ADDITION REACTIONS IN THE 1-AZIRINE SERIES

A. V. Eremeev and R. S. Él'kinson

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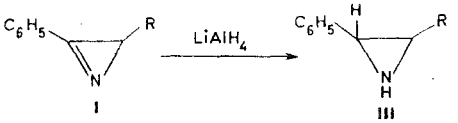
The addition reactions of 1-azirines were examined. The possibility of the use of 1-azirines as starting compounds in the synthesis of diverse nitrogen-containing acyclic, bicyclic, and heterocyclic compounds was demonstrated.

The chemistry of 1-azirine has been undergoing intensive development for the last 10 years. This development is due to the uniqueness of the structure of 1-azirine — it is a three-membered nitrogen heterocycle that contains a C=N bond and displays high reactivity in cycloaddition, thermolysis, and photolysis reactions. The synthesis, cycloaddition reactions [2], and utilization of 1-azirines for the construction of heterocyclic systems have been examined in reviews [1-4]. However, the reactivities of 1-azirines in addition reactions have been examined only extremely superficially in [1, 3, 4]. Such reactions in the 1-azirine series are doubtless of interest in the search for methods for the synthesis of functionally substituted aziridines and diverse acyclic, heterocyclic, and bicyclic systems [5-10], as well as in the solution of one of the most general problems of organic chemistry, viz., the addition of reagents to systems that contain a π bond.

The existence of nucleophilic (N) and electrophilic (C) centers in 1-azirines is responsible to a great degree for the peculiarities of their chemical properties.

I. Reduction of 1-Azirines by Complex Metal Hydrides

Metal hyrides reduce 1-azirines to the corresponding aziridines:

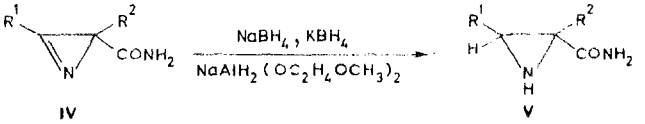


I II III

I R=CH_3 97%; II R=C_6H_5 85%

This reaction has been used primarily to prove structures [7]; however, the high yields and stereospecificity [6, 8] make it a convenient method for the synthesis of cis-2,3-disubstituted aziridines. The stereospecificity of the reaction is determined by the possibility of the addition of a hydride ion only on the unsubstituted side of azirines I and II [8].

The reaction of 2,3-diaryl-3-carbamoylazirines IV with sodium and potassium borohydrides and sodium alkoxyaluminum hydrides in benzene leads to 2,3-diaryl-3-carbamoylaziridines V; the amido group of azirine IV is not reduced by even 2 moles of the reducing agent [10]:



IV V

$R^1=R^2=C_6H_5$; $R^1=C_6H_5$, $R^2=p$-ClC_6H_4; $R^1=C_6H_5CH_2$, $R^2=C_6H_5$

II. Reactions Involving Nucleophilic Addition to 1-Azirines

Carbanions. 2,4-Diphenylpyrrole (IX) is formed in 73% yield in the reaction of 2-phenylazirine (VI) with acetophenone in the presence of the methylsulfinyl carbanion [11]:

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
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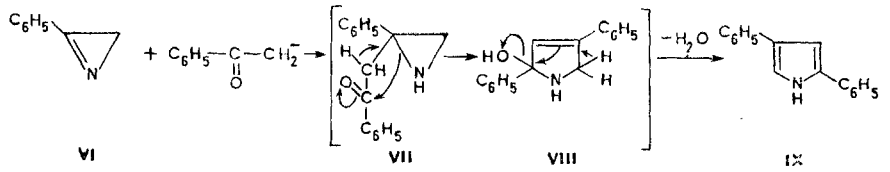
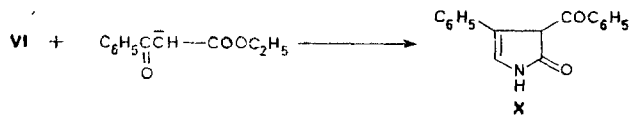
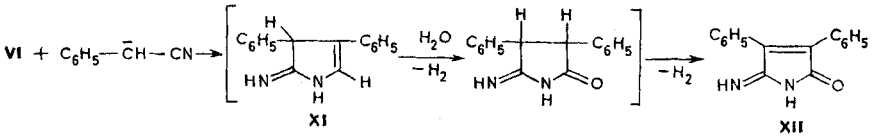


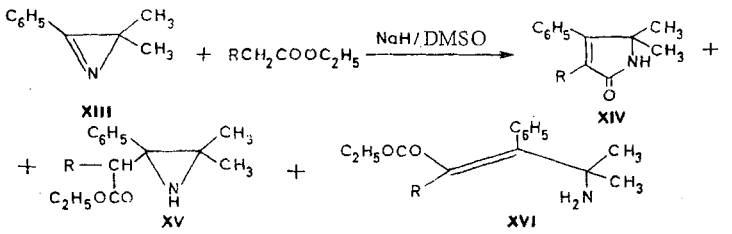
Similarly, azirine VI reacts with ethyl benzoylacetate to give 3-benzoyl-4-phenyl-2-oxopyrroline (X):



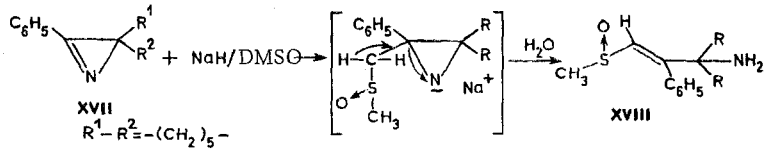
In the case of benzyl cyanide the reaction gave, instead of the expected 2-amino-3,4-diphenylpyrrole (XI), 2-oxo-5-imino-3,4-diphenylpyrroline (XII), the formation of which is postulated as being the result of reaction of the initially formed aminopyrrole XI with water and subsequent dehydrogenation to pyrroline XII:



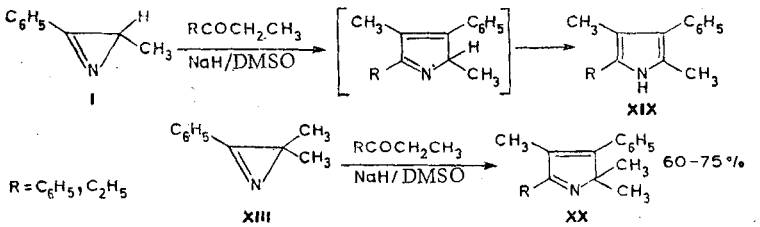
In the case of 3,3-dimethyl-2-phenylazirine (XIII) the reaction with ethyl alkyl(aryl)-acetates in the presence of sodium hydride in dimethyl sulfoxide (DMSO) gives substituted 2-oxopyrroline XIV, ester XV, and amino ester XVI [12]:



Azirine XVII reacts with sodium dimsyl at 25°C to give amino sulfoxide XVIII [13]:

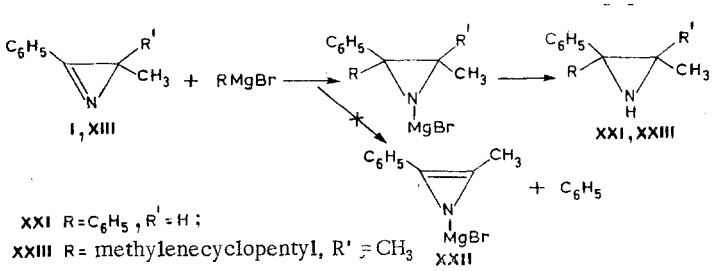


1-Azirines react with ketone or nitrile carbanions to give pyrroles in high yields [13]:



This reaction is considered to be the most convenient method for the synthesis of 2H-pyrroles [13].

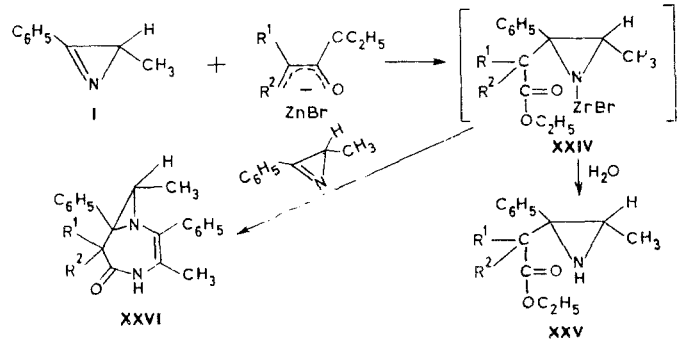
Cryptobases. 1-Azirines react with Grignard reagents to give aziridines XXI [7, 14]; as in the case of the reaction with lithium aluminum hydride, stereospecificity of the reaction is observed [15]. This reaction is anomalous for ketimines [16]. The Grignard reagent usually splits out the α-hydrogen atom of the ketimine to give an enamino anion, which then undergoes conversion to an enamine (2-azirine XXII in this case). However, the latter could not be isolated [7]:



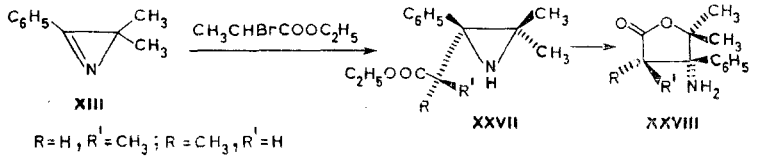
XXI R=C_6H_5, R'=H;
XXIII R= methylenecyclopentyl, R' = CH_3

Organolithium compounds and Grignard reagents obtained from γ-haloallenes react with 1-azirines to give the corresponding aziridines XXIII [17].

1-Azirines react with Reformatskii reagents to give aziridines XXV and XXVI [18]:

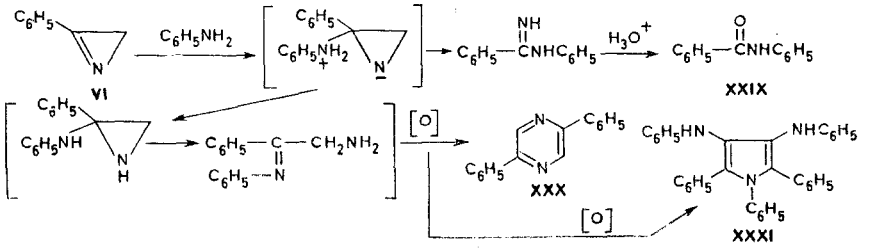


The Reformatskii reaction of α-bromo esters with 3,3-dimethyl-2-phenylazirine (XIII) gives diastereomeric aziridines XXVII, which are converted to amino lactones XXVIII under the influence of HF in pyridine [19]:



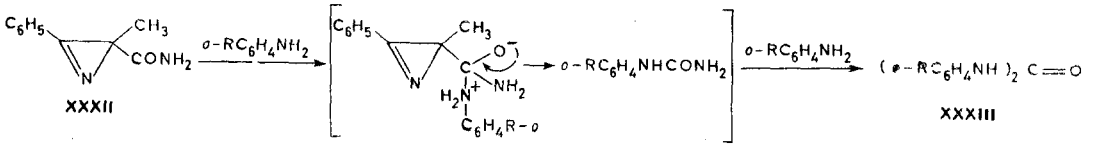
R=H, R'=CH_3; R=CH_3, R'=H

Bases. Six types of compounds, viz., benzanilides, pyrazines, phenacylanilines, indoles, pyrroles, and enediamines, are formed as a result of the reaction of 2-phenylazirine (VI) with substituted anilines and subsequent acid hydrolysis [20]. In particular, primarily benzanilide (XXIX), as well as 2,5-diphenylpyrazine (XXX) and 3,4-dianilino-1,2,5-triphenylpyrrole (XXXI), is obtained with aniline. The formation of XXIX-XXXI is due to initial nucleo-



philic attack by the amine on the carbon atom of the C=N bond through a step involving an intermediate aziridinium [sic] anion, which undergoes conversion via three pathways proposed by the authors.

In contrast to azirine VI, 3-carbamoylazirines react with o-chloroaniline and o-toluidine to give N,N'-diarylureas XXXIII with the liberation of ammonia [21, 22]:

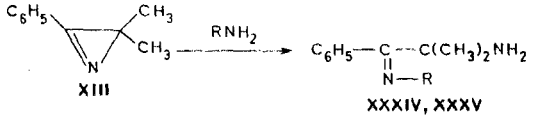


XXXII

XXXIII

R = Cl, CH_3

Aliphatic amines react with azirine XIII to give α-aminoisobutyrophenone imines [23, 24], evidently as a result of decomposition and subsequent rearrangement of the initially formed 2-aminoaziridines — products of 1,3 addition of the nucleophilic reagent to 3,3-dimethyl-2-phenylazirine.

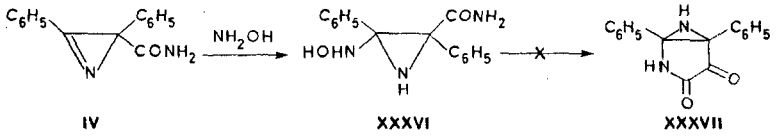


XIII

XXXIV, XXXV

XXXIV R = CH_3, XXXV R-R = -(C_6H_{11})-

The reaction of 3-carbamoyl-2,3-diarylazirine (IV) with hydroxylamine should be considered to be an excellent example of the preparation of functionally substituted aziridines [25]:



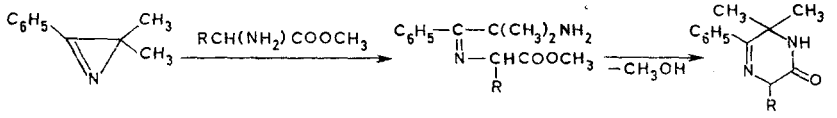
IV

XXXVI

XXXVII

The absence of intramolecular cyclization product XXXVII can be considered to be the result of a stereospecific reaction to give only trans isomer XXXVI.

A reaction that leads to a new type of heterocyclic compound, viz., 1,2,3,6-tetrahydro-2-pyrazinones XXXIX-XLVII, was discovered in an investigation of the reactions of azirine XIII with methyl esters of natural amino acids [26]. It was established in the case of the sodium salt of glycine that the corresponding Schiff bases of α-aminoisobutyrophenone, the subsequent cyclization of which leads to substituted ketotetrahydropyrazines, are formed initially:



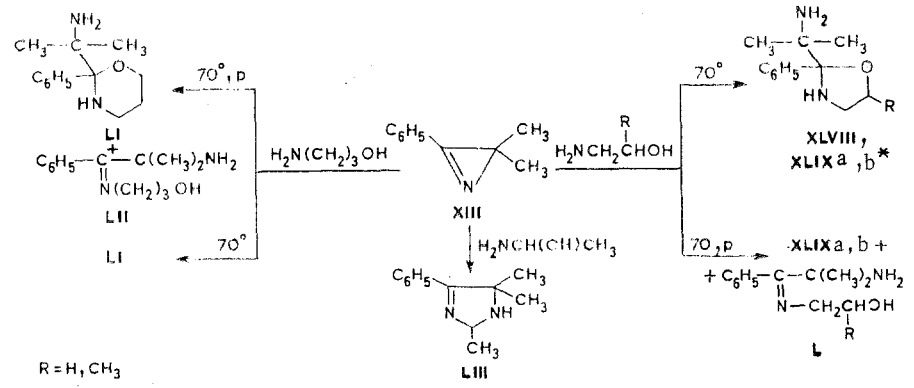
XIII

XXXVIII

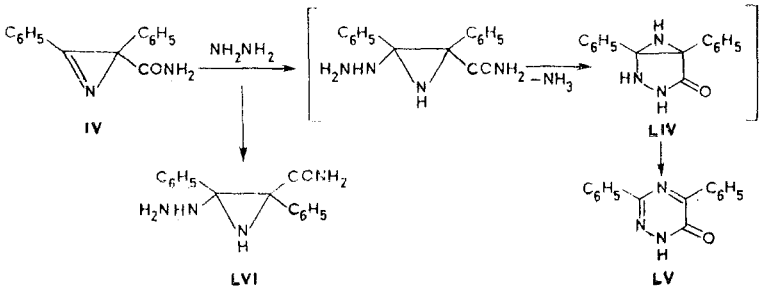
XXXIX-XLVII

XXXIX R = H; XL R = CH_3; XLI R = $CH(CH_3)_2$; XLII R = $CH_2C_6H_5$; XLIII R = CH_2COOCH_3; XLIV R = $(CH_2)_2COOCH_3$; XLV R = 3-indolyl; XLVI R = $(CH_2)_2SCH_3$; XLVII R = CH_2SCH_3

2,4,5-Substituted oxazolidines XLVIII and XLIXa,b and 2-substituted perhydro-1,3-oxazines LI, respectively, are primarily formed in the reaction of azirine XIII with β,γ-amino alcohols; side products, viz., Schiff bases of α-aminoisobutyrophenone, are obtained at elevated temperatures. The reaction of azirine XIII with 1-aminoethanol gives substituted 3-imidazoline LIII [27].

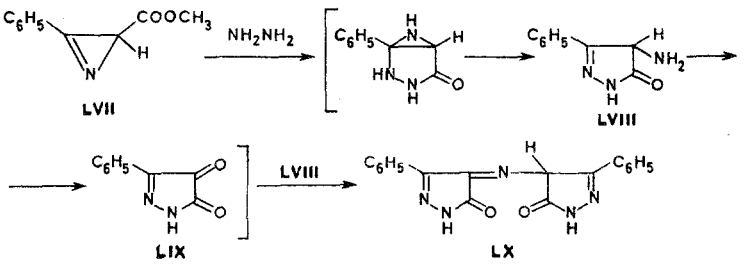


The reaction of azirine IV with hydrazine and phenylhydrazine was studied in [28, 29]. It is assumed that the resulting 1,2,4-triazin-6-one is obtained through a step involving bicyclic aziridine LIV, which undergoes opening of the aziridine ring and conversion to LV. The reaction also proceeds similarly with phenylhydrazine. In addition to the formation of triazine derivative LV, hydrazinoaziridine LVI, which evidently has a trans configuration and therefore does not undergo cyclization, was obtained in 10% yield.

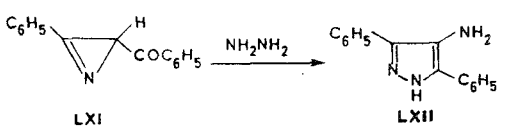


In this connection it should be noted that the nucleophilic addition of lithium aluminum hydride [7] and Grignard reagents [15] to 1-azirine is realized stereoselectively with the primary formation of cis isomers.

Azirine-3-carboxylic acid ester LVII and 3-carbamoylazirines that have one hydrogen atom in the 3 position react with hydrazine to give rubazonic acid [29]:

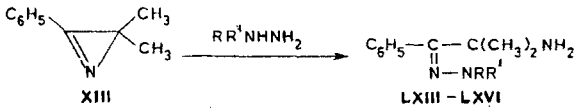


The formation of 4-amino-3,4-diphenylpyrazone (LXII) from ketone LXI and hydrazine is in agreement with the facts set forth above [30]:



Opening of the azirine ring to give α-aminoisobutyrophenone hydrazones and semicarbazone LXIII-LXVI occurs in the reaction of azirine XIII with hydrazine and its derivatives [31, 32]:

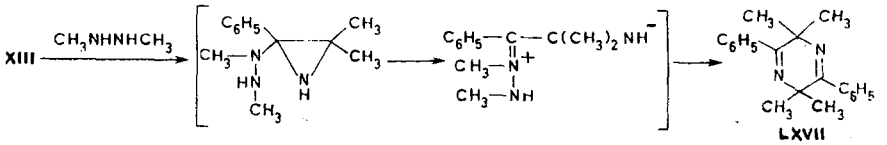
*Compounds XLIXa,b are isomers that differ with respect to the orientation of the CH_3 group.



XIII LXIII – LXVI

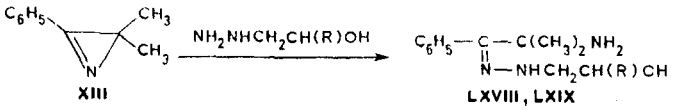
LXIII R=R¹=H; LXIV R=R¹=CH₃; LXV R=CH₃, R¹=H; LXVI R=CONH₂, R¹=H

sym-Dimethylhydrazine reacts with azirine XIII to give dihydropyrazine LXVII [31, 32]:



LXVII

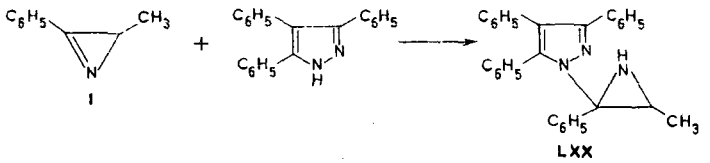
In a similar reaction with azirine XIII β-hydrazino alcohols form β-aminobutyrophenone β-hydroxyalkylhydrazones LXVIII and LXIX [27]:



LXVIII R=H, LXIX R=CH₃

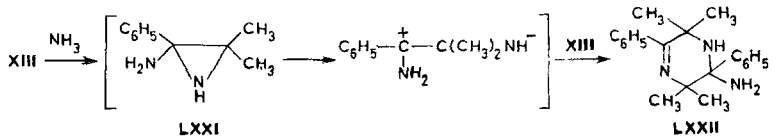
The initially formed adducts, viz., 2-hydrazinoaziridines, are evidently inclined to undergo isomerization to dipolar azomethine systems, the subsequent stabilization of which is achieved by transfer of a proton to the nucleophilic center to give α-aminoisobutyrophenone derivatives.

A rare example of the production of 2-aminoaziridines is the addition of triphenylpyrazole to 3-methyl-2-phenylazirine (I), as a result of which aziridine LXX is formed in 61% yield [33]:



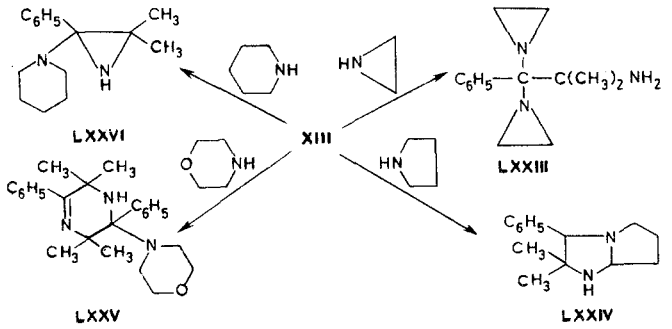
LXX

However, 2-amino-1,2,3,6-tetrahydropyrazine LXXII is formed in the reaction of azirine XIII with ammonia [23, 24]:

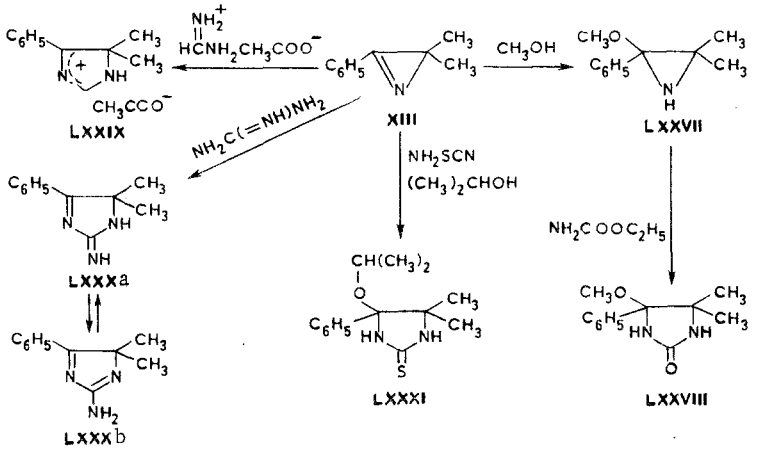


LXXI LXXII

Depending on the nature of the nucleophilic reagent, diaziridinopropane LXXIII, 1,4-diaza[3.3.0]bicyclooctane LXXIV, 2-morpholino-1,2,3,6-tetrahydropyrazine LXXV, and 2-piperidinoaziridine LXXVI, respectively, are formed in the reaction of azirine XIII with cyclic amines (aziridine, pyrrolidine, morpholine, and piperidine) [23, 24] (see following page):

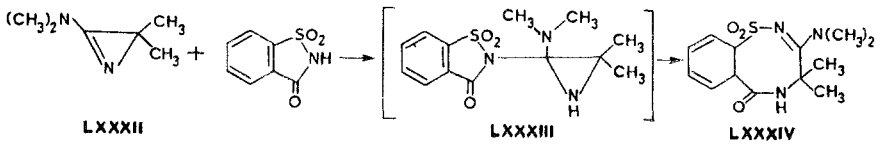


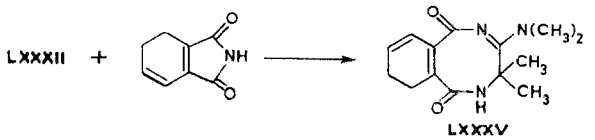
It is assumed that in this case the initial products are the corresponding 2-aminoaziridines, which, like LXXVI, undergo decomposition to give a dipolar system, the subsequent transformations of which are determined by the structure of the amine fragment.



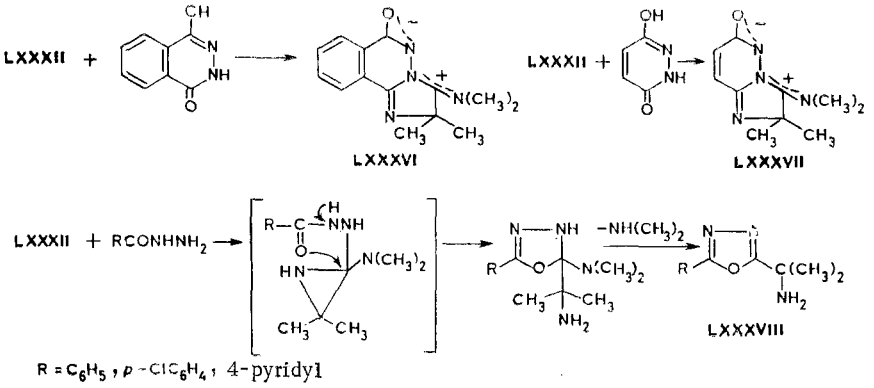
The formation of imidazole systems in reactions involving the nucleophilic addition of amides, urethane, and rhodamine to 3,3-dimethyl-2-phenylazirine has been demonstrated [34, 35]. The probable reaction pathway consists in the formation of a 2-alkoxyaziridine — the product of solvolysis of starting azirine XIII — the subsequent reaction of which with the amine component leads to the formation of an imidazole derivative with the simultaneous ejection of fragments that leave readily.

The reactions of 2-dimethylamino-3,3-dimethylazirine LXXXII) with NH-acid compounds such as saccharin and phthalimide lead to eight-membered heterocyclic systems LXXXIV and LXXXV as a result of hypothetical intramolecular rearrangement of addition product LXXXIII with subsequent ring expansion [36]:

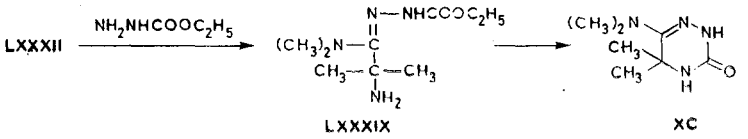




Azirine LXXXII reacts with phthalhydrazine and maleic hydrazide to give zwitterionic compounds LXXXVI and LXXXVII [37, 38] and with aromatic carboxylic acid hydrazides to give substituted 1,3,4-oxadiazoles LXXXVIII:

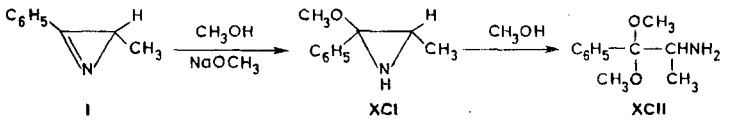


A similar reaction with ethyl carbazinate gives amino ester LXXXIX, which is readily cyclized to 4,5-dihydro-1,2,4-triazin-3-one (XC):

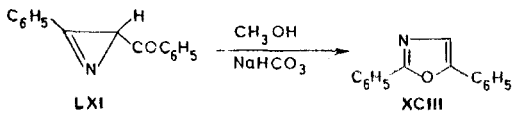


Similarly, LXXXII reacts with oxamoyl- and oxalohydrazides to give substituted triazines [39].

Azirine I adds alcohol in the presence of catalytic amounts of the alkoxide to give alkoxyaziridine XCI and acetal XCII [6]:

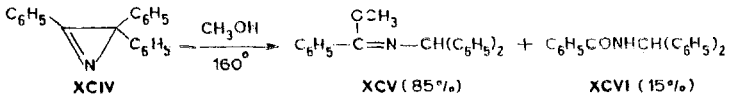


On the other hand, oxazole XCIII was isolated when azirine LXI was heated in methanol [30]:



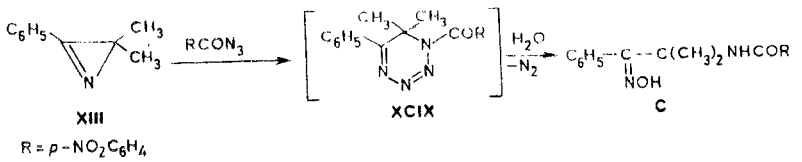
It is assumed that the initially formed alkoxyaziridine undergoes rearrangement to oxazole XCIII in this case.

1-Azirines XCIV reactions with alcohols in the presence of catalytic amounts of the alkoxide at 160°C with cleavage of the C–C bond to give imido esters XCV and amides XCVI [40]:



Only the corresponding alkoxyaziridines could be isolated in the reaction of 3,3-dimethyl-2-phenylazirine (XIII) with alcohol.

Organic Azides. The reaction of p-nitrobenzoyl azide with azirine XIII leads to α-aminoisobutyrophenone oxime C [41], evidently through intermediate tetrazine XCIX, as in the addition of azides to nitriles and isonitriles. A similar reaction of azirine XIII with ethyl α-azidocinnamate gives an equilibrium mixture of minio-enamine tautomeric forms of α-aminoisobutyrophenone oxime (CI and CII) and a small amount of ethyl 3-phenylazirine-2-carboxylate (CIII), which is formed as a result of partial thermal decomposition of the starting vinyl azide:

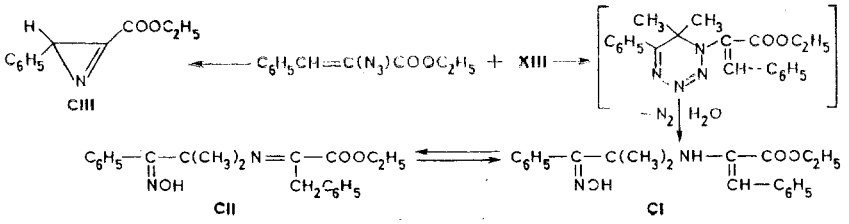


XIII

R = p-$NO_2C_6H_4$

XCIX

C

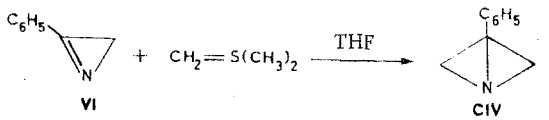


CIII

CII

CI

Ylids. One of the most interesting reactions involving nucleophilic addition to 1-azirine was realized in [42]. 1-Azabicyclo[1.1.0]butane CIV (60% yield) was obtained for the first time by treatment of 2-phenylazirine (VI) with dimethylmethylenesulfurane in tetrahydrofuran (THF):

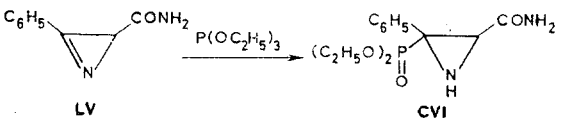


VI

CIV

III. Addition of Organophosphorus Compounds to 1-Azirines

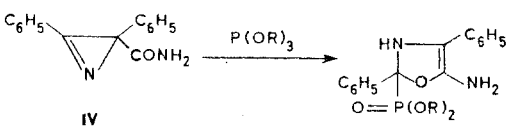
The reaction of 3-carbamoyl-2-phenylazirine (CV) with triethyl or trimethyl phosphite in ethanol leads to 2-aziridinylphosphonates in 60% yields [43]:



LV

CVI

However, oxazolines XVII were obtained in the reaction of 3-carbamoyl-2,3-diphenylazirine (IV) with trialkyl phosphites [43]:

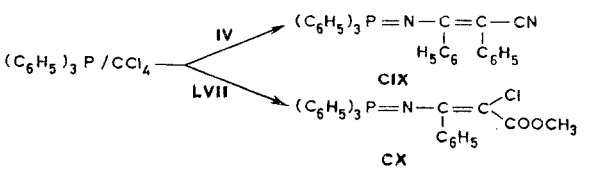


IV

CVII

2,5-Dicarbamoyl-3,6-diphenylpyrazine (CVIII), which is evidently the product of dimerization of starting azirine CV, was obtained as a result of the reaction of azirine CV with diethyl phosphite [43].

Instead of the expected substituted azirines, phosphoranes CIX and CX were isolated when azirines IV and LVII were treated with triphenylphosphine and carbon tetrachloride [44]:



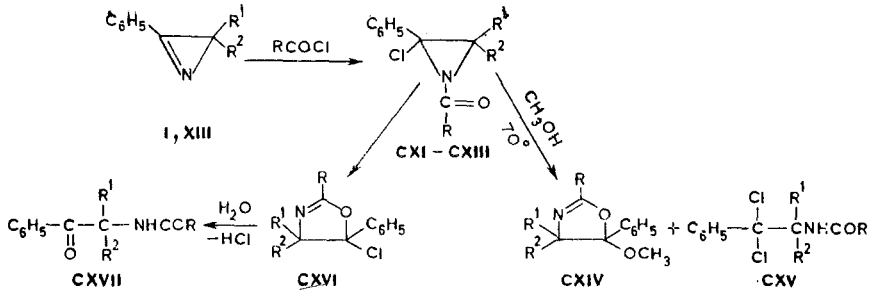
CIX

CX

IV. Electrophilic Addition of Acid Chlorides and Anhydrides to 1-Azirines

The low basicity of 1-azirine, which is determined by the significant p character of the orbital of the unshared electron pair of the nitrogen atom [45, 46] and is comparable to the basicity of acetonitrile [7], is responsible for a number of peculiarities in the behavior of 1-azirines in electrophilic addition reactions.

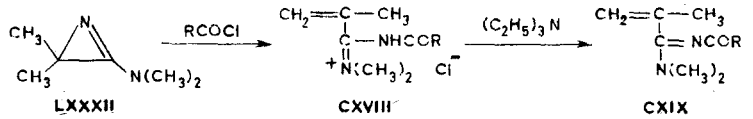
1-Azirines I and XIII react with acid chlorides to give N-benzoyl-2-chloroaziridines CXI-CXIII [7, 47-49].



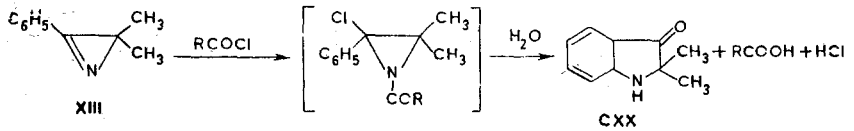
CXI, CXIV, CXV R = C_6H_5; CXII R = phthalimidomethyl; CXIII R = $CH_3C_6H_4SO_2NHCH(CH_3)$

Aziridines CXI are usually unstable and are converted to oxazolines CXIV and dichloro amides CXV upon heating and also in polar solvents [48]. Azirine XIII reacts almost quantitatively with N-phthalylglycine and N-tosylalanine acid chlorides to give N-acyl-2-haloaziridines CXII and CXIII, which readily undergo successive isomerization to 2-oxazolines CXVI and keto amides CXVII even without heating and in nonpolar solvents [49].

1,2 Cleavage of the azirine ring to give N-acylamidines CXIX occurs in the reaction of azirine LXXXII with acid chlorides [50]:

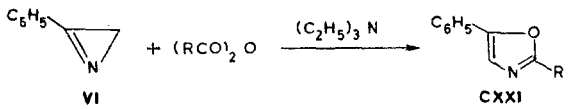


A study of the reactions of azirine XIII with unsaturated acid chlorides led to the discovery of a new type of rearrangement of N-acyl-2-haloaziridines to 2,2-disubstituted indoxyl CXX, which is accompanied by splitting out of an unsaturated acid [49]:

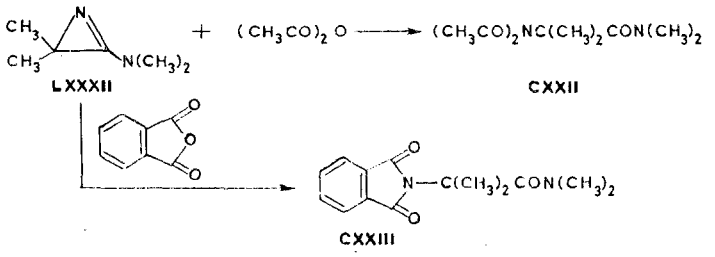


R = $CH_3CH{=}CH{-}$; $CH{=}CHOC(-CH{=}CH-){=}CH$; $C_6H_5CH{=}CH{-}$; $C_6H_5C{\equiv}C{-}$

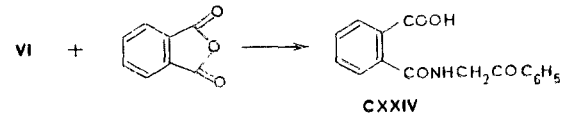
Oxazoles CXXI are formed in the reaction of azirine VI with acid anhydrides in the presence of triethylamine [11]:



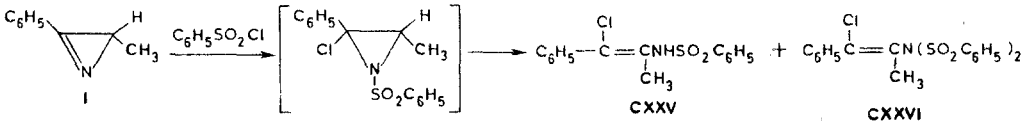
Dimethylaminoazirine LXXXII reacts with acetic and phthalic anhydrides to give, as a result of cleavage of the $C_{(3)}$–N bond, diacylamino derivatives CXXII and CXXIII, respectively [50]:



Azirine VI reacts with phthalic and maleic anhydrides to give N-phenacyl(phthalyl) and N-maleinyl monoamides CXXIV [11]:

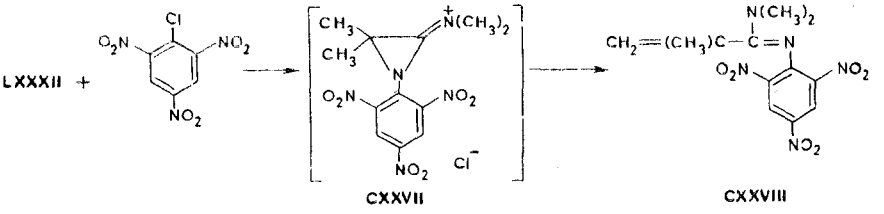


The reaction of azirine I with benzenesulfonyl chloride gives a mixture of sulfonamides CXXV and CXXVI [51]:



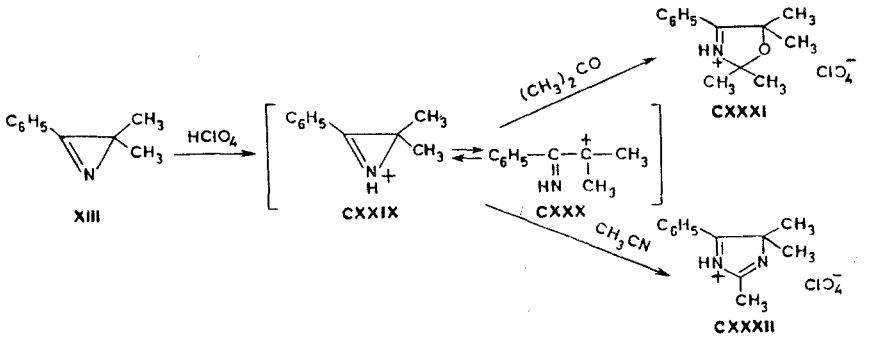
The possibility that N-sulfonylaziridines are intermediates in this reaction is not excluded since the rearrangement of N-sulfonylaziridines to vinyl sulfonamides is known [51].

Aminoaziridine CXXVII, the subsequent deprotonation and 1,2 cleavage of the ring of which lead to acrylamidine CXXVIII, is evidently formed in the reaction of azirine LXXXII with picryl chloride as a result of nucleophilic aromatic substitution [52]:



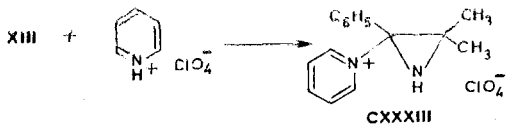
V. Reactions Involving the Addition of Acids to 1-Azirines and Acid Catalysis

The acid-catalyzed reactions of 3,3-dimethyl-2-phenylazirine (XIII) with acetone, acetonitrile, pyridine, and aniline have been investigated [53, 54]. The formation of stabilized carbonium ion CXXX, the addition of which to the C=O bond of acetone or the C≡N bond of acetonitrile leads to substituted oxazolinium (CXXXI) and imidazolium (CXXXII) perchlorates, was proposed in a study of the reaction of protonated (with anhydrous perchloric acid) azirine CXXIX with acetone and acetonitrile [53]:



Similar results were obtained in a study of the BF_3 etherate-catalyzed reaction of 1-azirines with nitriles [55].

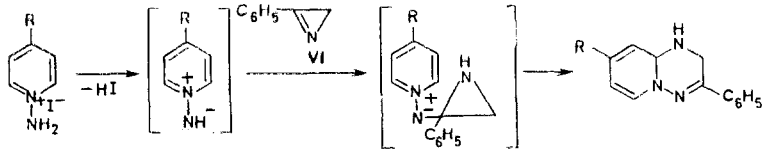
Azirine XIII reacts with pyridinium perchlorate to give stable perchlorate CXXXIII [53]:



CXXXIII

A similar structure has been proposed for the intermediate in the synthesis of 1-azirines by the Neber reaction [5].

N-Iminopyridinium hydriodides CXXXIV react with 2-phenylazirine in the presence of alkali to give pyridotriazines CXXXV [56]. Initial nucleophilic attack on azirine VI by the iminopyridinium ion with subsequent intramolecular rearrangement of resulting ylid CXXXVI to pyridotriazine CXXXV is proposed [56]. Azomethinylid systems similar to ylid CXXXVI have been previously proposed as intermediates [28, 29]:

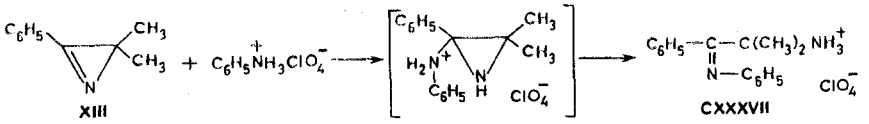


CXXXIV
R = H, CH_3

CXXXVI

CXXXV

Treatment of azirine XIII with anilinium perchlorate in acetonitrile gives perchlorate CXXXVII [54] instead of the expected addition product (similar to salt CXXXIII):

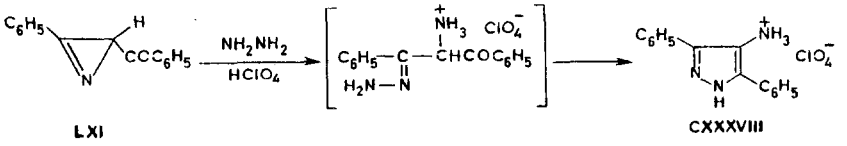


XIII

CXXXVII

The initial formation of N-(3,3-dimethyl-2-phenyl-2-aziridinyl)anilinium perchlorate, which, as a result of proton transfer, undergoes 1,3 cleavage of the ring to give salt CXXXVII, is assumed.

Azirine LXI reacts with hydrazinium perchlorate to give aminopyrazole CXXXVIII [30]. A reaction mechanism similar to the scheme of the reaction of azirine with anilinium perchlorate is assumed [54]:

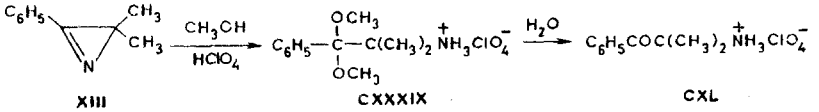


LXI

CXXXVIII

However, the α-amino β-diketone hydrazone perchlorate undergoes cyclization to aminopyrazole CXXXVIII.

The acid-catalyzed methanolysis of azirine XIII gives dimethyl ketal CXXXIX, by hydrolysis of which amino ketone perchlorate CXL is obtained [53]:



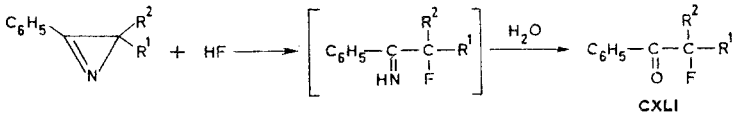
XIII

CXXXIX

CXL

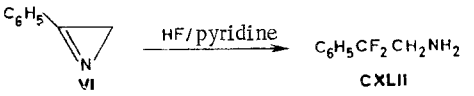
One of the most thoroughly investigated reactions of 1-azirines is acid-catalyzed hydrolysis to amino ketones [57-60]. However, the rather low yields of the latter do not make it possible to use this reaction for preparative purposes.

Addition of Acids. 1-Azirines are readily cleaved by HF, and subsequent hydrolysis leads to the corresponding α-fluoro ketones in 50-90% yields [61-63]:



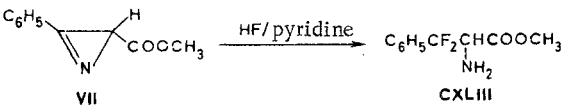
CXLI

A β,β-difluoro amine (67% yield) is formed when 2-phenylazirine (VI) is treated with HF in pyridine [62, 63]; the yield increases when triethylamine is added to HF in pyridine [62].



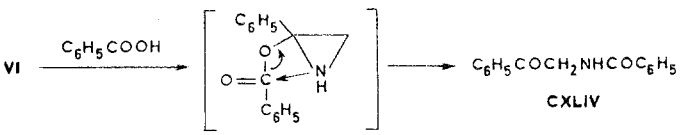
VI CXLII

The reaction of azirinecarboxylic acid esters with HF in pyridine is a new method for the synthesis of β,β-difluoro α-amino acid esters [63, 64]:



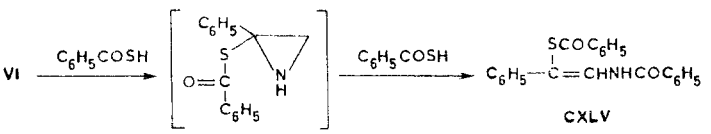
VII CXLIII

2-Phenylazirine (VI) reacts with benzoic acid to give α-(benzamido)acetophenone (CXLIV) [11]:



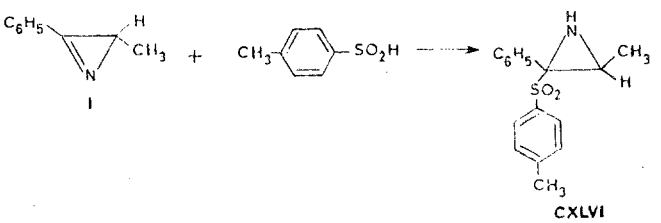
CXLIV

The formation of an intermediate thioaziridine, the subsequent benzoylation of which leads to N-benzoyl-α-benzoylthio-β-aminostyrene (CXLV), is proposed in the reaction of azirine VI with thiobenzoic acid [11]:



CXLV

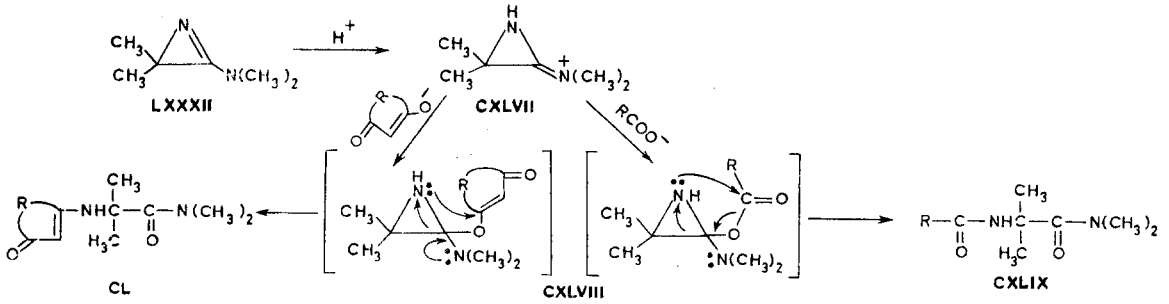
Azirine I reacts with p-toluenesulfinic acid to give an addition product, viz., tosylaziridine CXLVI [65]:



I CXLVI

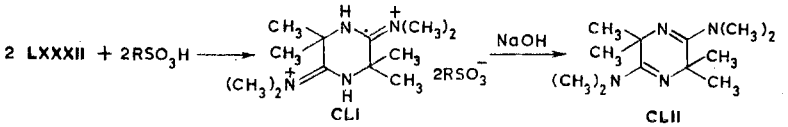
α-Halo carboxylic acids undergo conversion to α-halo amides similar to CXLIV upon reaction with 2-phenylazirine (VI) [66].

The reactions of azirine LXXXII with carboxylic acids or with cyclic 1,3-diketones give 2-amino-N,N-dimethylisobutyramides CXLIX and CL [67]:



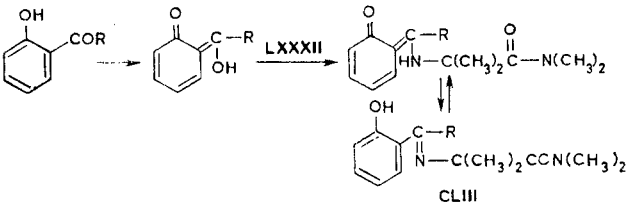
It is assumed that the resulting aminoaziridinium cation CXLVII reacts readily with nucleophilic carboxylate and enolate anions to give aminoaziridines CXLVIII, which, as a result of 1,2 cleavage of the ring with simultaneous transfer of an acyl group or its vinylog, are converted to amides CXLIX and CL, respectively. A similar scheme of the reactions of 1-azirines with carboxylic acids was also proposed in [11, 66].

Formylcycloalkanones and sulfinic acids react similarly with azirine LXXXII, whereas sulfonic acids form salt CLI, the alkaline hydrolysis of which leads to dihydropyrazine CLII [68]:

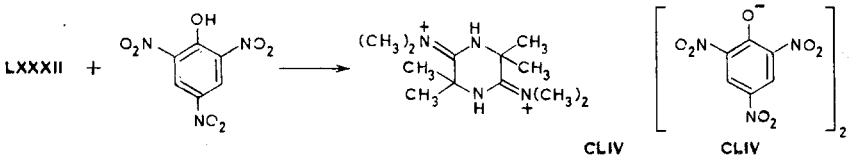


VI. Addition of Phenols and Hydroxamic Acids to 1-Azirines

2-Acylphenols react like cyclic 1,3-diketones [68] with azirine LXXXII [52]:

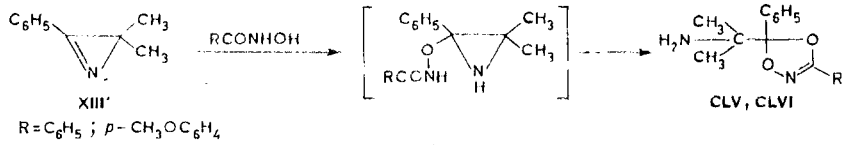


The mechanism of the reaction of azirine LXXXII with a more acidic phenol, viz., picric acid, is assumed to be similar [52] to the scheme of its reaction with strong acids [68].



Substituted isobutyramides are obtained when azirine LXXXII is heated with aryl halides in benzene or acetone with subsequent hydrolysis [52].

The addition of hydroxamic acids to azirine XIII opens up a new method for the synthesis of 1,3,4-dioxazoles CLV and CLVI [69]:



The initially formed aziridinium cation evidently reacts readily with the nuclophilic hydroxamate anion to give the corresponding aziridines. The latter in turn undergo 1,2 cleavage of the ring to give 1,3,4-dioxazoles CLV and CLVI.

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RESEARCH ON UNSATURATED LACTONES.

91.* SELECTIVE OXIDATION OF THE BROMOMETHYL GROUP IN SUBSTITUTED 2-BUTEN-4-OLIDES

A. A. Avetisyan, V. V. Ovsepyan, and G. G. Tokmadzhyan

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The selective oxidation of the bromomethyl group to a formyl group was realized by the direct action of dimethyl sulfoxide on 2-ethoxycarbonyl-3-bromomethyl-4,4-dialkyl(cycloalkyl)-2-buten-4-olides.

The production of aldehydes by the oxidation of a bromomethyl group by dimethyl sulfoxide (DMSO) was realized for the first time in 1957 [2] in a series of p-substituted bromomethyl aryl ketones. The reaction was subsequently extended to alkyl halides, and it was ascertained that in this case chlorides and bromides are oxidized by DMSO only through the corresponding tosylates and that aldehydes are obtained only from alkyl iodides by direct oxidation with DMSO [3, 4].

We have for the first time realized the similar oxidation of the bromomethyl group in a number of unsaturated γ-lactones by the direct action of DMSO on 2-ethoxycarbonyl-3-bromomethyl-4,4-dialkyl(cycloalkyl)-2-buten-4-olides.

*See [1] for communication 90.

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