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N-Nitrenes

B.V.Ioffe and M.A.Kuznetsov

This review gives an exhaustive summary of data on unstable intermediate species $RR'N-\ddot{N}$, containing a nitrogen atom with an incomplete electron shell, bonded to another nitrogen atom. These species are analogous to aminocarbenes, and play an important role in the chemistry of organic derivatives of hydrazine. Reactions in which the formation of N-nitrenes has been postulated have been systematised, and reactions involving their subsequent transformation with the separation of nitrogen, isomerisation, or addition to other reagents have been examined. The review covers papers dealing with the chemistry of N-nitrenes, published before mid-1971. The bibliography contains 145 references.

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I. INTRODUCTION

Progress in the chemistry of the carbenes in recent decades has led to an increase in interest in their analogues containing atoms with incomplete sextet electron shells, including the reactive intermediate compounds of formally univalent nitrogen $R-\ddot{N}$, the so-called nitrenes (the subject of several reviews[1-5] and a recent monograph[6]).

Among the nitrenes, a unique position is occupied by the labile compounds in which the "sextet" nitrogen atom is bonded to another nitrogen atom:



(I)

Compounds of type (I) are called N-nitrenes or aminonitrenes, to distinguish them from C-nitrenes or O-nitrenes, containing $C-\ddot{N}$ and $O-\ddot{N}$ bonds respectively. The terms diazene, azene, azalene, and azamine have also been used in the literature for structures of type (I).[1] The term "diazene" is now applied to monosubstituted derivatives of di-imide R-N=NH, and this can lead to confusion. The other names have not been widely used.

We shall use the terms "N-nitrene" and "aminonitrene" as equivalent names, the nature of the radicals R and R′ (I) being indicated in the name:

H_2N-N	aminonitrene
$(CH_3)_2N-N$	dimethylaminonitrene
C_6H_5NH-N	phenylaminonitrene etc.

In more complex compounds, in which the central nitrogen atom of the aminonitrene is present in a ring, it is convenient to use the names of the corresponding heterocyclic radicals, for example



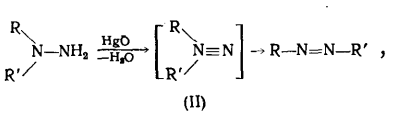
N-pyrrylnitrene .

An increasing number of facts indicate that N-nitrenes play a prominent role in the chemistry of the organic derivatives of hydrazine. Although the existence of these very unstable intermediate compounds in many instances has been only tentatively assumed, the ideas regarding aminonitrenes make it possible to understand a large number of the reactions of hydrazines, used in the production of synthetic materials and medicinal products, and in agriculture. The assumption that N-nitrenes are formed as intermediate products reveals common features in apparently completely different reactions and provides possibilities for predictions, useful analogies, and generalisations. Without a systematisation of ideas regarding N-nitrenes, the study and further development of the organic chemistry of hydrazine would be impossible.

The brief data on N-nitrenes in reviews of nitrenes[1-5], and the sections devoted to these compounds in the monograph cited[7] are inadequate and incomplete. The detailed article by Lemal in Lwowsky's book[6], published before this review was complete, covers the literature only as far as early 1969.

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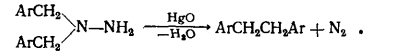
The first suggestion regarding the existence of unstable intermediate compounds with a nitrogen atom bound only to another nitrogen atom appeared as early as the end of the nineteenth century, with the need to explain the anomalous course of the oxidation of various hydrazines. In the oxidation of 1-allyl-1-phenylhydrazine and 1-allyl-1-*p*-tolylhydrazine with mercuric oxide, Michaelis and Luxemburg[8] obtained azo-compounds instead of the tetrazenes usually formed under these conditions, and they attributed this result to the rearrangement of a primary product with the unusual structure (II):



(II)

where $R = CH_2=CH-CH_2-$ and $R' = C_6H_5$ or p-$C_6H_4CH_3$. Formula (II) is not possible from the viewpoint of modern electronic theory, and it represents essentially the N-nitrene (I).

In the oxidation of dibenzylhydrazines with mercuric oxide, completely different anomalous products were obtained; nitrogen was liberated, and hydrocarbons were formed:

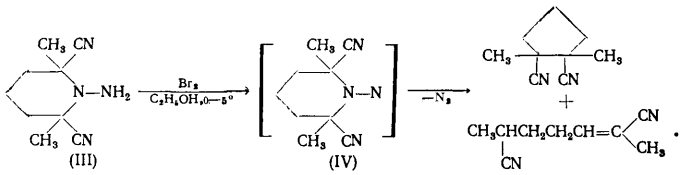


This reaction proceeds so smoothly that it was subsequently used for the preparation of derivatives of dibenzyl (the Busch–Weiss reaction)[10-12]. The replacement of one of the benzyl radicals by an aryl radical, however, leads

to the formation of arylhydrazones (or mixtures of arylhydrazones and tetrazenes)[13]:

$$\begin{matrix} Ar \\ Ar'CH_2 \end{matrix}\!\!>\!N\!-\!NH_2 \xrightarrow[0°,CHCl_4]{HgO} ArNHN{=}CHAr'\,.$$

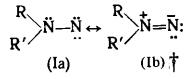
Later, it was established that the Busch–Weiss reaction is not restricted to benzylhydrazines; the oxidation of the cyclic hydrazine (III) with bromine leads to the liberation of nitrogen and the production of a mixture of dinitriles, which, in the opinion of the authors cited[14-17], are products of the decomposition of the N-nitrene (IV) formed as an intermediate product:



The hypothetical compound with a "sextet" nitrogen atom (V) was also regarded as an intermediate product in the thermal decomposition of a mixture of phenylhydrazine and its hydrochloride[18]:

$$[C_6H_5NH_2NH_2]^+ + C_6H_5NHNH_2 \rightarrow \underset{(V)}{[C_6H_5NH{-}N]} \rightarrow C_6H_5NH_2 + C_6H_6 + NH_3 + N_2 + H^+.$$

Since the nineteen-fifties, suggestions regarding the existence of intermediate species of this kind have begun to appear more frequently in papers on the chemistry of hydrazines. It has been considered that as a consequence of the presence of an unshared pair of electrons on the central nitrogen atom in these compounds, mesomerism is possible (Ia–Ib)



It has been suggested that mesomerism may lead to stabilisation and an increase in the lifetime of N-nitrenes compared with C-nitrenes or carbenes (see p. 106 of Ref. 7). Until recently, however, there was no information on the electronic structure of N-nitrenes or the relative roles of structures (Ia) and (Ib). In 1970, the structures of a number of the simplest N-nitrenes and their analogues were calculated[19] by the MO LCAO method with complete neglect of differential overlap and with allowance for all the valency electrons (the CNDO/2 method[20-22]). These calculations showed that aminonitrene itself $H_2N{-}N$ should have a planar configuration with N–N bond length 1.25 Å, which is smaller than the length of the N–N bond in hydrazine (1.46 Å) but longer than the length of the N=N bond in di-imide (1.2 Å)‡. The "sextet" nitrogen atom of the aminonitrene carries a fairly high negative charge (−0.217). For the nearest homologues of aminonitrene the negative charge on the terminal nitrogen atom is increased slightly as a consequence of the positive inductive effect of the alkyl substituents.

N-Nitrenes in which the unshared electron pair of the central nitrogen atom is involved in conjugation with substituents show the opposite effect—a definite, though small, decrease in the negative charge on the terminal nitrogen atom: −0.216 for N-pyrrylnitrene and −0.204 for phenylaminonitrene.

The populations of the π-AO of the terminal nitrogen atom in aminonitrene and its nearest homologues lie in the range 0.47–0.49, and the orders of the π-bonds between the nitrogen atoms in the range 0.81–0.84.

These results were obtained with the assumption that the ground state of the aminonitrenes is a singlet state. This assumption agrees with data on the stereochemistry of the addition reactions of various aminonitrenes at the double bond.

The comparatively large contributions of the polar structure (Ib), which reaches several percent, is an important characteristic feature of N-nitrenes, distinguishing them from C-nitrenes and from typical carbenes. The electrophilic properties characteristic of carbenes and associated with the presence of an incomplete electron shell can in the N-nitrenes be poorly defined and even masked by the distinct manifestation of the nucleophilic properties of the negatively charged terminal nitrogen atom with its high π-AO population. In this respect we must consider the nearest analogues of the N-nitrenes to be not the C-nitrenes but the so-called "nucleophilic carbenes", in particular the little-studied aminocarbenes.

Another characteristic structural feature of the N-nitrenes, which leaves a specific imprint on their reactions, is the presence of the nitrogen–nitrogen bond. As a consequence of the low energy of this bond, combined with the tendency, typical of many hydrazine derivatives, to decompose with the formation of the exceptionally stable nitrogen molecule, an extremely important role in the chemistry of the N-nitrenes is played by decomposition reactions, which are not characteristic of carbenes.

II. PREPARATION OF N-NITRENES

The fairly large number of reactions for which the formation of N-nitrenes in the intermediate stages has been postulated can be divided into two groups. One of these consists of reactions involving the formation and decomposition of unsymmetrically substituted hydrazine derivatives, including (formally at least) α-elimination according to the scheme

$$>\!N{-}N\!<^{X}_{Y} \rightarrow >\!N{-}N + XY\,.$$

These reactions invlude the oxidation of 1,1-disubstituted hydrazines by bromine in acid medium (XY = HBr), the alkaline cleavage of the hydrazides of sulphonic acids, the thermal decomposition of their N-sodium derivatives (XY = $NaSO_2P$), and also the incomplete reduction of N-nitrosamines in alkaline medium (X = OH, Y = H), the ozonolysis of hydrazones, and the reaction of secondary amines with difluoroamine HNF_2, in which the sources of the nitrenes—unstable hydrazine derivatives—are formed in the first stages of the processes.

† This mesomeric form can be regarded as a modern representation of the structure (II) proposed at an early date by Michaelis[8], whereas structure (Ia) is a more accurate general representation of structures of type (V).

‡ An interesting feature is that in an electron diffraction study of the compound N_2F_2, obtained by decomposing FN_3, it was found[23] that the intensity curves can correspond to a planar molecule of the form $\begin{matrix} F \\ F \end{matrix}\!\!>\!N{-}N$ with N–N bond length 1.16 Å.

Another less extensive group of methods for obtaining N-nitrenes consists of reactions involving the decomposition of various derivatives of hydrazine containing the fragment $\rangle N-N^{-}-Z^{+}$:

$$\rangle N-N^{-}-Z^{+}:$$

$$\rangle N-\bar{N}-\overset{+}{Z} \rightarrow \rangle N-N + Z \ .$$

The decomposition of N-azido-compounds (Z = N_2) and sulphoximines (Z = R_2SO) takes place according to this scheme.

1. Formation of N-Nitrenes in Oxidation Reactions

The first proof of the formation of N-nitrenes in oxidation reactions was obtained by McBride and Kruse[24]. In the oxidation of the simplest 1,1-dialkylhydrazines by halogens or alkali metal halates in strongly acidic medium (pH 0), the solutions showed characteristic absorption in the near ultraviolet, which could be interpreted as a consequence of the formation of the acid (VI) conjugate with (I):

$$\underset{R'}{\overset{R}{\rangle}}N-NH_2 \xrightarrow[-2HBr]{H^+,Br_2} \underset{R'}{\overset{R}{\rangle}}\overset{+}{N}=NH \rightleftarrows \left[\underset{R'}{\overset{R}{\rangle}}N-\ddot{N} \leftrightarrow \underset{R'}{\overset{R}{\rangle}}\overset{+}{N}=\bar{N}\right] + H^+ \ .$$

(VI) (I)

This acid, which was called the diazenium cation, is fairly stable in strongly acidic solutions. Neutralisation of the solutions gave the corresponding tetrazene $R_2N-N=N-NR_2$.

The existence of species of type (VI) was also proved as follows. Acid solutions of Me_2NNH_2 and Et_2NNH_2 were oxidised separately, then mixed and neutralised. The mixtures formed contained all three possible tetrazenes—the two symmetrical and the unsymmetrical.

Dimethyldiazenium perchlorate (VII) was isolated by the reaction of dimethylhydrazine with iodine and silver perchlorate:

$$Me_2NNH_2 + I_2 + 2AgClO_4 \rightarrow \underset{(VII)}{[Me_2\overset{+}{N}=NH]\,ClO_4^-} + 2AgI + HClO_4 \ .$$

Work on the electrochemical oxidation of 1,1-dimethylhydrazine[25] and 1,1-diphenylhydrazine[26,27] in acid solutions also established the formation of relatively stable products of the two-electron oxidation; the presence of these products was confirmed by coulometry and chronopotentiometry[25] and by ultraviolet spectroscopy. It was noted that these substances can be reduced to the original hydrazines in yields of up to 95%, but when the solutions are left to stand they slowly decompose.

Further proof of the formation of N-nitrenes in oxidation reactions is provided by the fact that they can be trapped in the form of stable products of addition to the multiple bonds[28-34] and the products of the cyclo-addition of diazenium salts at multiple bonds[27,35-39], and also by the reactions of N-nitrenes with dimethyl sulphoxide[28,31].

The oxidation of 1,1-disubstituted hydrazines by bromine in strongly acidic aqueous solutions has been dealt with in a number of papers[14,15,17,24,35,36,40-43]. Potassium iodate[44] and bromate[24,43,45] are sometimes used as oxidant, but yellow mercuric oxide is used most frequently[8-13,44,46-61]. The reaction with mercuric oxide is usually carried out in aqueous or absolute alcohol, and less frequently in CH_2Cl_2,[50,53,55,59] $CHCl_3$,[10,11] CCl_4,[12,56] ether[61], butanol, and dimethyl sulphoxide[57]. Activated manganese dioxide[32,53,56,59,60,62,63] and nickel dioxide[60,64] in CH_2Cl_2, potassium permanganate in acetone[16,55], N-bromosuccinimide[55,60], selenium dioxide and iodobenzene diacetate[60], *t*-butyl hypochlorite[17,65], chlorine[65], and per-acids[66] have also been used.

Lead tetra-acetate has recently been used for the oxidation of 1,1-disubstituted hydrazines[28-33,36,51,60,67-81]. The reaction is usually carried out in benzene or CH_2Cl_2.

1-Chlorobenzotriazole[82] and the diethyl ester and phenylimide of azodicarboxylic acid[83] have been used as oxidants.

In all instances it is assumed that intermediate formation of the N-nitrene takes place according to the general scheme

$$\underset{R'}{\overset{R}{\rangle}}N-NH_2 \xrightarrow[-2H]{-2e^-} \left[\underset{R'}{\overset{R}{\rangle}}N-\ddot{N} \leftrightarrow \underset{R'}{\overset{R}{\rangle}}\overset{+}{N}=\bar{N}\right] \ . \qquad (1)$$

The directions of the reactions of the N-nitrenes formed in the first stage of the reaction, and the structures of the final products, are determined by the conditions of the oxidation and also by the nature of the radicals R and R′ in the original hydrazine. If R and R′ are aliphatic or aromatic radicals, oxidation under mild conditions usually gives the tetrazenes, which are regarded as the "normal" products of the oxidation of unsymmetrical secondary hydrazines. N-Nitrenes with heterocyclic, benzyl, and certain other radicals, however, have a greater tendency to undergo other reactions, so that the oxidation of these hydrazines may take place "anomalously", with the formation of not tetrazenes but other nitrogen compounds or hydrocarbons.

The oxidation has been carried out with 1,1-dibenzylhydrazine and its derivatives[9-13,17,47-49,63,79], including optically active compounds[47,48], and also with heterocyclic compounds which can be regarded as analogues of 1,1-dibenzylhydrazine: 1-amino-2,6-diphenylpiperidine[44,46,54], 1-amino-2,5-diphenylpyrrolidine[58], and other compounds containing condensed aromatic rings[53,55,56,64,84]. The oxidation of 1-amino-2,5-diphenylpyrrole and 1-amino-2,3,4,5-tetraphenylpyrrole[56], 1-amino-1,3,4-triazole, and its 2,5-dimethyl- and 2,5-diphenyl-derivatives[78] has been studied. Studies have been reported of the oxidation of 1,1-dialkylhydrazine[24,25,34,35,40,41,45,61,83,85], 1-alkyl-1-benzylhydrazine[21,32], and also of 1,1-diarylhydrazine[26,27,63,86], and 1-aryl-1-benzylhydrazine[13]. The oxidation of 1,1-disbustituted hydrazines with allyl and aryl radicals was studied earlier[8,86].

Overberger and coworkers oxidised 1-amino-2,6-dicyano-2,6-dimethylpiperidine[14-17,42], 1-amino-2,6-dicyanopiperidine, and 1-amino-2,6-dicarbamidopiperidine[57]. The oxidation of N-aminopiperidine, N-aminomorpholine[63], and N-aminophthalimide[80] has been studied.

Considerable attention has been paid to the oxidation of compounds of the 1- and 2-aminobenzotriazole[60,68-72,77,82], 1-aminonaphtho[1,8,-*d*,*e*]triazine[73-75], and 1-amino-4,5-diphenyltriazole[82] series, in connection with the intermediate formation of dehydroaromatic systems—dehydrobenzene and 1,8-dehydronaphthalene.

1-Amino-oxindole and its derivatives[51,65] have been oxidised, and various 3-cinnolinols were obtained as final products.

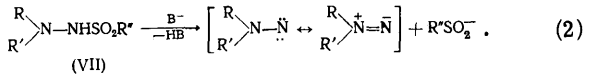
3-Aminobenzoxazoline-2-one[28,29,36], the N-aminoimides of various dibasic acids[29-32], and various other N-aminoheterocyclic compounds[29,32,33,67] were oxidised with the aim of carrying out addition reactions of the intermediate N-nitrene at the multiple bond.

3-Amino-benzo-1,2,3-triazine-4-one and its derivatives[76] were oxidised in an attempt to obtain benzocyclopropenone. The reaction of semicarbazide with per-acids has been carried out[66].

It should be emphasised that in early work on the oxidation of 1,1-disubstituted hydrazines the suggestion that N-nitrenes are formed in intermediate stages was used only to explain anomalous reactions, whereas it is now assumed that they are also formed in "normal" oxidation.

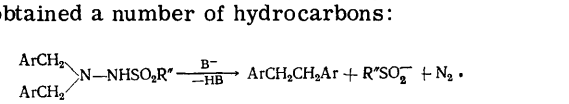
2. Decomposition of the Hydrazides of Sulphonic Acids and Their N-Sodium Derivatives

The action of alkalis on 1,1-disubstituted hydrazides of sulphonic acids (VII) leads not to their saponification but to their decomposition to the salts of the sulphinic acids and N-nitrenes, which undergo further reactions:

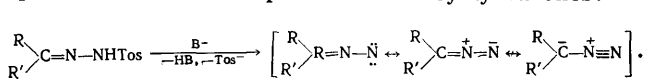


(VII) (2)

This reaction is named after its discoverer Carpino[87,88]. In the decomposition of dibenzylsulphonylhydrazines, Carpino obtained a number of hydrocarbons:



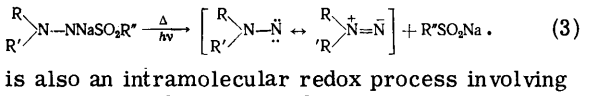
The formation of N-nitrenes from the hydrazides of sulphonic acids can be regarded as analogous to the preparation of diazo-compounds from tosylhydrazones:



In both instances an intramolecular redox process takes place, in which the hydrazine residue undergoes two-electron oxidation and the sulphonic acid residue is reduced to the sulphinate ion. In this sense the Carpino reaction is similar to the Busch–Weiss intermolecular oxidation of 1,1-disubstituted hydrazines; the final products of these reactions are also similar.

Lemal[89,90] observed a decrease in the rate of hydrolysis of 1,1-disubstituted hydrazides of sulphonic acids in strongly alkaline solutions. It was suggested that a condition for the reaction is the presence of alkali and free sulphonyl hydrazide.

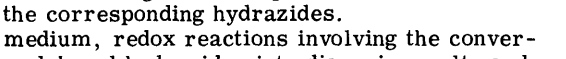
The alkaline decomposition of 1,1-disubstituted sulphonyl hydrazides is closely related to the thermal decomposition[75,90-93] or photolysis[75] of their N-sodium derivatives:



(3)

This is also an intramolecular redox process involving the oxidation of the hydrazine residue to the aminonitrene and the reduction of the sulphonic acid residue to the sodium salt of the sulphinic acid. The final products of this reaction are analogous to the products of the action of alkalis on the corresponding hydrazides.

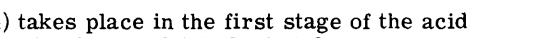
In acid medium, redox reactions involving the conversion of the sulphonyl hydrazides into diazenium salts and salts of sulphinic acids, which dissociate to give diazenium cations and sulphinate ions[94], also take place



(4)

Reaction (4) takes place in the first stage of the acid hydrolysis of 1-alkyl- and 1,1-dialkyl-2-tosylhydrazines, and the diazenium ion formed undergoes a number of further reactions.

Dissociation according to scheme (4) is also apparently the first stage of the ready exchange of sulphonic acid residues between sulphonyl hydrazides and salts of sulphinic acids[89,94]:



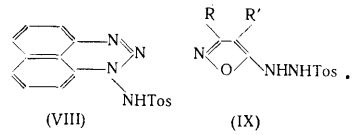
The exchange has been studied in alkaline and neutral media. The establishment of equilibrium in this exchange has been demonstrated by the NMR method, and the kinetics of exchange have been studied. It has been established that the reaction is of first order with respect to the original hydrazide and of zero order with respect to the salt (at a salt concentration greater than the equivalent concentration).

The action of alkali on 1,1-disubstituted sulphonyl hydrazides and the decomposition of their N-sodium derivatives have been most frequently studied with the readily available and easily purified tosyl hydrazides[55,56,59,62,75,87,88,91-93,95-101] and benzenesulphonyl hydrazides[87,88,91,96,101,102]. The hydrazides of alkylsulphonic acids have been less extensively studied[87,88,101].

The substituents on the tertiary nitrogen atom have been varied widely. Dibenzylhydrazides[87,88,95,96] and their derivatives[87,88] and analogues[55,62,92,97,98] have been studied. The alkaline cleavage of the 1-aryl-1-benzylhydrazides of sulphonic acids has been carried out[101,102]. The reactions of hydrazides with alkyl[90,91,96,102] and allyl[93] substituents have also been studied.

The Carpino reaction has been carried out with the tosylates of 1-aminopyrrole[91], 1-amino-2,5-diphenylpyrrole, and 1-amino-2,3,4,5-tetraphenylpyrrole[56], and also with 9-benzenesulphonimidocarbazole[91].

Hoffmann and coworkers[75] obtained 1,8-dehydronaphthalene by the alkaline hydrolysis of compound (VIII):



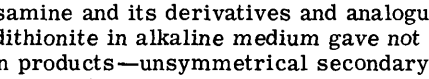
(VIII) (IX)

The alkaline cleavage of monosubstituted hydrazides was used in synthesis for the elimination of the hydrazine group in compound (IX)[99,100].

Most studies of the alkaline decomposotion of sulphonyl hydrazines have been carried out in aqueous or aqueous-alcoholic solutions of NaOH or KOH[55,56,59,62,87,88,91,92,97,98,101,102]. Other solvents used include ethylene glycol[56] and diethylene glycol[88], and, less frequently, aqueous K_2CO_3 solution[99,100], triethylamine in dimethylformamide[87], and pyridine[92].

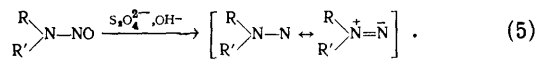
3. Formation of N-Nitrenes in the Reduction of N-Nitrosamines

In 1957 it was discovered[103] that the reduction of dibenzylnitrosamine and its derivatives and analogues with sodium dithionite in alkaline medium gave not the usual reduction products—unsymmetrical secondary hydrazines R_2NNH_2—but hydrocarbons of the dibenzyl series:



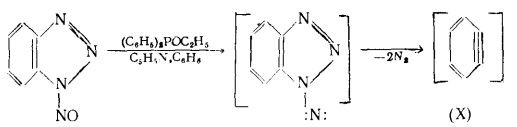
The anomalous reduction of nitrosamines to hydrocarbons has been called the Overberger–Lombardino reaction. Since the products were found to be the same as the products of the oxidation of the corresponding

hydrazines, it was suggested that the same intermediate compounds—N-nitrenes—are formed in the two instances:



(5)

Reactions involving the anomalous reduction of nitrosamines were observed with dithionite in alcoholic alkali[47,48,58,84,103,104], lithium in liquid ammonia[104], and a benzene solution of ethyl diphenylphosphinite $[(C_6H_5)_2POC_2H_5]$.[105] Anomalous reduction is undergone not only by dibenzylnitrosamine itself[103,104] but also by N-nitroso-derivatives of benzylphenylamine, diphenylamine, and 2,6-dimethylpiperidine[103], 2,6-diphenylpiperidine[103,104], 2,5-diphenylpyrrolidine[58], and the optically active α,α'-dimethyldibenzylamine[47,48]. The formation of dehydrobenzene (X) was observed in the reduction of 1-nitrosobenzotriazole[105]:

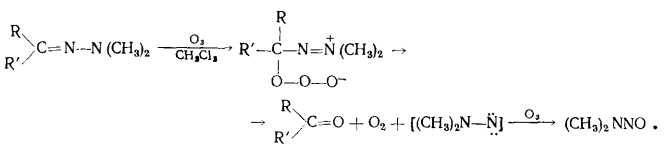


It is at present difficult to assess the possibility of formation of N-nitrenes in the reduction of N-nitrosamines taking place "normally", since the necessary experimental data are not available.

4. Ozonisation of Compounds Containing the $>C=N-N<$ Group

It has been known for a long time that in the ozonisation of compounds containing the $>C=N-N<$ group, aldehydes or ketones are formed[106,108]; the compositions of the other products of the reaction, and its mechanism, were not studied until recently. In 1961, papers were published on the ozonisation of the double bond in azines[109] and on the action of ozone on pyrazole and some of its homologues[110]; the authors of these papers assume that N-nitrenes are formed as intermediate products.

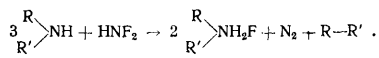
On the basis of kinetic data[111], the following mechanism for the ozonisation of the C=N bond in dimethylhydrazones was suggested:



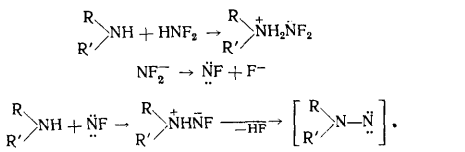
The N-nitrene formed may react with the solvent or be oxidised to the N-nitroso-compound[111].

5. Reaction of Difluoroamine with Amines and Phenylhydrazones

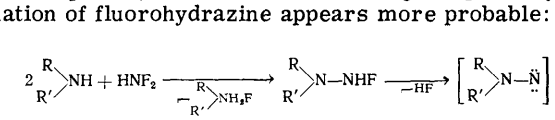
Bumgardner and coworkers[95] studied the reaction of primary and secondary amines with difluoroamine in an excess of the amine:



The deamination of dibenzylamine with difluoroamine, the reduction of N-nitrosodibenzylamine with sodium dithionite, and the alkaline cleavage of 1,1-dibenzylhydrazine tosylate give dibenzyl in similar yields. On this basis it was concluded that N-nitrenes are formed in an intermediate stage of the deamination. The authors cited[95,112] put forward the following mechanism:

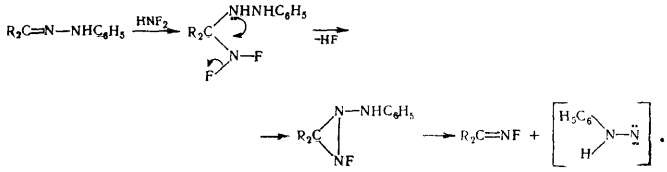


In our opinion, a mechanism involving the primary formation of fluorohydrazine appears more probable:



The reaction with difluoroamine has usually been carried out at room temperature. A variety of primary amines have been taken for the reaction—saturated[95] and unsaturated[37] amines, 3,5,5-trimethylpyrazoline[95], N-methylaniline[113], and the small-ring compounds azetidine[95] and aziridines[95,114].

It has also been assumed that N-nitrenes are formed in the reaction of difluoroamine with the phenylhydrazones of acetone and formaldehyde[113]:

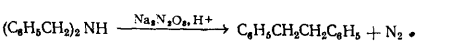


Stronger evidence in support of all the above reaction mechanisms is required.

6. Formation of N-Nitrenes in the Reaction of Angeli's Salt with Secondary Amines

Lemal[96,115] described the reactions of a number of secondary amines with Angeli's salt $Na_2N_2O_3$§. Dibenzylamine, pyrrolidine, piperidine, morpholine[96], pyrroline, and its *cis*- and *trans*-2,5-dimethyl-derivatives[115] were studied.

Dibenzyl was obtained from dibenzylamine:



Other amino-compounds also gave products identical to the products of the reactions of the corresponding N-nitrenes, so that Lemal, without putting forward a reaction mechanism, concluded that the formation of N-nitrenes as an intermediate stage of the reaction of amines with Angeli's salt is possible.

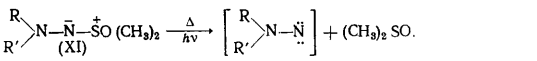
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§ Angeli's salt has the sodium α-oxyhyponitrite structure[116]:

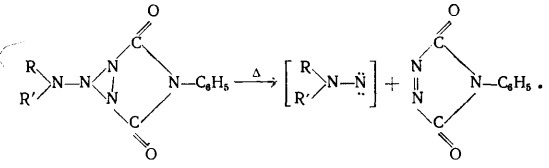


7. Formation of N-Nitrenes in the Decomposition of Their Adducts and N-Azides

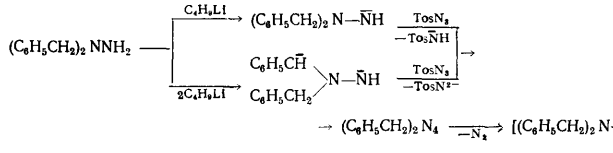
Sulphoximines (XI), obtained by the addition of N-nitrenes to dimethyl sulphoxide, give N-nitrenes again as a result of photolysis[29] or thermal decomposition[31,67]:



The formation of N-nitrenes in the decomposition of N-aminotriaziridines, obtained by the addition of N-nitrenes across an N=N bond, has been assumed[83]:



A recent paper[117] dealt with the decomposition of N-azides, giving N-nitrenes and their decomposition products. The N-azides were obtained by the exchange of hydrazide anions and $TosN_3$; the intermediate N-azide was not isolated. Dibenzylamino-N-azide and the corresponding N-nitrene were obtained in this way:



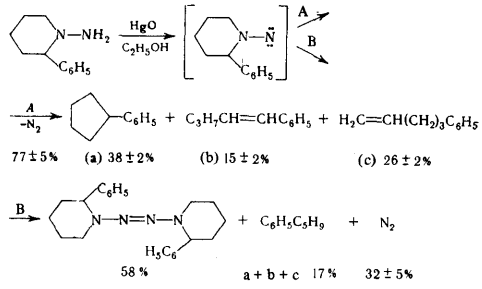
III. REACTIONS OF N-NITRENES

The previous section examined briefly reactions in which the intermediate formation of N-nitrenes has been assumed. The products of these reactions result from the subsequent transformation of the N-nitrenes. If we follow the traditional classification of chemical reactions according to the number of reactants and products, we can divide all known reactions of N-nitrenes into three types: 1) decomposition; 2) isomerisation; and 3) addition.

Examples of reactions of the first type are provided by the Busch–Weiss, Carpino, and Overberger–Lombardino reactions, in which the N-nitrenes decompose to hydrocarbons and nitrogen. The rearrangement of N-nitrenes to the isomeric hydrazones belongs to the second of the reaction types listed above, and examples of the third type are fairly widely encountered: they include the formation of tetrazenes, characteristic of N-nitrenes, and also the addition of various aminonitrenes across double bonds.

The direction of the reaction depends on many factors, which can be classified as internal factors, determined by the nature of the N-nitrene (its structure), and external factors determined by the conditions under which the reaction is carried out. The role of the medium has been little studied and is difficult to take into account. The same N-nitrenes react in different ways under different conditions, and even such an unstable species as dibenzylaminonitrene can be reduced to 1,1-dibenzylhydrazine without decomposition, whereas the comparatively stable aromatic imidonitrenes, under the conditions of the thermal decomposition of sulphoximines at 400–450°,[118] decompose with the liberation of nitrogen.

The lifetime of a given N-nitrene, and hence the reactions which it can undergo, can vary over a wide range, particularly under the conditions of heterogeneous reactions. If the probability that the N-nitrene meets and reacts with another molecule is appreciable, intermolecular reactions are observed, whereas if this probability is low, the N-nitrene decomposes before it is able to react with another molecule. This obvious situation is effectively illustrated by data on the oxidation of 1-amino-2-phenylpiperidine (XII) by yellow mercuric oxide[52].



When compound (XII) is added rapidly to a suspension of mercuric oxide in alcohol, the N-nitrene formed is able, before decomposition, to meet a molecule of the original hydrazine and react with it, giving chiefly the product of the bimolecular reaction—the tetrazene—and the decomposition products (hydrocarbons) are obtained in only 17% yield (path B). When the reagent is added slowly, the probability of the above encounter is low, and the decomposition of the N-nitrene is almost complete (path A).

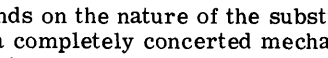
Thus in order to predict the direction of a reaction it is necessary to take into account many factors; these often have opposite effects which cannot yet be estimated quantitatively. Moreover, the picture is usually complicated by various secondary processes.

With all this in mind, we shall consider below the chief reactions of N-nitrenes and the small amount of information which has accumulated on the reaction mechanisms.

1. Decomposition of N-Nitrenes

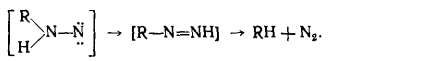
One of the most interesting and general features of N-nitrenes is their ability to decompose with the liberation of nitrogen and the formation of hydrocarbons. This reaction has been observed for N-nitrenes obtained in the most varied ways. In summarising the available data, it may be noted that the mechanism of the decomposition of N-nitrenes depends on the nature of the substituents and may vary from a completely concerted mechanism to a biradical mechanism.

The most extensively studied decomposition is the decomposition of aminonitrenes with the rupture of two bonds, for example the decomposition of dibenzylaminonitrene and its derivatives into dibenzyl and nitrogen:



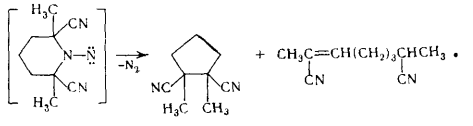
This reaction, discovered by Busch and Weiss in 1900, has attracted the attention of many research workers in subsequent decades. Dibenzyls have been obtained in the oxidation of 1,1-disubstituted hydrazines[9–12,47–49,88,104], in the anomalous reduction of nitrosamines[47,48,84,104], in the Carpino reaction[55,62,87,88,97,101], in the deamination of dibenzylamine by difluoroamine[95] or $Na_2N_2O_3$,[96] and in the decomposition of dibenzylamino-N-azide[117].

Decomposition to the corresponding hydrocarbons is also undergone by monosubstituted N-nitrenes, possibly after their rearrangement into the azo-compound[18,37,95,99,100,113,114]:



Problems related to the existence and stability of compounds of the type R–N=NH have been examined[119].

In the decomposition of N-nitrenes, in addition to combination of the residues R and R′, disproportionation with the formation of unsaturated compounds may also take place. Reactions of this kind were first observed in the oxidation of 1-amino-2,6-dicyano-2,6-dimethylpiperidine by bromine[14–17], when 2,6-dicyanohept-2-ene was obtained in addition to *cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclopentanes:

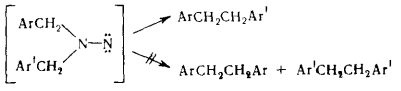


A large number of examples of reactions of this kind were subsequently studied[42,44,46–48,52,54,57,58].

The question of the mechanism of the decomposition of N-nitrenes was first raised in 1955, when a radical mechanism was proposed for the decomposition of 2,6-dicyano-2,6-dimethylpiperidyl-N-nitrene[17]. Later[44], however, it was suggested that the decomposition of aminonitrenes of this kind, and also of aminonitrenes with substituents of the benzyl type is a three-centre concerted decomposition. The data at this stage of the studies were summarised by Overberger[120]. Later, an E_2-mechanism was proposed[42], but this was later rejected when it could not explain new experimental facts[52,54,57].

A criterion for the correctness of a mechanism for the decomposition of aminonitrenes with radicals of the benzyl type must be consistent with the following experimental facts.

1. In the decomposition of aminonitrenes with different radicals, it has not been possible to isolate mixed cross-products of the combination[49,84,93,104]:

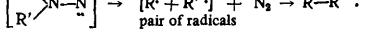


2. Decomposition with combination of the radicals takes place only if both[49,50,52,93] or at least one[52] of the substituents in the N-nitrene is capable of stabilising the intermediate state. These substituents are the benzyl, allyl, and nitrile radicals, and the carbamide and furfuryl groups. It is also known that in order to obtain a high yield of the products of the combination, the substituents should have a small volume, otherwise alkenes are formed preferentially[57].

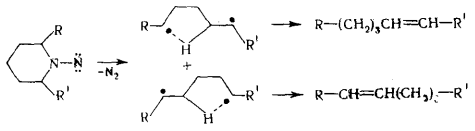
3. For N-nitrenes with R and R′ radicals of the benzyl type, no definite conclusion can be reached regarding the influence of the inductive or mesomeric effect of a substituent in the ring on the rate of decomposition or the yield of hydrocarbons[87,88,101]. The absence of a relationship of this type is characteristic of radical reactions.

4. The stereospecificity of the decomposition of aminonitrenes in which the substituents form a cyclic system is extremely high[44,46,57,58,103,104]. For the optically active α,α′-dimethyldibenzylaminonitrene, the stereospecificity of the decomposition decreases sharply[47,48,84].

Almost all these results are consistent with the radical mechanism of decomposition, proposed by Overberger, with a strong cage effect, which prevents the formation of cross-products and increases the stereospecificity of the reaction[58]:

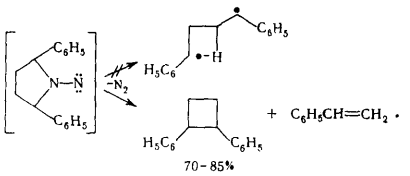


The formation of alkenes in the decomposition of six-membered rings, in Overberger's opinion, involves a five-membered intermediate state:



The relative amounts of combination products and alkenes will in this instance depend on steric factors.

In the decomposition of N-(2,5-diphenylpyrrolidino)nitrene, 1,4-diphenylbutenes are not formed[58], apparently due to the highly strained nature of the corresponding intermediate state (which must be four-membered):

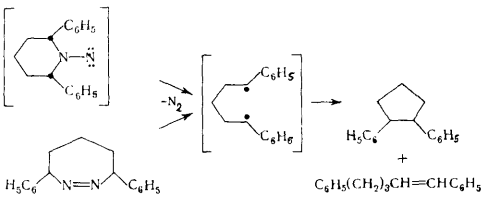


The process proceeds further with the partial formation of styrene.

The decomposition of N-nitrenes can be compared with the decomposition of the corresponding azo-compounds, the radical mechanism of which was established by the EPR method[121].

At first, the non-stereospecific nature of the thermal decomposition of the azo-compounds was noted[122,123]. Later, however, a number of authors[121,124–129] showed that under conditions favouring a marked cage effect, the decomposition of azo-compounds is extremely stereospecific. The model compounds in this work were *cis*- and *trans*-2,5-disubstituted Δ^1-pyrazolines[121,124–128] and 3,6-dicyano-3,6-dimethyl-3,4,5,6-tetrahydropyridazine[129].

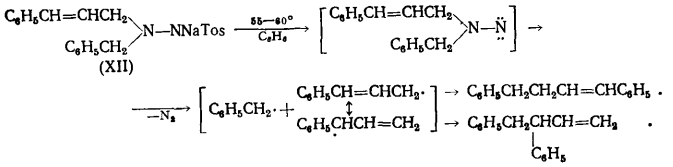
Evidence that the mechanisms of these reactions are the same is provided by the similarity in the isomeric composition of the products obtained in the decomposition of N-(*cis*-2,6-diphenylpiperidyl)nitrene[44,46,103,104] and in the decomposition of *cis*-3,7-diphenyl-1,2-diazacycloheptene-1[124]:



The products of the decomposition of N-(*cis*-2,5-diphenylpyrrolidino)nitrene[58] and the thermal decomposition of *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine[130] are also similar.

The proposed radical mechanism is effectively confirmed by the results of the decomposition of the sodium derivatives of tosylhydrazines with different allyl and benzyl radicals[93]. Thus the decomposition of compound

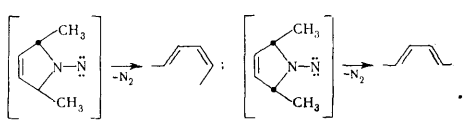
(XII) gave not only 1,4-diphenylbut-1-ene but also 3,4-diphenylbut-1-ene, in the ratio 3 : 1, with a total yield of ~ 100%:



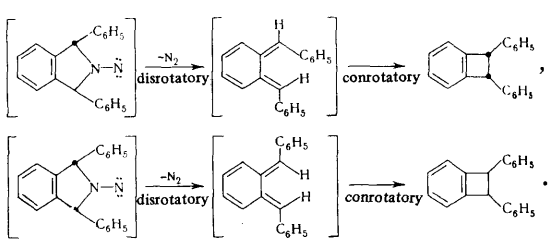
This result indicates the intermediate formation of free allyl and benzyl radicals. The absence of the cross-products—dibenzyl and diphenylhexadienes—indicates a strong cage effect.

The biradical decomposition of the aminonitrenes should however be regarded only as one possible extreme. The other extreme possibility is the concerted mechanism of decomposition.

The decomposition of a number of aminonitrenes obeys the Woodward–Hoffmann rules for concerted processes. These rules define the stereochemistry of the decomposition and are observed in those instances where these processes for the aminonitrene are allowed and are energetically more favourable than the radical processes. A common feature of the concerted processes of the decomposition of aminonitrenes is the formation of a system with a greater unsaturation than the original system. The polyene obtained may react further, and its subsequent reactions are also determined by the Woodward–Hoffmann rules. Examples of such processes are the decomposition of various N-(3-pyrrolino)nitrenes[115,132] and N-(1,3-dihydroisoindolino)nitrenes[53,55,59,64,92,98]. Lemal[115] established by means of correlation diagrams that the decomposition of N-(3-pyrrolino)nitrene should be disrotatory, and he confirmed this experimentally. The model compounds were N-(*cis*- and *trans*-2,5-dimethylpyrrolino)nitrenes:

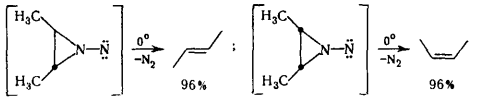


The decomposition of N-(1,3-dihydroisoindolino)nitrenes has attracted considerable attention, since it was expected to give various benzocyclobutenes. This process takes place in two stages, and for the example of N-(*cis*- and *trans*-1,3-dihydro-1,3-diphenylindolino)nitrenes it was shown[53,59,92,98] that the stereochemistry of both stages obeys the Woodward–Hoffmann rules. The yields and compositions of the products depend markedly on the conditions of the reaction[59]:

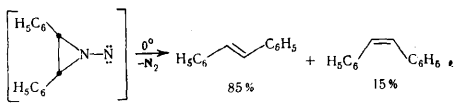


The decomposition of unsubstituted N-(1,3-dihydroisoindolino)nitrene[53,55,92,98] and the tri- and tetraphenyl-derivatives with substituents in the 1,3-positions[64] has also been studied. The intermediate products showed a tendency to undergo other concerted reactions, also possible in these systems, with the formation of various polycyclic compounds.

The decomposition of N-aziridinonitrenes gives alkenes. Data on the stereochemistry of the decomposition of three-membered rings with the formation of alkenes are contradictory, and there is still lack of agreement regarding its mechanism. Until recently it was considered that the decomposition of N-aziridinonitrenes was completely stereospecific, and this was demonstrated by the deamination of *cis*- and *trans*-2,3-dimethylaziridines by difluoroamine[114] (see also Ref. 133):

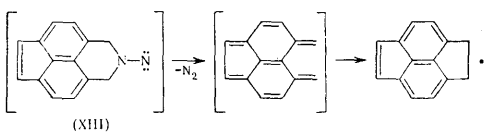


The decomposition of N-(*cis*-2,3-diphenylaziridino)nitrene is non-stereospecific, however[32]:



It was shown that under the conditions of the reaction, the isomerisation of *cis*-stilbene into the *trans*-isomer does not take place. Here, it is true, it may be assumed that the mechanism of the decomposition is intermediate between the biradical and the purely concerted mechanisms, but even this does not explain all the results obtained.

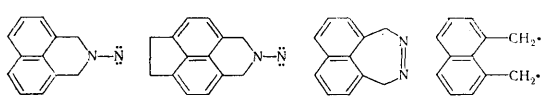
The decomposition of aminonitrenes with large rings has been little studied up to the present and has not been examined from the viewpoint of the preservation of orbital symmetry. The only example as yet is the decomposition of the aminonitrene (XIII), which gives dihydropyracylene in 8–15% yield[62]:



(XIII)

It may be assumed that this reaction takes place in two stages: linear cheletropic[131] decomposition of the aminonitrene takes place first, followed by electrocyclic closure of the ring with 12 π-electrons.

It should be noted that the aminonitrenes (XIV) and (XV) with similar structures do not decompose to nitrogen and hydrocarbons[55,62,97].

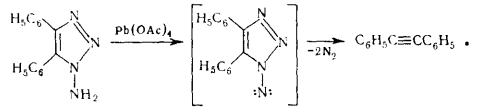


(XIV) (XV) (XVI) (XVII)

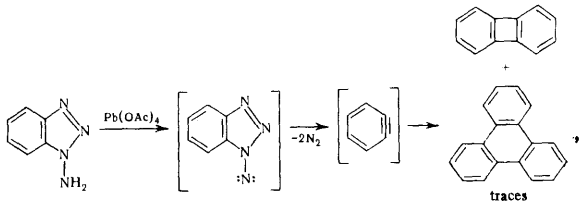
Concerted decomposition in these systems is impossible, but it is not clear why biradical decomposition does not take place. The decomposition of the aminonitrene (XIV) and the corresponding azo-compound (XVI) should take place by the same mechanism with the formation, in the first stage, of the biradical (XVII) and a molecule of nitrogen. The thermal decomposition of compound (XVI), however, as expected, gives the acenaphthene in 59% yield[55], and the aminonitrene (XIV) does not decompose to give nitrogen and hydrocarbons. No explanation for this has yet been put forward.

Let us now consider processes, involving the decomposition of aminonitrenes, in which more than two bonds in the original molecule are broken. This group includes the cleavage of 1- and 2-(1,2,3-triazolyl)nitrenes, and various other reactions.

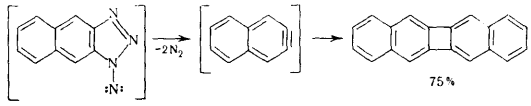
1-(1,2,3-Triazolyl)nitrene decomposes with the liberation of two molecules of nitrogen and the formation of hydrocarbons. In this way, 1-amino-4,5-diphenyl-(1H)-triazole gave tolane[82]:



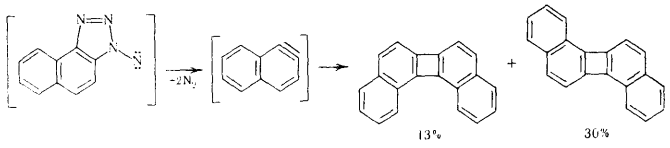
Hydrocarbons were obtained by the following reactions: from 1-aminobenzotriazole[60,69-71,82,105]:



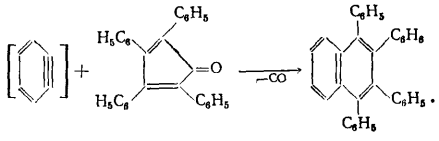
from 1-amino-[1H]-naphtho[2,3-*d*]triazole[72]:



from 1-amino[1H]-naphtho[1,2-*d*]triazole[72]:

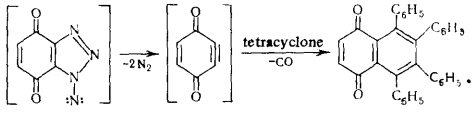


All these products are dimers of the corresponding dehydro-derivatives. The "arenes" obtained can also be trapped by "tetracyclone" (2,3,4,5-tetraphenylcyclopentadienone)[69,82,105]:

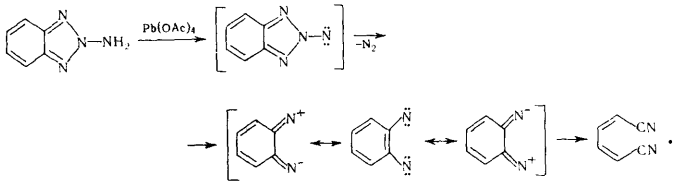


The yield of tetraphenylnaphthalene is almost quantitative, indicating the quantitative formation of dehydrobenzene in this reaction.

1-Aminobenzotriazoles with different substituents in the benzene ring also undergo splitting[69,71,77]. A similar method gave "benzynequinone" (dehydroquinone)[68,77], which with tetracyclone gave tetraphenylnaphthaquinone in 40–60% yield:

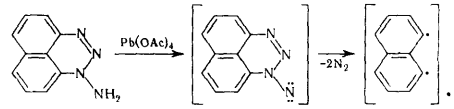


The oxidation of 2-aminobenzotriazole gives the dinitrile of *cis-cis*-mucic acid[70,71,82]:



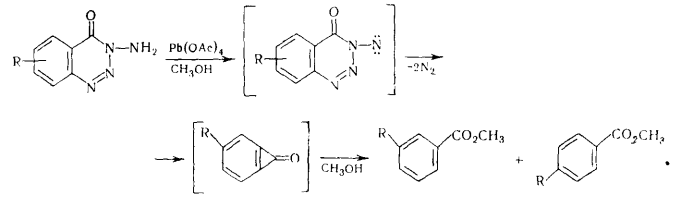
Oxidation by lead tetra-acetate leads to the partial formation of the *cis-trans*-dinitrile, apparently as a consequence of isomerisation under the conditions of the reaction. The milder conditions of oxidation by iodobenzene diacetate give only the *cis-cis*-isomer[71]. The formation of the dinitrene in an intermediate stage of the reaction is confirmed by the fact that the dinitrile of mucic acid was also obtained by the oxidation of *o*-phenylenediamine[71] by lead tetra-acetate and by the thermal decomposition of *o*-phenylenediazide[134]. Both of these reactions involve the intermediate formation of the dinitrene. *cis-cis*-2,5-Dimethoxymuconitrile was obtained by oxidising 1,4-dimethoxy-2,3-phenylenediamine[77].

The oxidation of 1-aminonaphtho[1,8-*d*,*e*]triazine gives 1,8-dehydronaphthalene[73-75]:

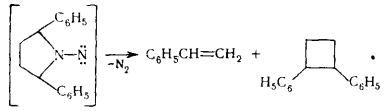


1,8-Dehydronaphthalene could not be obtained either by the thermal decomposition or by the photolysis of the sodium derivative of the tosylate of this compound. 1,8-Dehydronaphthalene is an exceptionally reactive compound. It reacts with solvents[73,74] and also adds on to C=C[73-75] and N=N[74] bonds.

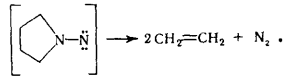
In 1969, an attempt was made to prepare benzocyclopropenone by the oxidation of 5- or 6-substituted 1-aminobenzotriazolin-8-ones, but the reaction in methanol gave only the methyl esters of the corresponding benzoic acids[76]:



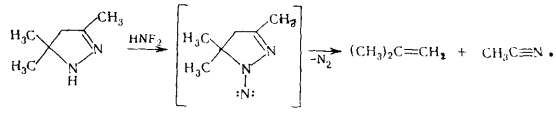
The decomposition of aminonitrenes containing a five-membered ring with different degrees of unsaturation is of considerable interest. This is important for the study of systems in which concerted decomposition is impossible. It was noted above that one of the products of the decomposition of N-(2,5-diphenylpyrrolidino)nitrene is styrene[58]:



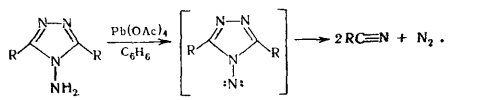
With unsubstituted N-(pyrrolidino)nitrene, dissociation into three components is the only route taken in the splitting:



This splitting with rupture of the 1–2, 1–5, and 3–4 bonds is fairly typical of nitrenes with a five-membered ring. It has been established[95] that when 3,5,5-trimethyl-Δ^2-pyrazoline is treated with difluoroamine, the N-nitrene formed decomposes to nitrogen, acetonitrile, and isobutene:



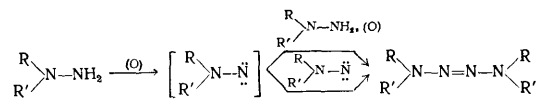
In the oxidation of 1-amino-1,3,4-triazoles with different substituents in positions 2 and 5, the liberation of 55–90% of the nitrogen and the formation of the corresponding nitriles was observed[78]:



1-Aminopyrrole derivatives, however, do not decompose in this way, but form tetrazenes and subsequently pyrrole derivatives[56,78,91]. It was therefore suggested that, other conditions being equal, the direction of the reaction is determined by the ease of rupture of the bond 3–4.[78] The explanation for the decomposition of the triazole derivatives is that the energy of the N–N bond here is smaller by 40 kcal mole^{-1} than the energy of the C–C bond 3–4 in pyrrole. This hypothesis, however, cannot explain the decomposition of aminonitrenes in the two previous instances, where the energy of the bond 3–4 is fairly high.

2. Formation of Tetrazenes

Since the time of Fischer[135] it has been known that Δ^2-tetrazenes are the chief products of the oxidation of 1,1-disubstituted hydrazines by a wide variety of oxidising agents. This "normal" oxidation is now also regarded as involving the interaction of the initially formed N-nitrenes with the original hydrazine or (which is less likely) their dimerisation[7,52]:

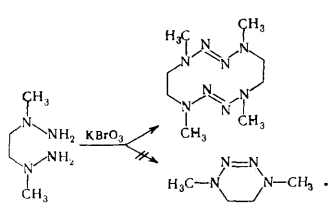


Tetrazenes are also formed in other instances on dimerisation of intermediate N-nitrenes, if the latter are sufficiently stable under the conditions of the reaction[24,55,56,66,91].

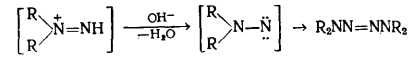
Fairly frequently, the tetrazenes formed are unstable under the conditions of the reaction and decompose with the separation of a molecule of nitrogen and the formation of secondary amines[56,78,90,91].

The possible stereoisomerism of Δ^2-tetrazenes has not been studied until recently, but recent papers deal with the isolation of *cis*- and *trans*-3,3-azobis-(2-oxazolidinone)[136] and the *cis*- and *trans*-isomers of the tetrazene obtained by oxidising N-aminophthalimide[80]. The oxidation usually gives the thermodynamically more stable *trans*-structure, but the *cis*-form can also be obtained on heterogeneous oxidation[80,136].

An attempt to prepare the *cis*-tetrazene by the oxidation of 2,5-diamino-2,5-diazahexane (this would be 1,4-dimethyl-1,4,5,6-tetrahydro-1,2,3,4-tetrazine) gave the twelve-membered cyclic bis-tetrazene[45]:

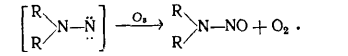


McBride developed a method for preparing tetra-alkyltetrazenes by oxidising 1,1-dialkylhydrazines with bromine in acidic aqueous solution followed by neutralisation[24,34,40,44]. The diazenium ion formed in the first stage, on neutralisation, gives the N-nitrene, which then dimerises to give the tetrazene:



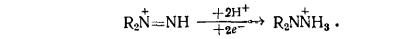
3. Oxidation and Reduction of N-Nitrenes

These reactions have been insufficiently studied. The oxidation of N-nitrenes to the corresponding nitrosamines was observed under ozonisation conditions[110,111]:



It was suggested that in the electrochemical oxidation of 1,1-dimethylhydrazine in acid medium, one possible reaction of the diazenium ion is its oxidation to the nitrosamine[25].

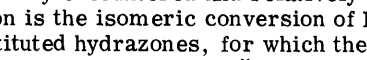
Reduction of N-nitrenes apparently takes place in the reduction of N-nitrosamines to hydrazines. It is known that diazenium ions in acid medium can be reduced by chemical (by $SnCl_2$ or Zn in H_2SO_4) or electrochemical methods[25,26]. The corresponding 1,1-disubstituted hydrazines are obtained in yields close to 100%:



4. Rearrangements of N-Nitrenes

The rearrangements of N-nitrenes have been studied in considerable detail, but a satisfactory mechanism has not yet been proposed for any of these reactions.

The most widely encountered and relatively fully studied reaction is the isomeric conversion of N-nitrenes into monosubstituted hydrazones, for which the name "diazene–hydrazone rearrangement" has been proposed[90]:

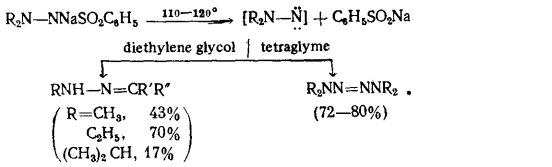


The formation of hydrazones in the oxidation of 1-aryl-1-benzylhydrazines by mercuric oxide was detected at an early date[13]. Later, examples of this rearrangement were studied for arylbenzylaminonitrenes[101,102], arylalkylaminonitrenes[101,113], and dialkylaminonitrenes[25,85,89,90,102]. The rearrangement has usually been carried out in alkaline medium, and only one example in acid medium is known[25].

That the rearrangement is intramolecular is indicated by the absence of the products of the cross-reaction in the alkaline cleavage of a mixture of the tosylates of 1-benzyl-1-*p*-chlorophenylhydrazine and 1-*p*-chlorobenzyl-1-phenylhydrazine (only benzaldehyde *p*-chlorophenylhydrazone and *p*-chlorobenzaldehyde phenylhydrazone were isolated)[101]. The reaction is of first order with respect to the hydrazide anion, and the rate-determining step is the separation of the sulphinate ion.

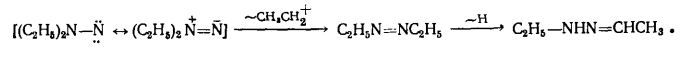
The mechanism of the diazene–hydrazone rearrangement was the subject of a special study[90] in which the N-sodium derivatives of the 1,1-dialkylhydrazides of benzenesulphonic acids were heated to 110–120° in the organic solvents tetraglyme and diethylene glycol. It was found that the composition of the decomposition products depends markedly on the nature of the solvent: in the aprotic tetraglyme, tetrazenes were obtained in good

yields, whereas in diethylene glycol, only the hydrazones or a mixture of the hydrazone and the tetrazene were obtained:

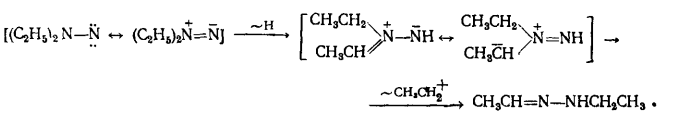


Three possible mechanisms for the rearrangement of the aminonitrenes to hydrazones were examined[90].

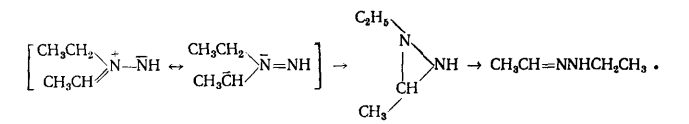
1. Migration of one of the substituents on the central nitrogen atom to a neighbouring atom carrying a negative charge, in the form of the carbo-cation; the azo-compound formed then undergoes isomerisation to the hydrazone:



2. A mechanism which differs from the preceding mechanism in the order of migration of the proton and the carbo-cation and which assumes the intermediate formation of not the azo-compound but an unstable ylide:

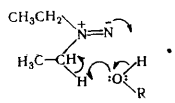


3. A mechanism involving a valency rearrangement of the initially formed ylide into the diaziridine, which then undergoes isomerisation to the hydrazone:



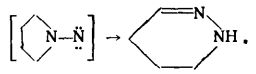
Neither azo-compounds nor diaziridines were detected among the products of the rearrangement. Since special experiments showed that under the conditions of the rearrangement[90] azoethane undergoes only partial isomerisation, and the corresponding diaziridine does not undergo isomerisation at all, mechanisms 1 and 3 were rejected.

The role of the hydroxyl-containing solvent is regarded as being to facilitate the migration of the proton by the formation of a six-membered cyclic intermediate complex with the participation of the aminonitrene:



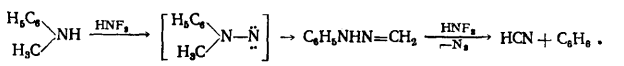
Experiments with compounds labelled with ^{15}N,[102] however, did not confirm the second proposed mechanism either. From the mechanism with the primary formation of an ylide, it follows that for a nitrene with a labelled terminal nitrogen atom the hydrazone formed should contain the tracer atom in the amino-group $RCH{=}N{-}N^{*}HCH_2R$, but the labelled atom was found to be the imide nitrogen atom of the hydrazone $RCH{=}N^{*}{-}NHCH_2R$, that is the rearrangement as it were involved not the carbo-cation RCH_2^+ but the alkylidene residue $RCH\langle$. Further study of the mechanism of the rearrangement of aminonitrenes to hydrazones is thus required.

Some heterocyclic aminonitrenes can undergo diazene–hydrazone rearrangement with expansion of the ring as a result of the inclusion of a second nitrogen atom in it. Thus Δ^2-tetrahydropyridazine was obtained from derivatives of N-aminopyrrolidine[96]:



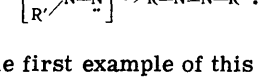
The yield was 55–70%, depending on the method used to generate the nitrene. This reaction indicates new methods for the preparation of heterocyclic nitrogen compounds which are difficult to obtain.

The diazene–hydrazone rearrangement has been postulated in the reaction of difluoroamine with N-methylaniline[113]:

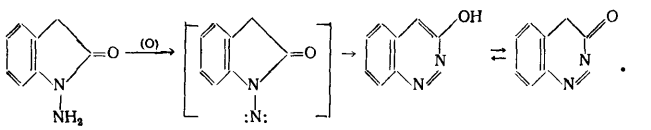


It should however be noted that formaldehyde phenylhydrazone was not obtained in the alkaline cleavage of 1-phenyl-1-methylhydrazine tosylate[101].

Another form of rearrangement of N-nitrenes involves their conversion into azo-compounds:

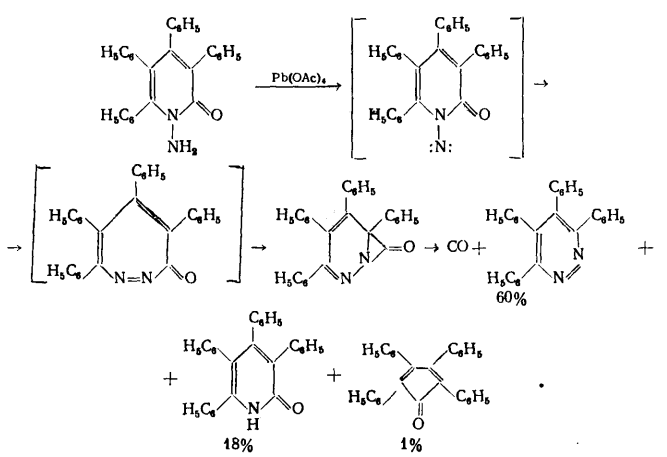


Historically, the first example of this reaction can be taken to be the formation of azo-compounds from 1-allyl-1-arylhydrazines on oxidation with mercuric oxide[8,86]. After this, no new example of the preparation of azo-compounds from 1,1-disubstituted hydrazines was described, although the analogous reactions of heterocyclic compounds were discovered by Baumgarten[51,65] and Rees[67]. In the oxidation of 1-amino-oxindole and its derivatives by lead tetra-acetate[51], *t*-butyl hypochlorite, and chlorine[65], Baumgarten observed rearrangement to 3-cinnolinol:



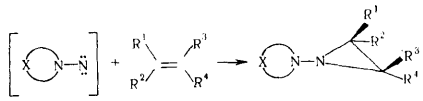
An interesting feature is that oxidation by chlorine gave the highest yield (up to 93%).

Rees and Yelland[67] discovered a similar rearrangement in the oxidation of N-amino-2,3,4,5-tetraphenylpyridone:



5. Addition of N-Nitrenes Across Multiple Bonds

The first report of the addition of N-nitrenes across the C=C bond of alkenes and conjugated dienes appeared only in 1967[28], but a fairly large amount of data has now accumulated[28,29,31-34,137], indicating the important synthetic and theoretical aspects of these reactions.



Preliminary reports of the addition of aminonitrenes to N=N[83] and C≡C[30] bonds have also appeared. All these reactions are (1+2)-cyclo-addition reactions.

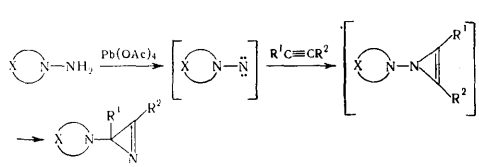
The specific features of the addition of N-nitrenes to multiple bonds are determined to a considerable extent by the negative charge on the sextet nitrogen atom and the high population of its π-orbital[19], as a consequence of which the simplest aminonitrenes exhibit nucleophilic, and not electrophilic properties, like the carbenes. In addition reactions, aminonitrenes with electron-accepting substituents which increase the electrophilic nature are used—most frequently N-amido- and N-imidonitrenes and similar compounds[28-34,137]. The addition of other types of aminonitrene to multiple bonds has not yet been observed. Aminonitrenes with very similar structures often show quite different behaviour, however, and it is difficult to predict the direction of a reaction.

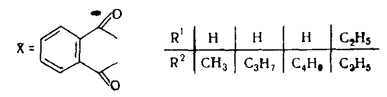
Both nucleophilic[28,29,32-34,97] and electrophilic[23,31,33,34,137] alkenes and dienes[28,29,34] have been taken for the addition reactions. Recently, to increase the yield of products, attempts have been made to use alkenes with electron-accepting substituents, but an unambiguous relationship between the yield of products and the electrophilic nature of the alkene has not yet been established[34]. An interesting feature is that *trans*-1,2-dichloroethylene and trichloroethylene give aziridines in 60–90% yield, whereas 1,1-dichloroethylene and *cis*-1,2-dichloroethylene do not form adducts at all[34]. It must be assumed that the yield of aziridines apparently characterises not so much their formation directly in the addition reaction as the stability of the resulting extremely unstable[33,34,137] aziridines under the conditions of the reaction, on isolation and purification.

The reaction of aminonitrenes and dienes gave the corresponding vinylaziridines in 35–71% yields. Adducts across both double bonds, or products of 1,4-addition, are not formed[28,29,34].

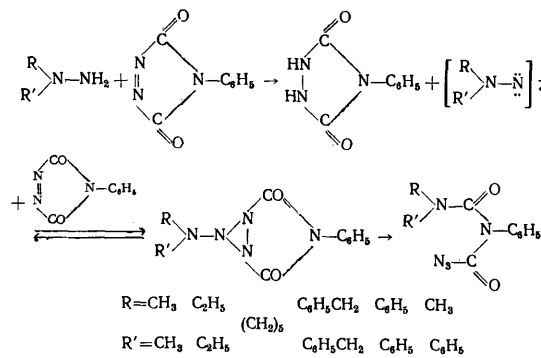
A remarkable feature is the complete stereospecificity of the addition of aminonitrenes to the C=C bond[28,29,31-34,137]. If Skell's postulates[138,139] regarding the stereochemistry of the addition of carbenes across multiple bonds are extended to aminonitrenes, it may be assumed that aminonitrenes react with a double bond exclusively in the singlet state[29,34].

In the addition of aminonitrenes across the C≡C bond, 2H-azirines are obtained in relatively low yields (5–15%)[30]. These reactions are of interest in that the 1H-azirine formed in the first stage is antiaromatic, so that it immediately undergoes rearrangement into the 2H-azirine, which is the final reaction product:



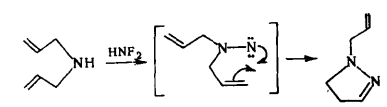


It is stated[83] that the products of the addition of aminonitrenes to the N=N bond are triaziridines. The diethyl ester and phenylimide of azodicarboxylic acid have been used as aminonitrene acceptors. In the last instance the reaction is represented:



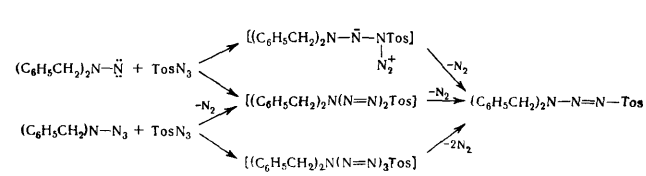
The triaziridines were isolated and characterised by their ultraviolet spectra and melting points.

With dialkylaminonitrenes, intramolecular reaction of the N-nitrene with the multiple bond was observed; the reaction mechanism was not discussed[37]:

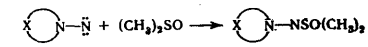


6. Reactions of N-Nitrenes with Tosyl Azide and Dimethyl Sulphoxide

In the reaction of dibenzylaminonitrene, formed from dibenzylamino-N-azide, or possibly, of the azide itself with tosyl azide at 0°, one of the products is 3,3-dibenzyl-1-tosyltriazene (yield 13–28%)[117]:

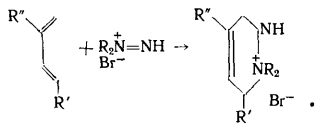


The aminonitrenes which can add to double bonds were taken for the reaction with dimethyl sulphoxide[29,31,67]. The products obtained were called sulphoximines[29,67] or iminoxysulphuranes[31]:

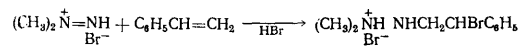


7. Reactions of Diazenium Salts

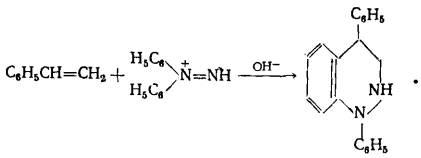
The diazenium cations formed on protonation of N-nitrenes have proved to be very active dienophiles, and this has been used for the preparation of quaternary Δ^4-tetrahydropyridazinium salts [35,36,38,39]:



The ability of 1,1-dimethyldiazenium bromide to undergo the Diels–Alder reaction with isoprene or divinyl under mild conditions was discovered by McBride and Urry [35] and later studied in detail by Zelenin and Bezhan [38,39,140] with many 1,1-dialkyldiazenium bromides, isoprene, chloroprene, and piperylene. Even cyclohexa-1,3-diene, which reacts only with very active azo-compounds, gives an adduct with 1,1-dimethyldiazenium bromide in 80% yield. The structural direction of these reactions is the usual direction for diene synthesis: 1-substituted dienes (piperylene) give the ortho-isomers, and 2-substituted dienes (isoprene and chloroprene) the para-isomers. The product of the oxidation of 1,1-di-isopropylhydrazine in acid medium, however, did not undergo the diene synthesis. The branched structure of the framework of the diazenium cations is apparently of considerable importance [39,140]. In the reaction of dimethyldiazenium bromide with isoprene, the formation of small quantities (12%) of tiglic aldehyde dimethylhydrazone was observed [35]. The reaction of the 1,1-dimethyldiazenium cation with styrene and indene leads to the formation of hydrazinium salts [36]:



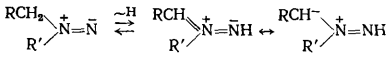
When the solution is neutralised, these salts may be converted into diazetidinium salts, and also undergo more extensive decomposition. The reaction of styrene with 1,1-diphenyldiazenium perchlorate in acetonitrile, however, leads after neutralisation to the formation of 1,4-diphenyl-1,2,3,4-tetrahydroquinoline [27]:



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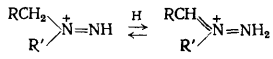
A number of papers published in 1971 supplement and extend our knowledge of aminonitrenes.

New data on the conversion of dialkylaminonitrenes into dialkylhydrazones [141] indicate that this reaction is a general reaction for aminonitrenes generated under different conditions, and can be regarded as indicating the important role of tautomeric equilibria



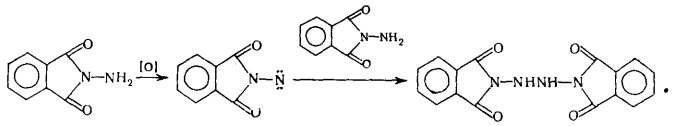
in the subsequent reactions of the aminonitrenes.

The analogous tautomerism of the protonated forms of aminonitrenes—the diazenium cations:



is apparently the first stage of the splitting of diazenium cations at the $C=N^+$ bond with the formation of carbonyl compounds when solutions of diazenium salts and the corresponding 2,4-dinitrophenylhydrazones are boiled—in the reaction with 2,4-dinitrophenylhydrazine [142].

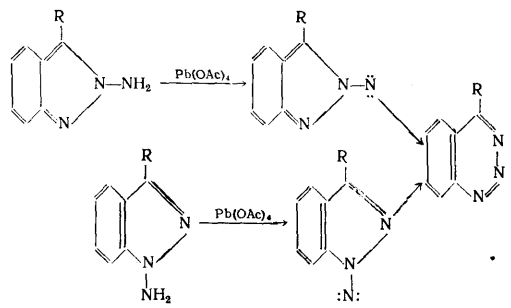
In the oxidation of various N-aminolactams with lead tetra-acetate and iodobenzene diacetate, the corresponding tetrazanes were isolated [143]:



These are capable of undergoing further oxidation to Δ^2-tetrazenes, providing evidence in support of the previously proposed mechanism of oxidation of 1,1-disubstituted hydrazines to Δ^2-tetrazenes via the tetrazanes, obtained in the reaction of intermediate N-nitrenes with the original hydrazines [7,52] (see also section III, 2 of this review).

The formation of esters of benzoic acid in the oxidation of 5- and 6-substituted 1-aminobenzotriazolin-8-ones with lead tetra-acetate in CH_2Cl_2 [144] may take place not only via the decomposition of intermediate aminonitrenes to cyclopropenones and two molecules of nitrogen [76] but also via the formation of indazolones, which have been isolated as the adducts with tetracyclone.

In the oxidation of 3-substituted 1- and 2-aminoindazoles, instead of the liberation of nitrogen, expected by analogy with the behaviour of the corresponding aminobenzotriazoles [69–72], the reaction gave 1,2,3-benzotriazines [145] in almost quantitative yields



This rearrangement of the intermediate aminonitrenes is extremely similar to other examples of ring expansion in aminonitrenes [51,65,67].

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