SYNTHESIS OF NITROGEN HETEROCYCLES BY MEANS OF NITRENES. II. FIVE-MEMBERED HETEROCYCLES WITH SEVERAL HETEROATOMS (REVIEW)*

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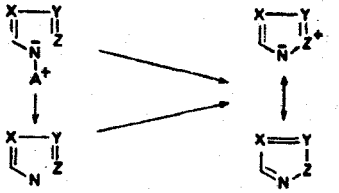
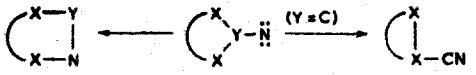
The intramolecular cyclization of heteroanalogs of 1,3-butadien-1-ylnitrenes, the expansion and contraction of the rings of hetarylnitrenes, the incorporation of nitrenes, and the intermolecular dipolar cycloaddition of acylnitrenes to unsaturated compounds, which leads to the formation of five-membered nitrogen heterocycles with several heteroatoms, are examined.

Analogies (at least formal analogies) with the reactions involved in the formation of a pyrrole ring through nitrenes [1] can be found for many reactions of nitrenes that lead to five-membered nitrogen heterocycles with several heteroatoms. These processes include primarily the intramolecular cyclization of heteroanalogs of 1,3-butadien-1-ylnitrenes. Nevertheless, as in the case of carbon-chain nitrenes, a heteroring can also be formed in this case with bypassing of the nitrene step by concerted decomposition of its precursor:

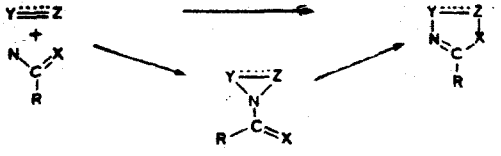


As in the carbocylic series, some hetarylnitrenes undergo ring expansion or contraction:



Like the pyrrole ring, a five-membered ring with several heteroatoms can be constructed as a result of intramolecular incorporation of a nitrene in a Z—N δ bond (most often in the C—H bond):

Reactions of nitrenes that are used specially for the preparation of cyclic systems with several heteroatoms are also known. This group of reactions includes, for example, the intermolecular dipolar cycloaddition of several nitrenes (most often acylnitrenes) to a multiple bond. Of course, in such cases one must bear in mind that the final reaction product may also be formed as a result of expansion of the ring of the intermediate three-membered heteroring:



*See [1] for Part I.

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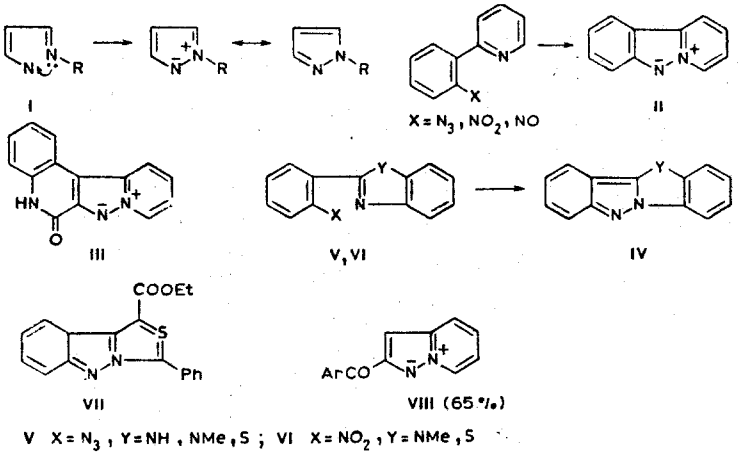
Pyrazoles and Their Analogs

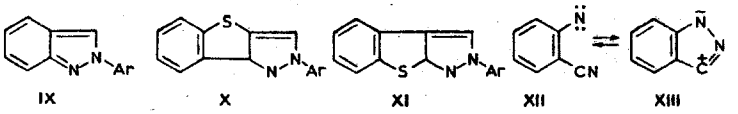
The most common method for the construction of a pyrazole ring through nitrenes is isomerization of 4-aza-1,3-butadienylnitrenes (I). The intramolecular reaction of the sextet nitrogen atom with the unshared pair of electrons of another nitrogen atom is similar to the intermolecular addition of nitrenes to tertiary amines [2].

The formation of pyrido[1,2-b]indazoles II and their heteroanalogs III (in 45%-95% yields) was observed in the thermolysis or photolysis of 2-(o-azidoaryl)pyridines and in the deoxygenation of nitroso- and nitroarylpyridines with triethyl phosphite [3-5]. It is possible that azide added to the C=N bond of the pyridine ring with subsequent splitting out of nitrogen from the intermediate tetrazoloindazole under the conditions of thermolysis of the azide. However, the photolytic pathway for the formation of pyridoindazole II most likely includes the formation of a triplet arylnitrene, the precursor of which is assumed to be 2,2'-di(2-pyridyl)azobenzene [6]. Similarly, condensed indazoles IV were obtained by both thermal decomposition of azides V (in 66-96% yields) and by deoxygenation of nitro compounds VI (in 54-83% yields) with triethyl phosphite [7, 8]. Intensely violet (λ_{max} 542 nm) thiazolo[3,4-b]indazole VII is formed in the deoxygenation of 4-(o-nitrophenyl)-5-ethoxycarbonylthiazole [9].



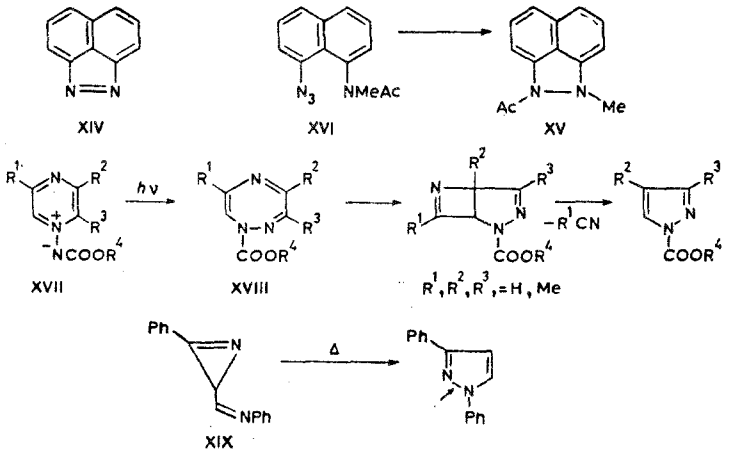
As a rule, the thermal cyclization of 2-(β-azidovinyl)pyridines to 1,7a-diazaindenes III and VIII gives the products in high yields; nitrenes that have a C=C bond in both the acyclic and carbocyclic fragments can participate in reaction [10].

The C=N bond in nitrene I may be located outside of the ring. Thus 2-aryl-2H-indazoles IX are formed in 40-95% yields in the deoxygenation of o-nitroso(or o-nitro) benzalanilines [11, 12] or by thermolysis of the analogous azides [13, 14]. Benzothienopyrazoles X and XI were obtained from the anils of aldehydes of the thiophene series [15] (in 65-75% yields in the case of thermolysis of the azides and in 20-40% yields in the case of deoxygenation of the nitro derivatives). It has been shown that o-cyanophenylnitrene XII is in equilibrium with ylid XIII [16].



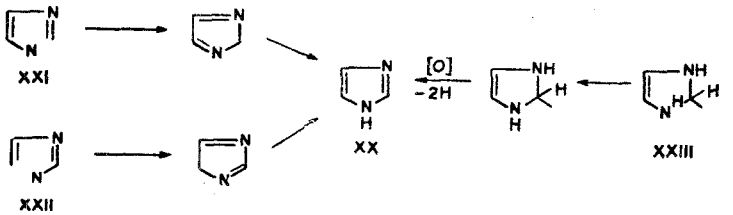
Benzo[c,d]indazole XIV is formed by irradiation of 1,8-diazidonaphthalene in a matrix at 77°K as a result of intramolecular attack on the azido group by the sextet nitrogen atom in the intermediate 8-azido-1-naphthylnitrene [17]. Dihydrobenzindazole XV was obtained in 18% yield by thermolysis of azide XVI [18].

Contraction of the ring of 2-pyrimidinylnitrenes leads to 1-cyanopyrazoles in 5-33% yields [19]. The formation of 1-ethoxycarbonylpyrazoles (in 35-48% yields) through intermediate triazepines XVIII was noted in the case of irradiation of ylids XVII [20]. The thermal decomposition of azirine XIX gives 1,3-diphenylpyrazole as a result, in the opinion of Padwa and co-workers [21-23], of equilibrium isomerization of the azirine to a nitrene of the I type.

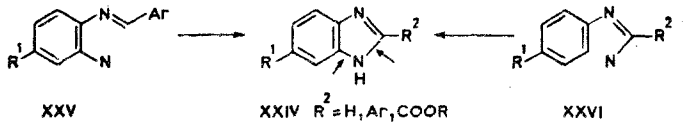


Imidazoles and Benzimidazoles

The 1H-imidazole ring (XX) can be constructed by isomerization of 3-aza- or 2-aza-1,3-butadienylnitrenes (XXI, XXII) through the intermediate 2H- or 4H-imidazoles; the intramolecular incorporation of 3-aza-1-butenylnitrenes XXIII in the C—H bond with subsequent dehydrogenation of the intermediate 4-imidazolines also leads to 1H-imidazoles

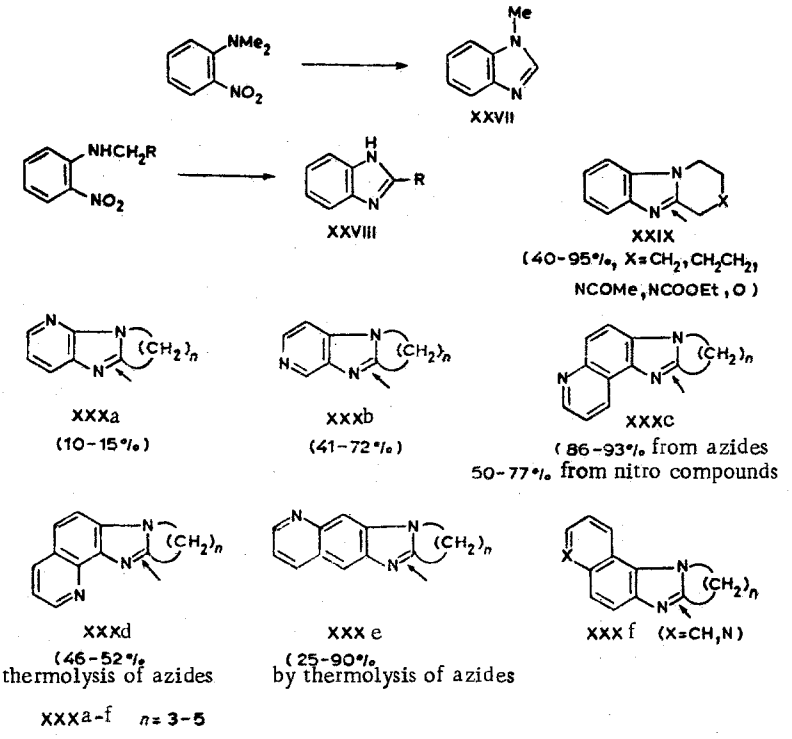


2-Arylbenzimidazoles XXIV are formed in 40-70% yields in the cyclization of arylnitrenes XXV obtained by thermolysis of o-azidoanils [24] or by deoxygenation of o-nitroanils [25] of aromatic aldehydes. More detailed study has been devoted to the formation of benzimidazoles XXIV from azomethine nitrines XXVI, which were obtained by photolysis of diphenyldiazamethane (52%) [26-27], thermolysis or photolysis of 1,5-diaryltetrazoles (10-25%) [28-31], photolysis of N-(N-arylbenzimidoyl)sulfonimides (30-95%) [32], photolysis (or less frequently, thermolysis) of 3,4-diaryl- and 3-ethoxycarbonyl-4-aryl-Δ^2-1,2,4-oxadiazolin-5-ones (60-86%) [33-35], or by α elimination of the anions of o-chlorobenzoic or benzenesulfonic acids from the corresponding O-substituted derivatives of amidoximes (72-90%) [36, 37].

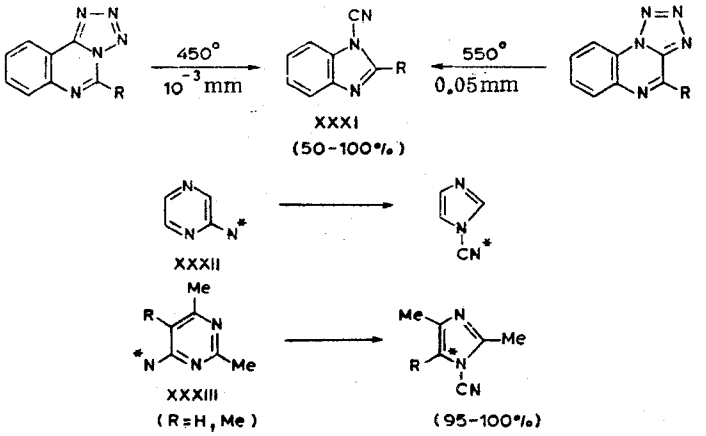


Like their heteroanalogs, N-alkyl- or N-cycloalkyl-o-aminophenylnitrenes of the XXIII type are converted to condensed imidazoles [14]. The thermolysis of o-azidoanilines in nitrobenzene or the reduction of o-nitroanilines with ferric oxalate leads to 1-substituted imidazoles of the XXVII type (from N,N-disubstituted anilines) or to 2-substituted imidazoles XXVIII (from monosubstituted anilines) [38, 39]. Condensed imidazoles XXIX and XXXa-f were similarly obtained [39-45] (here and subsequently, the bond that is formed during cyclization of the nitrene is indicated by an arrow).

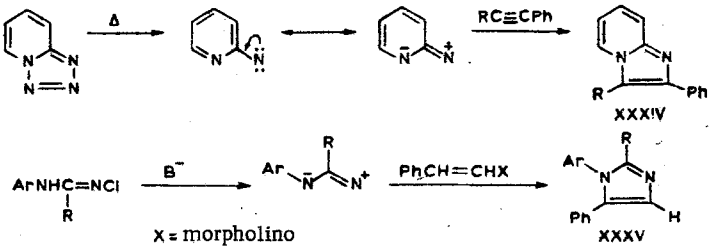
The thermal fragmentation of 2-pyrrolidinophenylsulfonyl azide through 2-pyrrolidinophenylnitrene leads to pyrrolidino[1,2-a]benzimidazole in 18% yield [46]. 1-Cyanobenzimidazoles XXXI can be obtained by contraction of the ring of both 4-pyrimidinyl- [47] and 2-pyrazinylnitrenes [19, 47, 48]. Contraction of the ring of labeled pyrazinylnitrene XXXII



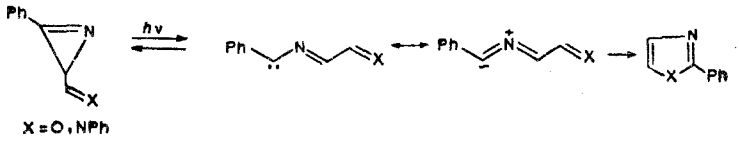
leads to 1-cyanoimidazole containing ^{15}N in the cyano group, whereas pyrimidinylnitrene XXXIII is converted to an imidazole with the label in the ring [47].



A fundamentally different method for the synthesis of imidazole derivatives XXXIV and XXXV proceeds through 1,3-cycloaddition of azomethine nitrenes to acetylenes or enamines [49, 50].



The thermal decomposition of phenyl azides (but not α-azido ketones of the aliphatic series) leads to 4-aryl-2-aroylimidazoles (in 45-85% yields) [51, 52]; 2,4,5-triphenylimidazole was obtained by thermolysis of benzyl azide in the condensed phase [53, 54]. Whereas the thermal decomposition of an azirine of the XIX type gives a substituted pyrazole (see above), during photolysis it is converted quantitatively to 1,2-diphenylimidazole through the intermediate nitrile ylid [21-23, 55].



X=O, NPh

Benzimidazo[2,1-a]isoquinoline was obtained by deoxygenation of 1-(o-nitrophenetyl)-tetrahydroisoquinoline [56].

Hydrogenated Diazoles

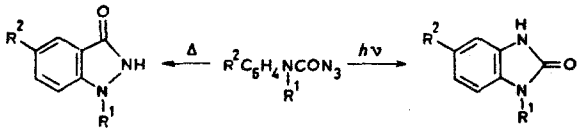
The formation of di- and tetrahydro derivatives of pyrazole and imidazole in reactions with the participation of nitrenes has been relatively rarely observed. As a rule, the 4-imidazolines that are formed in the cyclization of 3-aza-1-butenylnitrenes XXIII are dehydrogenated under the reaction conditions to imidazoles XX (see above). However, in some cases it has been possible to isolate compounds of the XXXVI type in 50-75% yields by cyclization of nitrenes XXXVII generated by thermolysis of the azides in nonoxidizing solvents (in diglyme, for example) or by deoxygenation of the nitro compounds with trimethyl phosphite [52, 57].

XXXVII XXXVI

R=H, NO_2 ; X=CH_2, NMe, O

1-Allyl-2-pyrazoline was obtained in 33% yield by intramolecular rearrangement of diallylaminonitrene, but it was not possible to cyclize other allylaminonitrenes in this way [58]. The cyclization of N-chlorotrimethylenediamine to pyrazolidine in the presence of bases can be regarded as an example of the intramolecular incorporation of a nitrene in the N—H bond [59].

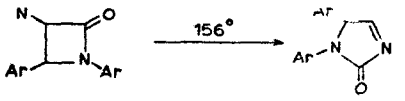
The intramolecular incorporation of diphenylcarbamoylnitrene, obtained by photolysis of azide XXXVIII (R^1 = Ph, R^2 = H), in the aromatic C—H bond led to benzimidazolin-2-one XXXIX in 57% yield [60]. Isomeric indazolones XL were obtained in ∿90% yields by thermolysis of azides XXXVIII in xylene [60-63]. The thermolysis or photolysis of azides XXXVIII (R^1 = CH_2Ph) leads to the expected benzimidazolones XXXIX, together with their debenzylated derivatives [64-66] and indazolones XL (R^1 = CH_2Ph) [67].



XL XXXVIII XXXIX

The formation of 2,4,5-triphenyl-2-imidazoline (in 29% yield) in the gas-phase pyrolysis of benzyl azide is regarded as being the result of the reaction of benzylnitrene with benzalimine [54]. Benzimidazolone XXXIX (R^1 = R^2 = H, in 40% yield) and its N-acetyl derivative were obtained by heating o-phenylenediamine with aroyl azides, while N-carbamoylbenzimidazolones XXXIX (R^1 = $CONR_2$, R^2 = H, ∿70% yield) were obtained by thermal decomposition of the diazide of o-phthalic acid in the presence of amines; however, the basis of these transformations is the rearrangement of the aroyl azides to isocyanates and reaction of the latter with amines [68].

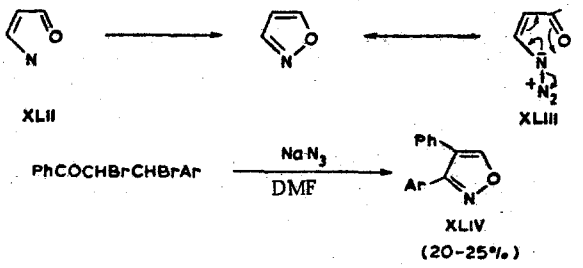
Expansion of the ring of 2-oxo-3-azetidinylnitrenes leads to the formation of 3-imidazolin-2-ones XLI [69].



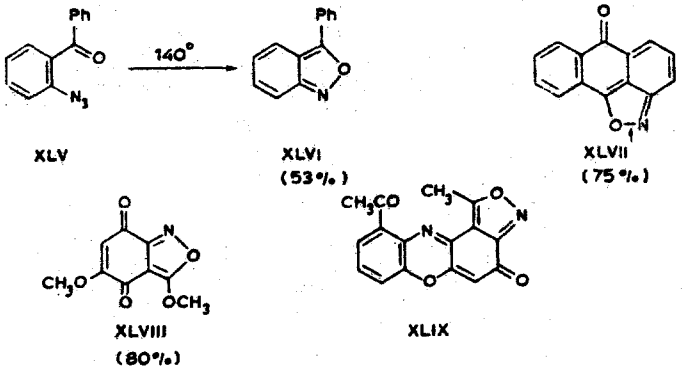
XLI
(20-70%)

Oxazoles, Isoxazoles, and Their Analogs

One should expect that the isomerization of cis-4-oxa-1,3-butadienylnitrenes XLII may serve as a method for the construction of an isoxazole ring. In fact, isoxazoles were obtained in good yields in an attempt to synthesize cis-β-azidovinyl ketones from the corresponding chloroderivatives and sodium azide [70, 71]. A "nitrene" mechanism has been proposed for the formation of isoxazoles [72, 73], but the conditions under which the reaction is carried out (from −20 to +20°C in strongly polar solvents) more likely correspond to concerted cyclization of azides XLIII, in which the formation of an N−O bond proceeds simultaneously with splitting out of nitrogen. The action of NaN_3 in proton-donor solvents of HN_3 on aroylacetylenes also leads to isoxazoles in 15-75% yields [74, 75]. The method for the synthesis of 3,5-diarylisoxazoles (XLIV) was improved somewhat after substituted dibromobenzalacetophenones were proposed as the starting reagents [76].

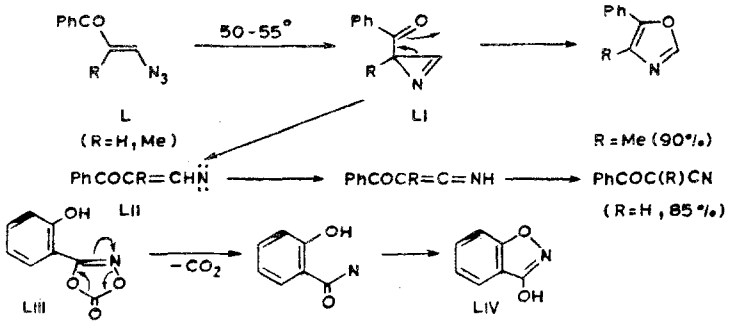


o-Azidobenzophenone (XLV) and 1-azido- and 1,4- and 1,5-diazidoanthraquinones, which are potential precursors of nitrenes of the XLII type in which the C=C bond is aromatic, undergo cyclization to anthranil (XLVI) or its condensed analogs (for example XLVII) under thermolysis conditions [77, 78]. Condensed isoxazoles XLVIII and XLIX were obtained by treatment of the corresponding chlorobenzoquinone or chlorophenoxazinone with sodium azide in methanol [79].



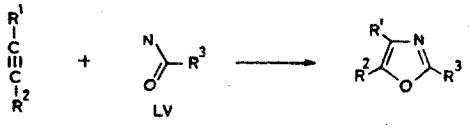
Several mechanisms [80, 81] have been proposed for the thermolysis of o-azidobenzophenones, which is accelerated by electron-acceptor substituents and inhibited by electron-donor substituents; however, preference should be given to the concerted character of the process [81]. Another method for the synthesis of anthranils (in 55-70% yields) — deoxygenation of o-nitrocarbonyl compounds with triethyl phosphite [8, 25, 82, 83] — does not exclude the formation of nitrenes of the XLII type. The COOR group can also participate in the formation of an isoxazole ring; for example, azidomethylenemalonic ester is converted at 110°C to 5-ethoxy-4-ethoxycarbonylisoxazole in 70% yield [84].

trans-β-Azidovinyl ketones L are decomposed at higher temperatures than the cis isomers to give primarily β-keto nitriles and (or) isoxazoles [72, 85]. It is assumed that rearrangement of the 2H-azirine LI with cleavage of the C−C bond precedes the formation of the oxazole, while a 1,2-hydride shift in singlet nitrene LII precedes the formation of the nitrile [72]. However, isoxazoles are formed in the photolytic decomposition of trans-azidovinyl ketones [86, 87]. This is associated with the reaction of the oxazoles and isoxazoles through intermediate 2-acyl-2H-azirines LI [21, 88, 89]; the existence of an isoxazole — nitrene XLII — azirine LI equilibrium has been demonstrated [21, 90-97].

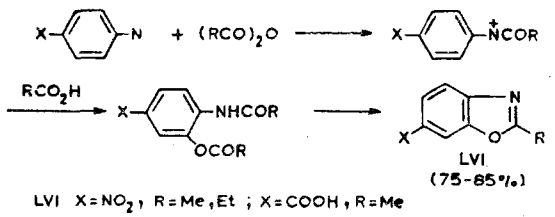


(o-Hydroxybenzoyl)nitrene, which is formed in the thermolysis of dioxazolone LIII, is converted to benz[d]isoxazole LIV in 95% yield [98, 127].

The most general method for the synthesis of oxazoles (in up to 35% yields) with the participation of nitrenes is the addition of carbonylnitrenes LV to acetylenes [99-103]. 1H-Azirines have not been detected as intermediates in even a single case, and the reaction is often regarded as 1,3-cycloaddition of the carbonylnitrene to the C≡C bond [104-106]. The process is usually carried out with excess acetylene in order to suppress the addition of two nitrene particles and in low-polarity solvents in order to reduce the rate of cycloaddition of the azides (the precursors of nitrenes LV), which form triazoles. The reaction products will possibly be more homogenous under photolysis conditions.



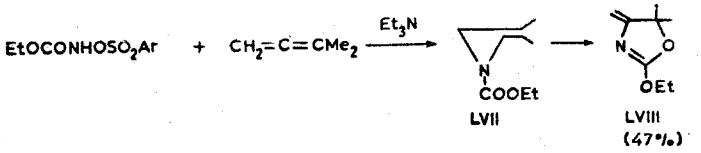
The simplest vinyl azides may gave oxazoles in good yields when they are treated with carboxylic acid chlorides in the presence of aluminum chloride: 2H-azirines and 1-acyl-2-chloroaziridines are formed successively as intermediates [107]. α-Azidocarbonyl compounds are converted to 2,5-disubstituted oxazoles in the presence of acyl chlorides and triphenylphosphine (in up to 30-60% yields) [108]; 2-arylbenzoxazoles (in up to 53-60% yields) were obtained by reductive cyclization of o-nitro- [109] and o-azidophenyl benzoates [110], and also by heating the products of the reaction of aroyl azides with o-aminophenoxides in the presence of polyphosphoric acid (PPA) [68]. The pyrolysis of aryl azides in a mixture of polyphosphoric and carboxylic acids was found to be a promising method for the synthesis of condensed oxazoles [111-113]. The mechanism of the formation of benzoxazoles LVI includes the reaction of an arylnitrene with an anhydride [112] and assumes activation of the aromatic ring by electron-acceptor substituents [113]. This method was used to obtain 2-methyl-substituted 8-nitronaphtho[1,2-d]oxazole (in 25% yield), oxazole[4,5-c]quinoline (in 65% yield), oxazolo[5,4-g]quinoline (in 45% yield), oxazolo[5,4-c]isoquinoline (85%), oxazolo[4,5-g]-indazole (60%), and a number of other condensed oxazole derivatives [111, 112].



Oxazolines

Only one method for the synthesis of 2-oxazolines with the participation of nitrenes — intermolecular addition to the C=C bond of alkoxycarbonylnitrenes generated by α elimination [114], thermolysis, or photolysis of azides [115-117] and of aroylnitrenes obtained by photolysis of azides [118-122] or trimethylammonium amidates [123] — has been described. Olefins [119-121], vinyl ethers [118, 119, 122, 123], allenes [114, 116], isoprene [115], and keteneimines [117] have served as the unsaturated compounds. 1-Ethoxycarbonylaziridines, which were converted to 2-oxazolines by heating, were isolated in the case of isoprene, 3-methyl-1,2-butadiene [114], and isopropenyl acetate [124]. It is possible that the reaction also proceeds with the formation of unstable 1-acylaziridines in other cases. Ethoxy-

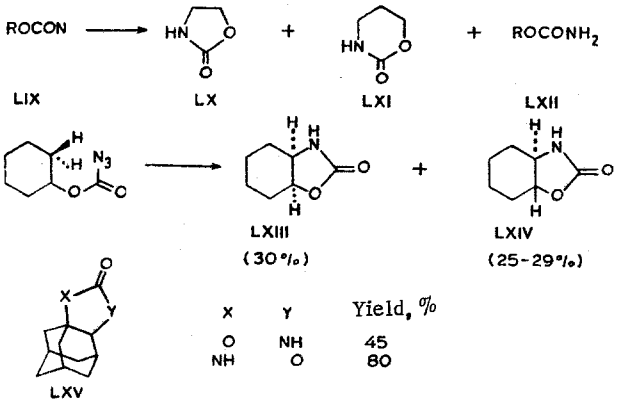
carbonylnitrene adds only to the C=C bond of keteneimines to give 2-ethoxy-4-arylimino-2-oxazolines in 70% yield [117]. 2-Ethoxy-5,5-dimethyl-4-isopropylidene-2-oxazoline was obtained in 29% yield by thermolysis of ethoxycarbonyl azide in the presence of tetramethylallene [116]. Ethoxycarbonylnitrene initially adds to the least substituted C=C bond of unsymmetrical allenes; however, 1-ethoxycarbonylaziridine LVII undergoes subsequent rearrangement to oxazoline LVIII, the structure of which corresponds formally to the addition of a nitrene to the most substituted allene C=C bond [114]. 5-Alkoxy-2-aryl-2-oxazolines (20-40%) were obtained by a similar reaction [118, 119, 122, 123], while dipolar 1,3-cycloaddition of carbonyl azides to alkyl vinyl ethers leads to mixtures of 4- and 5-methoxy-2-oxazolines [125].



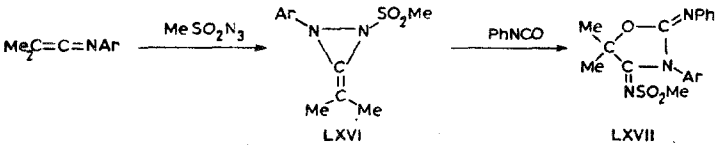
4-Oxazolines are formed by isomerization of phenoxycarbonylnitrene [126] or o-hydroxybenzoylnitrene generated by thermolysis of 1,4,2-dioxazolone LIII [127] and also by thermal isomerization of 3,3-dimethyl-2-acetyl-1-ethoxycarbonylaziridine, obtained by the addition of ethoxycarbonylnitrene to the C=C bond of mesitylene oxide [128].

2-Oxazolidones

A method for the preparation of 2-oxazolidines by the intramolecular incorporation of singlet alkoxycarbonylnitrenes, obtained by photolysis or thermolysis of azides [2, 104-106, 129], in the C—H bond has been well described. This reaction has much in common with the formation of 2-pyrrolidones from singlet alkanoylnitrenes, but nitrenes of the LIX type undergo rearrangement to oxazolidones LX in higher yields (60-80%) [2, 130, 131]. 2-Oxotetrahydro-1,3-oxazines LXI and alkyl carbamates LXII can be obtained as side products. The ratio of the yields of LX and LXI is determined by the difference in the reactivities of alkanoylnitrenes LIX with respect to incorporation in primary, secondary, and tertiary C—H bonds (1:10:30) [132]. For example, a mixture of LX-LXII in a ratio of 26:28:1 is formed in the thermolysis of propyl azidoformate in chloroform [133]. However, if only the secondary C—H bonds participate in the formation of five- and six-membered heterocycles, the LX:LXI ratio is somewhat less than unity; the yields of cyclic compounds decrease as the length of the carbon chain in nitrene LIX increases, and the yield of the carbamate increases [132, 134, 135]. If incorporation occurs in the C—H bond of an asymmetric carbon atom, its configuration is retained in the oxazolidone [136]. The nitrene formed from cyclohexyl azidoformate attacks both the cis- and trans-C—H ring bonds with equal probability to give a mixture of LXIII and LXIV [137]. In the case of rigid polycyclic systems the ratio between the five- and six-membered reaction products of the LX and LXI type is determined by the geometry of the transition state [2, 133, 137-141]. Thus the photolytic or thermal decomposition of 1- and 2-adamantyl azidoformates leads only to five-membered heterocycles LXV [133, 138].



Oxazolidine-2,4-dione derivatives of the LXVII type were isolated in 30-50% yields when alkylidenediaziridines LXVI, which are formed by reaction of methylsulfonyl azide with N-aryl-keteneimines are treated with phenyl isocyanate [142].

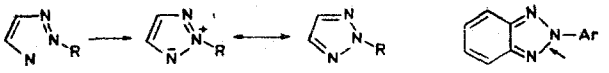


LXVI LXVII

Triazoles, Tetrazoles, and Their Condensed Analogs

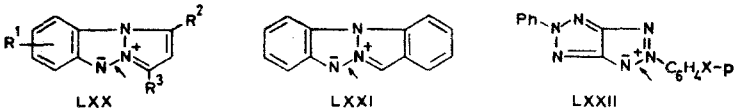
The formation of 1,2,3-triazoles is possible in the cyclization of 3,4-diaza-1,3-butadienylnitrenes LXVIII. In fact, 2-arylbenzotriazoles LXIX were obtained in high yields in the thermolysis of o-azidobenzenes or in the case of deoxygenation of o-nitroazobenzenes [11, 12, 143, 144]. However, this process, at least in the first case, takes place via a concerted mechanism [12].

The N—N bond in nitrene LXVIII can be a fragment of a heteroring: deoxygenation of 1-(o-nitrophenyl)-substituted pyrazoles and indazoles or decomposition of the analogous azides leads to pyrazolo- and indazolo[1,2-a]benzotriazoles LXX and LXXI [14, 144-146]. Singlet nitrenes participate in the formation of these compounds from both azides and from nitro derivatives; the yields of cyclization products of the LXX type increase as the electrophilicity of the sextet nitrogen atom and the basicity of the nitrogen atom undergoing



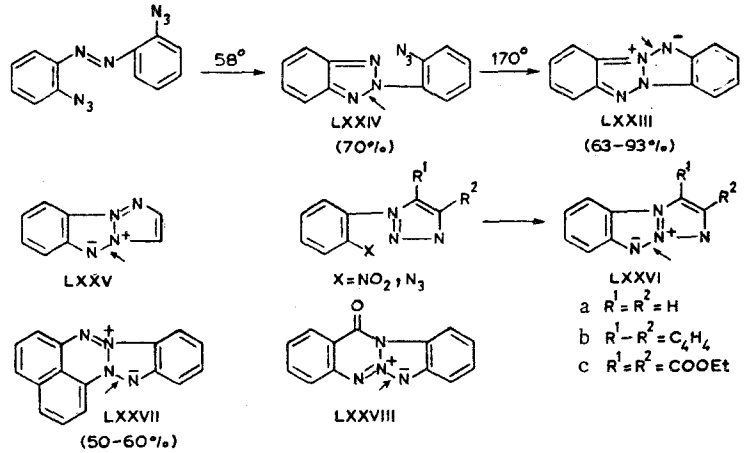
LXVIII LXIX (50-100%)

attack by the nitrene increase [144]. The hexaazapentalene—triazolo[4,5-d]triazole—system (LXXII) was obtained by thermolysis of 5-azido-4-phenylazo-2H-1,2,3-triazole [147].



LXX (0-65%; $R^1=R^2=R^3=H$, 45%) LXXI (23-30%) LXXII X=H, Me, Cl, Me_2N

Dibenzo-1,3α,4,6α-tetraazapentalene LXXIII is the product of cyclization of 2-(o-azidophenyl)- or 2-(o-nitrophenyl)benzotriazoles LXXIV [14, 148-152]. The formation of triazole LXXIV from 2,2'-diazidoazobenzene proceeds via a concerted mechanism at relatively low temperatures (58°C), whereas the formation of pentalene LXXIII (170°C) proceeds via a nonconcerted mechanism with the participation of a nitrene. Pentalene LXXIII was obtained immediately in 63% yield in the deoxygenation of 2,2'-dinitroazobenzene with excess triethyl phosphite [12]. Benzotetraazapentalene LXXV was isolated in 70% yield by deoxygenation of 2-(o-nitrophenyl)-2H-1,2,3-triazole with trimethyl phosphite [149]. The isomeric benzo- (LXXVIa, in 45-70% yield) and dibenzo-1,3α,6,6α-tetraazapentalene (LXXVIb, in 65-75% yield) were obtained by cyclization of the corresponding 1-aryl-1H-1,2,3-triazoles [148, 150]. Similarly, diethyl-1-(o-nitrophenyl)-1,2,3-triazole-4,5-carboxylate gives 14% tetraazapentalene LXXVIc when it is treated with triethyl phosphite, while triazolo[3,4-a]quinoxaline derivatives were isolated from the reaction with tributyl phosphite [150]. Similar cyclizations of benzo- and naphthotriazine derivatives lead to condensed LXXVII and LXXVIII systems [153-156].



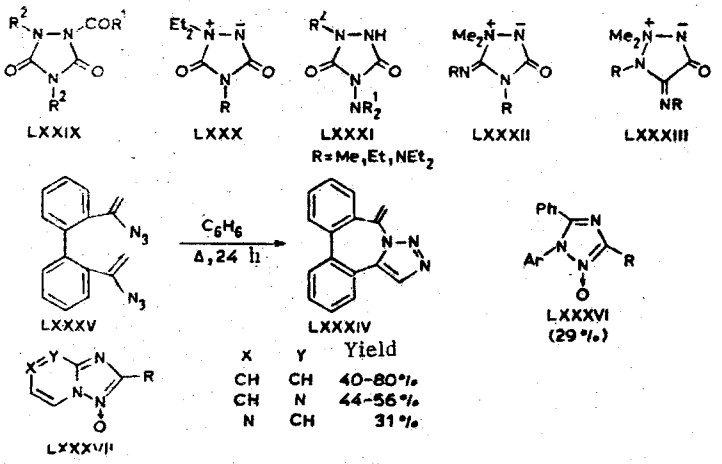
LXXIV (70%) LXXIII (63-93%)

LXXV X=NO_2, N_3 LXXVI a $R^1=R^2=H$ b $R^1-R^2=C_4H_4$ c $R^1=R^2=COOEt$

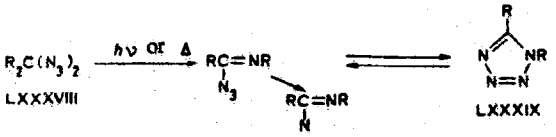
LXXVII (50-60%) LXXVIII

Urazoles and related structures (LXXIX-LXXXIII) are formed in the cyclization (thermal or photolytic) of alkoxy- or dialkylaminocarbonyl azides in the presence of alkyl isocyanates, as well as the analogous heterocumulenes [157-159]; however, it is assumed that these reactions proceed without the participation of nitrenes [157]. Dibenzoazepinortriazole LXXXIV was isolated in 17% yield in the thermolysis of bis(azidovinyl)diphenyl (LXXXV) [160].

1,2,4-Triazoles can be obtained by rearrangement of dialkylaminonitrenes generated from secondary amines and Angeli's salt ($NaHN_2O_3$) [161, 162] or by [3 + 2] cycloaddition of azomethine nitrenes such as 2-symtriazinylnitrene to nitriles [163]. The analogous cycloaddition of ylids of azomethine nitrenes and dimethyl sulfoxide to nitrile oxides gives 1H-1,2,4-triazole 2-oxides and their analogs (LXXXVI and LXXXVII) [164].

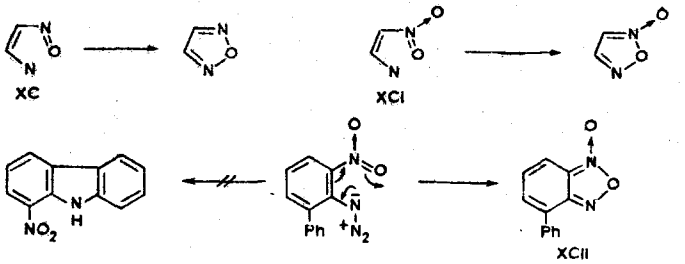


Tetrazoles LXXXIX are obtained in the case of thermal or photochemical rearrangements of gem-diazidoalkanes LXXXVIII as a result of isomerization of the intermediate azides of the imine acids. Tetrazoles and mainly their condensed derivatives are presently attracting a great deal of attention, since they may exist in equilibrium with azides of imine acids that are capable of undergoing conversion to azomethine nitrenes and subsequently to other heterocyclic compounds such as, for example, benzimidazoles and 1,2,4-oxadiazoles [27, 165-170].



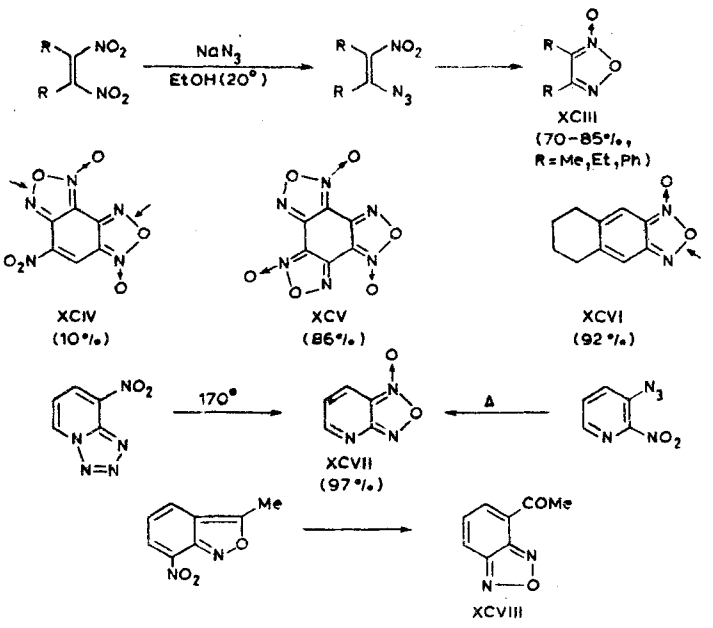
Oxadiazoles and Dioxazoles

The cyclization of cis-2-nitroso- and 2-nitrovinylnitrenes XC and XCI should lead to the formation of 1,2,5-oxadiazoles and, respectively, their oxides (furazans and furoxans). However, as in the case of other 1,3-butadienylnitrenes that have a heteroatom in the 4 position, the possibility itself of the existence of nitrenes in a number of cases is hypothetical. In particular, the lower decomposition temperatures of o-nitroazidobenzenes (20-30°C) than in the case of other aryl azides (140-170°C), the lower enthalpies of activation, and the negative entropy of activation indicate a concerted mechanism for the formation of the furoxans [38, 171-173]. This is also confirmed by the fact that 4-phenylbenzofuroxan (XCII) rather than 2-nitrocarbazole is formed in the thermolysis of 2-azido-3-nitrodiphenyl [38].

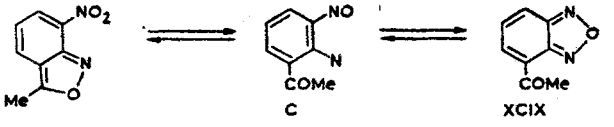


The simplest furoxans (XCIII) are obtained from cis-2-azido-1-nitroethylenes at the instant of their formation [174]. Not only o-azidonitrobenzenes [171, 172] but also o-nitro-

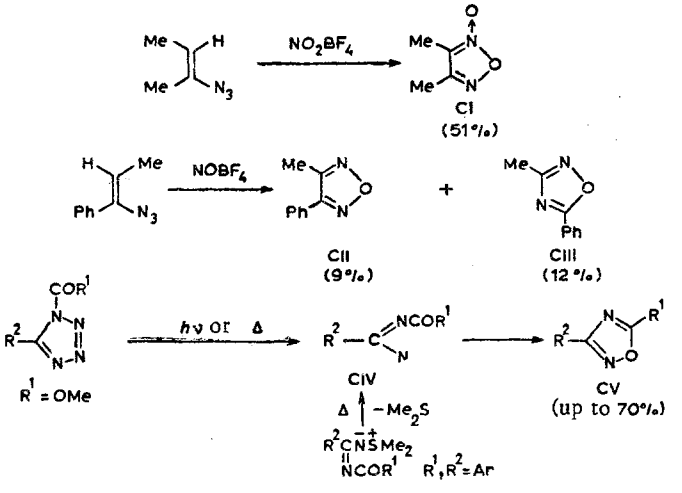
substituted nitrosobenzenes [12], anilines, or arylhydrazines [173, 175, 176] can be used as the starting compounds in the synthesis of benzofuroxans. Nitrobenzofuroxans and nitrobenzodi- and benzotrifuroxans XCIV and XCV were obtained by thermolysis of polyazidonitrobenzenes [175, 177]. Isomeric naphthofuroxans [173], tetrahydronaphthofuroxan XCVI [178], pyrido[2,3-c]furoxan (XCVII) [178, 179], and acetylbenzofurazan XCVIII [14] were similarly synthesized.



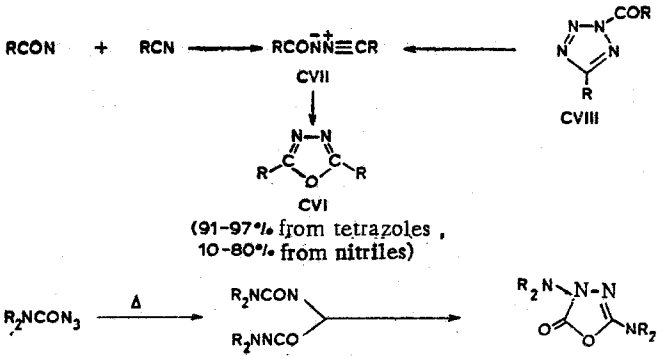
Benzofurazans are formed in the thermolysis of o-nitroazidobenzenes [12], in the deoxygenation of o-dinitrobenzenes [180] or furoxans [12], and by treatment of furoxans with nitrous acid [181] or sodium azide in DMSO [182]. The deoxygenation of 4-nitro-1-methylanthranil with triethyl phosphite leads to 4-acetylfurazan (XCIX) through intermediate nitrene C [183]. Naphtho[1,2]furazan was obtained in 65% yield by deoxygenation of 1,2-dinitrosonaphthalene, and the corresponding [3,4-d]pyridazine (36% yield) was obtained from 4,5-dinitroso-3,6-diphenylpyridazine [180].



Furoxan CI, furazan CII, and 1,2,4-oxadiazole CIII are formed by treatment of vinyl azides with nitronium or nitrosyl tetrafluoroborate at −10°C in aprotic solvents [184]. 4-Oxa-2-aza-1,3-butadienylnitrene CIV undergoes cyclization in the usual way to give 1,2,4-oxadiazole CV [165, 166, 185].

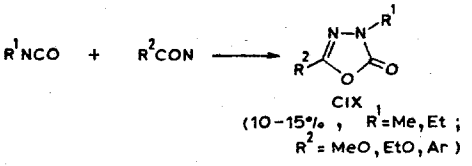


1,3,4-Oxadiazoles CVI are formed by cyclization of N-acylnitrilimides CVII, which are intermediates in the thermolysis of 2-acyltetrazoles CVIII (in this case the reaction proceeds without the participation of nitrenes) [30] or in the addition of carbonylnitrenes to nitriles [102, 131, 186, 187]. The latter reaction proceeds almost quantitatively, although the preparative yield of the oxadiazole is sometimes low.

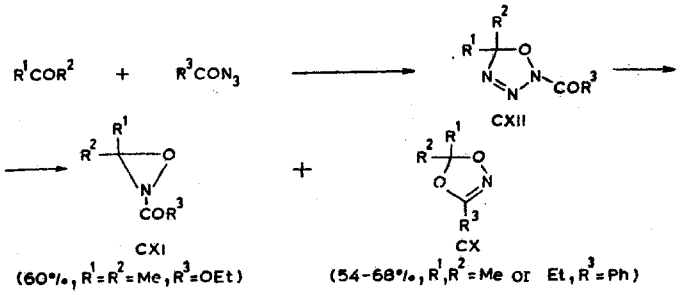


Nitrenes add to the C≡N bond with greater difficulty than to the C=C bond, but addition to the C≡N bond proceeds with greater ease than incorporation in the C—H bond. The reaction of ethoxycarbonylnitrene with acrylonitrile therefore leads mainly to 2-cyano-1-ethoxycarbonylaziridine, and the yield of oxadiazole CVI (R^1 = OEt, R^2 = CH_2 = CH) is only 14% [168]; oxadiazole CVI was obtained in 82% yield along with 2-oxo-5,5-dimethyltetrahydro-1,3-oxazine (15%) [133]. Thus there are several more or less similar methods for the synthesis of oxadiazoles of the CVI type; thus 2-methyl-5-phenyl-1,3,4-oxadiazole is formed by irradiation of 2-acetyl-5-phenyltetrazole [102] or by irradiation of acetyl azide in benzonitrile [102] or benzoyl azide in acetonitrile [188] (in 23, 1, and 30% yields, respectively).

The thermolysis of carbamoyl azides leads to carbamoylnitrenes and isocyanates, which, as a result of [3 + 2] cycloaddition, give Δ^2-1,3,4-oxadiazole-5-ones CIX [64]. Alkoxycarbonylnitrenes, obtained under the conditions of severe photolysis of alkyl azidoformates, or aroylnitrenes add to alkyl isocyanates to give oxadiazolones CIX together with urazoles LXXIX [157]. 2,4,5-Triphenyl-Δ^2-1,3,4-oxadiazoline was obtained by thermal decomposition of 2,5-diphenyltetrazole in the presence of benzaldehyde [30].

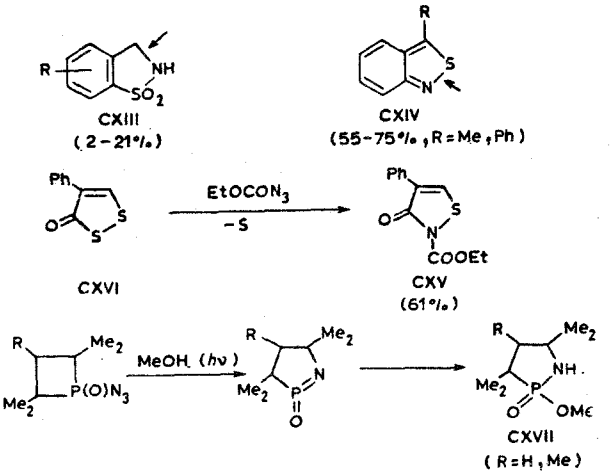


The addition of benzoylnitrene to the C=O bond of aliphatic or alicyclic ketones gives Δ^2-1,4,2-dioxazolines CX (in 30-75% yields) [188, 189]. The isomeric 2-acyloxaziridines CXI were isolated in individual cases [190, 191]; however, according to recent data [189], oxaziridines CXI and dioxazolines CX are formed independently of one another in the decomposition of 2-acyloxatriazolines CXII. It is extremely likely that other azoles are also obtained via a similar scheme that excludes the formation of nitrenes if the photolysis of the carbonyl azides takes place in the presence of compounds that contain polar C=X bonds.



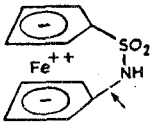
Azoles with Sulfur or Phosphorus Atoms in the Ring

2,3-Dihydrobenz[d]isothiazole 1,1-dioxides CXIII are formed as a result of intramolecular incorporation of o-methylsulfonylnitrenes in the C—H bond of a methyl group [192, 193];



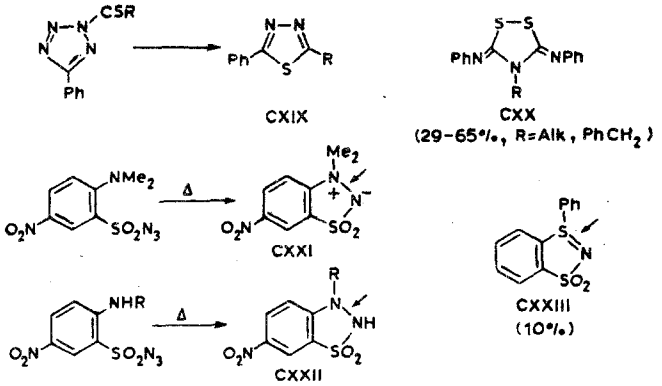
the thermal rearrangements of o-aroylbenzene-sulfonyl azides lead to similar compounds [194]. 4-Thia-1,3-butadienylnitrenes, which are obtained by thermolysis of o-azido-substituted aceto- and benzophenones, undergo cyclization to benzisothiazoles CXIV in the presence of hydrogen sulfide [194]. 3-Oxothiazoline ring CXV was constructed by heating ethoxycarbonylazide and dithiolone CXVI [195].

Methyl phosphonamidates CXVII (in 40-60% yields) are formed with ring expansion by UV irradiation of 1-azidophosphetane oxides in methanol [196]. Intramolecular incorporation of ferrocenylsulfonylnitrene in the C—H bond of the second ring led to ferrocenophan derivative CXVIII, which can be regarded as an analog of isothiazole [197, 198].

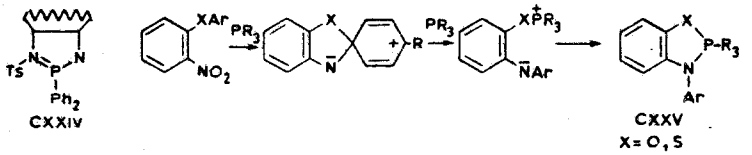


CXVIII
(67%)

1,3,4-Thiadiazole CXIX, which is the thia analog of oxadiazole CVI, was isolated in the thermal decomposition of the corresponding 2-thioacyltetrazole [30]. The reaction of primary alkyl azides with phenyl isothiocyanate (at 80-100°C) leads to 3,5-bis(phenylimino)-1,2,4-dithiazolidines CXX as a result of reaction of the intermediate 3-phenyliminothiaziridines with excess reagent [199]. Cyclic ammoniosulfamidates (for example, CXXI) or 2,3-dihydrobenzothiazole dioxides CXXII were obtained by thermolysis of o-dialkylaminoarylsulfonyl azides [46], while o-(phenylthio)phenylsulfonyl azide undergoes cyclization to 3-phenylbenzodithiazole-1,1-dioxide (CXXIII) [192].



Phosphadiazolines CXXIV are possibly formed when P,P-diphenyl-N-tosylphosphazene azide is heated in the presence of dicyclopentadiene [200], while oxazaphosphoranes CXXV are formed by deoxygenation of aryl o-nitrophenyl ethers with triethyl phosphite [201-203]. Like the deoxygenation of the corresponding thia analog, this reaction is still the only method for the synthesis of oxazaphosphorinanes and thiazaphosphorinanes [55, 201-203].



CXXIV

CXXV
X=O,S

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