc., 104, 161 (1982).
161. J.-P. Dulcere, S. Sellers, H. Koroniak, B. Shatkin, and T. Clark, J. Org. Chem., 47, 2298 (1982).
162. B. N. Solomonov, I. A. Arkhireeva, and A. I. Konovalov, Zh. Org. Khim., 16, 1670 (1980).
163. R. Askani, R. Kirsten, and B. Dugall, Tetrahedron, 37, 4437 (1981).
164. R. Jösel and G. Schröder, Ann. Chem., No. 9, 1428 (1980).
165. W. Reischl, E. Altmann, and E. Zbiral, Monatsh. Chem., 113, 427 (1982).
166. M. Meerssche, B. Tinant, G. Germain, and J. Declercq, Bull. Soc. Chim. Belg., 91, 205 (1982).
167. W. Klobucar, L. Paquette, and Y. Blount, J. Org. Chem., 46, 4021 (1981).
168. M. Chang and D. Dougherty, J. Org. Chem., 46, 4092 (1981).
169. R. Amey and B. Smart, J. Org. Chem., 46, 4090 (1981).
170. W. Adam, O. de Lucchi, and K. Hiel, Chem. Ber., 115, 1982 (1982).
171. L. Paquette, L. Hertel, R. Gleiter, M. Böhm, M. Beno, and G. Christoph, J. Amer. Chem. Soc., 103, 7106 (1981).
172. E. Fahr, M. Richter, W. Schmitt-Sody, and R. Elbert, Tetrahedron Lett., No. 34, 3269 (1980).
173. J. Hall, W. Bidgard, J. Fargher, and M. Jones, J. Org. Chem., 47, 1459 (1982).
174. J. Pincock and L. Druert, Tetrahedron Lett., No. 34, 3251 (1980).
175. W. Speckamp, Rec. Trav. Chim., 100, No. 10, 345 (1981).
176. H. Wamhoff and G. Kunz, Angew. Chem., 93, 832 (1981).
177. D. Jones, Chem. Commun., No. 13, 766 (1982).