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The present state of the chemistry of aminonitrenes and oxynitrenes

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ABSTRACT. The principal aspects of the chemistry of amino- and oxy-nitrenes—the nitrogen analogues of carbenes in which the sextet of the nitrogen atom is linked to another nitrogen atom or two oxygen—are examined. The available information about the methods of detection, structure, methods of generation, and properties of these usually unstable intermediate species are analysed critically. Attention is concentrated on the comparison of amino- and oxy-nitrenes, their rearrangements, and their interactions with unsaturated compounds.†

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I. Introduction

Vigorous studies on the nitrogen analogues of carbenes—the nitrenes X—N̈: (I)—have led to the creation of a large and rapidly developing field of chemistry.[1,2] The so called heteronitrenes, where the sextet of the nitrogen atom adjoins a heteroatom (see Scriven,[2] Chapter 5) and in the first place aminonitrenes (*N*-nitrenes or 1,1-diazenes) (I, X = R_2N), occupy a special place in this field. It is determined by the important role which aminonitrenes play in numerous reactions of organic hydrazine derivatives[3] and the wide variety of their synthetic applications, in particular for the preparation of *N*-aminoaziridine and other nitrogen heterocycles, which are otherwise difficult to obtain, and new classes of acyclic polynitrogen compounds. This is perhaps the most thoroughly investigated type of nitrenes and therefore special attention will be devoted to it in the present review. Information about the oxygen analogues of aminonitrenes—oxynitrenes (or *O*-nitrenes) (I, X = RO), which are of interest as possible intermediates in reactions of hydroxylamine derivatives, is much more scanty, but data obtained in recent years permit a comparative characterisation of these two types of nitrenes, which was lacking in the previous reviews.

The hypothesis of the existence of aminonitrenes, which arose in the middle of the 1950's (see Ioffe et al.,[3] Chapter 3) received rapid recognition and the last two decades have becomes a period of vigorous development of the chemistry of aminonitrenes. A number of methods for their generation and the variety of their reactions have rapidly increased and the first synthetic applications of the reactions of these unstable species became outlined. At the end of the 1960s, search was begun for evidence indicating the existence of the analogous oxynitrenes, which rapidly led to the successful synthesis of alkoxyaziridines, which stimulated the systematic investigation also of heteronitrenes of this kind. The principal results of this kind have been summarised in monographs[1–3] and a number of reviews.[4–7]

At the end of the 1970s there was a return to a more critical analysis of the accumulated data. A rigorous revision of the results began and more attention began to be paid to the demonstration of the involvement of *N*- or *O*-nitrenes in particular reactions and to the relation between their structure and behaviour. Studies on the reactivity of these nitrenes were concentrated on aspects promising from the synthetic point of view such as reactions with unsaturated groups, including heteroatomic groups, and a wider variety of intermolecular cyclisations. At the same time the search for milder methods for the generation of these species and their new reactions did not cease.

A series of fundamentally important results, which have significantly altered the features of this branch of the chemistry of nitrenes, have been obtained during the past decade. Most of them have not been included in the latest reviews[2,7] and we have therefore endeavoured to survey these data, covering the literature up to the middle of 1987.

II. Structure and properties

1. The results of quantum-chemical calculations

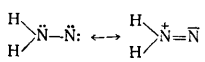
Quantum-chemical calculations have until recently been the only source of information about the structure of amino- and oxy-nitrenes. As a result of the adjoining positions of the heteroatoms with the unshared (lone) electron pairs (LEP), here preference was usually given to non-empirical methods. Furthermore, the incomplete electron cloud to the "nitrene" nitrogen atom requires allowance for configuration interaction in order to obtain reliable results. All these features have sharply complicated the calculations and have virtually restricted them to the simplest molecules, such as aminonitrene itself H_2NN (II) or hydroxynitrene HON. Admittedly, these compounds are incorporated in a kind of "set of tests" for the testing of new bases and new computational schemes and even new results appear annually for these species (see, for example, Decleva and Lisini[8] and the annual bibliography of non-empirical calculations in the "Journal of Molecular Structure"). However, there have been nevertheless few studies of real value to experimental chemists and among them one would wish to mention in the first place calculations of the structure of the simplest aminonitrene (II)

† This article was planned for publication in issue No. 7, 1989, which was devoted to the chemistry of carbenes.

by the general valence bond method taking into account the configuration interaction.[9]

These calculations made it possible for the first time to demonstrate reliably that nitrene (II) has a singlet ground state (S_0). The first triplet state (T_1) has an energy higher by 63 kJ mol^{-1} and the energy of the first excited singlet state (S_1) is higher by 212 kJ mol^{-1},[9] which corresponds to absorption in the visible region of the electronic spectrum at above 560 nm (the $S_0 \rightarrow S_1$ transition). The calculated first ionisation potential is 9.4 eV.[9] The calculated enthalpy of formation of aminonitrene is ΔH^{298} = 361 kJ mol^{-1}, i.e. is higher by 123 kJ mol^{-1} than ΔH^{298} for the isomeric *trans*-HN=NH and is higher by 103 kJ mol^{-1} than ΔH^{298} for *cis*-N_2H_2.[9,10]

In the ground state (S_0), the $H_2N\ddot{N}$: molecule is planar and the nitrogen–nitrogen bond length is 125 pm—a value typical for the N=N bond in azo-compounds. This indicates a decisive contribution of the polar structure (IIb) to the resonance stabilisation of aminonitrene via the transfer of the electron density of the LEP of the amino-nitrogen atom to the unoccupied *p* orbital of the nitrene atom:



(IIa) (IIb)

The large calculated dipole moment of aminonitrene (4D) is entirely consistent with this find, the nitrogen atom constituting the negative end of the dipole.[9]

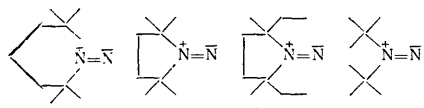
On exciting of the molecular of compound (II), the electron of one of the LEP of the nitrone nitrogen atom is transferred to the unoccupied *p* orbital. As a result, the molecule resembles a hydrazyl radical and the role of resonance stabilisation diminishes sharply. In agreement with this finding, the H_2NN molecule in the T_1 state is no longer planar (although the barrier to the inversion of the amino-nitrogen atom is only 0.8 kJ mol^{-1}), while the equilibrium N–N bond length increases to 137 pm.[9] At the same time it is nevertheless shorter than the N–N single bond in hydrazines (145 pm [3]); together with the appreciable dipole moment (2.35 D), this shows that in the triplet state of the nitrene (II), the LEP of the amino-nitrogen atom is appreciably delocalised. Similar changes in geometry occur also in $S_0 \rightarrow S_1$ transition.[9]

The calculated N–H bond energy is 180 kJ mol^{-1},[10] which makes it possible to estimate the C–N bond strength in substituted aminonitrenes as ~100 kJ mol^{-1}. Aminonitrenes should therefore be comparatively resistant to decomposition with rupture of the N–H or C–N bond which gives rise to the hope that they may be detected and identified.

2. The synthesis and properties of stable aminonitrenes

One of the ways of stabilising unstable intermediate species such as carbenes or nitrenes is their binding in complexes. At the beginning of the 1970s, the first complexes of *N*-nitrenes, including also the simplest aminonitrene (II),[11] with tungsten and molybdenum ions, were already discovered. Later complexes of aminonitrenes were obtained with rhenium, niobium, and tantalum,[12,16] as well as a series of iron-porphyrin complexes.[17,18] As a rule, these are very stable compounds and the properties of the aminonitrenes bound in them should naturally differ appreciably from those of the free species.

However, it was found that aminonitrenes can be detected in a state other than the complexes. As early as 1978, immediately after the calculations of Davis and Goddard,[9] a series of studies began to be published[19–26] on this synthesis (specifically the synthesis) and properties of stable aminonitrenes. It was shown that, when there are tertiary substituents at the amino-nitrogen atom, the dialkyl-aminonitrenes (III)–(VI), relatively stable at low temperatures, can be obtained by the classical method—the oxidation of the corresponding 1,1-disubstituted hydrazines by t-butyl hypochlorite in the presence of triethylamine[19–21,23–26] or active nickel peroxide:[226]



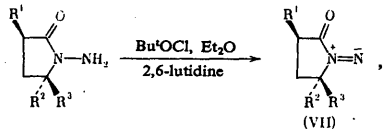
(III) (IV) (V) (VI)

cis (a), *trans* (b)

Bright crimson or purple solutions of the nitrenes (III)–(V) in ether are stable at –78 °C for several days and at –85 °C they can be actually purified by chromatography on Al_2O_3. However, they decompose rapidly on raising the temperature to 0 °C. The nitrene (VI) can be stored only at –127 °C, decomposing rapidly even at –90 °C.[25] The comparative stability of these compounds can be accounted for by the presence of the bulky tertiary substituents which prevent both intermolecular reactions (dimerisation to tetrazenes) and intramolecular reactions (for example rearrangement to hydrazones).

The structure of the *N*-nitrenes (III)–(VI) has been unambiguously demonstrated by a set of spectroscopic characteristics (Table 1), which demonstrate agreement with calculated data,[9] as well as by their reactions on raising the temperature (decomposition, dimerisation to tetrazenes), which are entirely similar to the familiar reactions of unstable dialkylaminonitrenes (see also Section IV). Indeed, in agreement with predictions,[9] the nitrenes (III)–(VI) have a broad absorption band with a fine structure in the visible region. The low intensity of this band and its hypsochromic shift following an increase in the polarity of the solvent agree with its assignment to the $n-\pi^*$ transition in the $\rangle\overset{+}{N}=\overline{N}$ chromophore, isoelectronic with the carbonyl group, while the position of the transition between the zero-point vibrational levels (λ_{0-0}) agrees well with the calculated estimate (~560 nm [9]). The marked difference between the electronic absorption and fluorescence spectra indicates a marked change in the equilibrium geometry, also predicted by calculations,[9] on transition from the ground (S_0) to the first excited singlet state (S_1). The high frequency of the ν(N–N) vibrations in the IR spectra (the assignment of the band has been confirmed by isotope substitution), which actually exceeds somewhat the usual frequency of the N=N double bond vibrations (1574 cm^{-1} in azomethane) agrees with the conclusion[9] that the nitrogen–nitrogen bond in the simplest aminonitrene has a significant double bond character. The frequency ν(N–N) in the IR spectra then virtually agrees with the fine structure interval in the fluorescence spectra of compounds (IV) and (V), which constitutes additional confirmation of the assignment. It is remarkable that, on passing from the six-membered amino-nitrene (III) to the five-membered aminonitrenes (IV) and (V), the characteristics of the IR and the electronic spectra change in the same way as for the isoelectronic cyclohexanone and cyclopentanone derivatives.[24] The structure of the hydrocarbon substituents in compounds (III)–(VI) follows from their ^{1}H NMR spectra, while the unusual character of the nitrene nitrogen atoms is reflected in the enormous value of its chemical shift (δ = 917 p.p.m.) in the ^{15}N NMR spectrum of the nitrene (III).

The even more stable cyclic acylaminonitrenes (VII) were synthesised by the same method in 1984:[27,28]



R^1=H, R^2=R^3=Ph (a);
R^1=H, R^2=Me, R^3=Ph (b);
R^1=Me, R^2=Ph, R^3=Me (c);
R^1=Me, R^2=Me, R^3=Ph (d);
R^1=R^2=H, R^3=Ph (e).

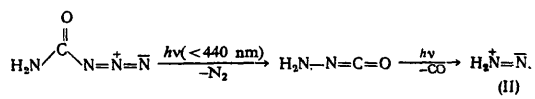
Compounds (VIIa–d) are stable in solutions at room temperature for several days and even weeks, but the nitrene (VIIe), having a hydrogen atom in the α-position, isomerises rapidly under these conditions to the corresponding tetrahydropyridazinone (see Section IV).

Table 1. The properties of the nitrenes (II)–(VII).

Compound	Electronic absorption spectrum: λ_{max} ($\lambda_{0\text{-}0}$), nm	Fluorescence spectrum (−196 °C): $\lambda_{0\text{-}0}$, nm	ν(N–N), cm^{-1}	$E^{\neq}_{decomp}$, kJ mol^{-1}
(II)	636	—	1574	—
(III)	543* (620)	684	1595	80—84
(IV)	497* (572)	607	1638	80—84
(V)	507* (568)	620	1630	80—84
(VI)	506	715	—	54
(VIIb)	520**	—	—	122

* $\varepsilon_{max} \simeq 18-20$.
** $\varepsilon_{max} \simeq 90$.

Finally, in 1984 it was possible to detect in a matrix and to characterise by IR and UV spectroscopy (see Table 1) also the simplest aminonitrene (II),[29] generated by the photolysis of the azide of carbamic acid (the Curtius rearrangement):



The isotopomers of the nitrenes (II) with two deuterium atoms and a nitrene ^{15}N were obtained in the same study, which made it possible to confirm the assignment of the IR bands, in particular the ν(N=N) band, whose frequency (1574 cm^{-1}) is much higher than for the isomeric *trans*-diazene HN=NH [ν(N=N) = 1529 cm^{-1} in the Raman spectrum[29]]. The spectroscopic properties of compound (II) fit one series with the properties of the substituted aminonitrenes (III)–(VI) (see Table 1) and agree well with the calculated estimates.[9] However, they differ sharply from Wiberg's "isodiazene",[30,31] to which the structure (II) was also attributed. According to the set of available data, Wiberg's report of the detection of the nitrene (II) on decomposition of the caesium salt of toluene-*p*-sulphonic acid hydrazide should probably be regarded as erroneous.

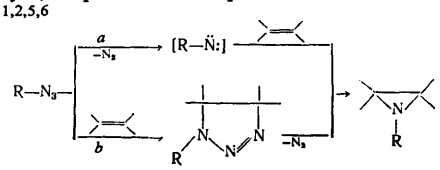
III. Methods of generation

The reactions in which the formation of amino- and oxy-nitrenes has been postulated are very numerous,[3–7] but the oxidation of 1,1-disubstituted hydrazines and alkoxyamines is most often employed for the generation of these species. The alkaline cleavage or thermolysis of the corresponding sulphonamides, the decomposition of sulphimines and sulphoximines, a series of cheletropic reactions, in particular the decomposition of *N*-aminoaziridines, and incomplete reduction of nitrosamines are of considerable interest. The neutralisation of the corresponding diazenium salts is a convenient method for the generation of dialkylaminonitrenes.[3]

The hypothesis of the existence of aminonitrenes was put forward initially to account for the so-called "anomalous" (with evolution of nitrogen and the formation of hydrocarbons) oxidation of 1,1-disubstituted hydrazines. The "anomalous" reduction of nitrosamines and the decomposition of sulphonic acid hydrazides was almost immediately included in this group of reactions. The similarity of the products of these reactions suggested a common intermediate—aminonitrene. Admittedly, the involvement of aminonitrenes in the normal course of these processes remained debatable. The next landmark was the stereospecific synthesis of *N*-aminoaziridine derivatives by the oxidation of a whole series of hydrazines in the presence of alkenes (see Section IV)—by analogy with the chemistry of carbenes, this was explained by the intermediate generation of aminonitrenes and their addition to the C=C bond. Naturally, the synthesis of *N*-alkoxyaziridines via the oxidation of *N*-alkoxyamines in the presence of alkenes, which soon followed, was immediately regarded as proof of the oxidative generation of alkoxynitrenes. Finally, the formation of a whole series of aminonitrenes in oxidation reactions was recently convincingly demonstrated by spectroscopic methods.

Hitherto, the main piece of evidence for the involvement of amino- or oxy-nitrenes in the reaction has usually been the similarity of the products of the given reaction to those of others for which the nitrene mechanism has already been established. Even more remote analogies are sometimes employed, for example, the analogy with the rules governing the occurrence of carbene reactions (Skell's postulate is usually invoked). Having demonstrated the nitrene mechanism of the reaction in relation to 1–2 examples, it is then usually subsequently extended to other similar reactions.

Such reasoning is entirely natural and acceptable in practice. However, it is at the same time extremely vulnerable. Indeed, it is actually clear that for the same process mechanism the composition of the products depends markedly on the specific reaction conditions: the method of generation of the nitrene, temperature, solvent, the presence of oxidants and reductants, the pH of the medium, etc. In order to compare the results, it is therefore necessary to resort in this instance to fairly bold extrapolations. On the other hand, typical "nitrene" products can sometimes be obtained without any involvement of nitrenes. A classical example is provided by the interaction of azides with alkenes, where, depending on the reaction conditions, aziridines can be formed both via nitrenes (pathway *a*) and wholly via the "azide" mechanism, as a result of the decomposition of the primary 1,3-dipolar addition products—2-triazolines (pathway *b*):[1,2,5,6]



Thus unambiguous demonstration of the nitrene mechanism of the reaction requires the consideration of very many of its aspects, in the first place a set of kinetic data. There have so far been few such studies in the chemistry of amino- and oxy-nitrenes and we usually deal merely with the hypothesis of the involvement of nitrenes in the reaction, which is not always sufficiently well founded. The data described below should be considered from precisely this point of view.

1. Oxidation of amino-compounds

Historically the first[3-6] and hitherto the most convenient and most widely used method for the generation of amino- and oxy-nitrenes (I) is the oxidation of corresponding hydrazines or hydroxylamines:

$$X{-}NH_2 \xrightarrow[-HY]{YZ} \left[X{-}N\begin{matrix}Z\\H\end{matrix}\right] \xrightarrow{-HZ} X{-}\ddot{N}: \quad ; \qquad (1)$$

(VIII) (I)

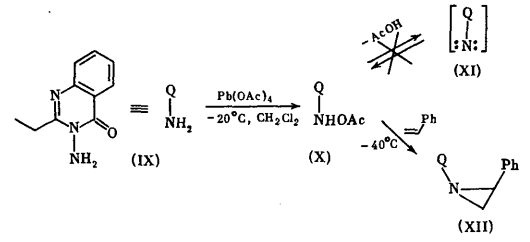
X=R_2N, RO.

The assortment of oxidants employed is extremely wide,[3-7] but the lion's share of the results have been obtained using 2–3 most popular reagents. Yellow mercury oxide was usually employed in the early studies. Nowadays lead tetraacetate (LTA), t-butylhypochlorite, and nickel peroxide are most often used.

The formation of the nitrenes (I) in a whole series of oxidation reactions has been demonstrated extremely reliably—it is sufficient to recall that stable aminonitrenes have been obtained by precisely this procedure (see above). However, we may note that, according to Eqn. (1), the oxidative generation of nitrenes should include at least two stages: the formation of the intermediate compound (VIII) and the subsequent α-elimination of HZ. The nature of the group Z is determined by the oxidant and it is evident that, depending on its leaving capacity, the tendency of the molecule of compound (VIII) to undergo α-decomposition varies significantly. In principle, the intermediate (VIII) may prove to be fairly stable and can participate in subsequent reactions without decomposing to the nitrene.[3] It is sometimes fairly difficult to distinguish reactions proceeding via the nitrenes (I) from reactions involving their precursors (VIII).

This problem has already been discussed in the literature.[3,32] In particular, it has been noted that, for certain oxidants the reactions with 1,1-disubstituted hydrazines afford only a small amount of the usual aminonitrene conversion products (hydrocarbons, hydrazones, etc.) and sometimes they are altogether absent. Such a discrepancy (the dependence of the results on the nature of the oxidant) clearly indicates a decisive role of the first oxidation stage. The oxidation of 1,1-disubstituted hydrazines by derivatives of tetravalent selenium may serve as an example.[33,34] According to the authors, intermediate compounds of type (VIII) with a N–Se bond are formed during this reaction but the process does not go as far as the formation of aminonitrenes.

The case where the reactions of the nitrene precursor (VIII) resemble those expected for the nitrene itself is much more insidious and unexpected. Thus a communication has been published recently stating that the low-temperature oxidation of *N*-aminoquinazolinone (IX) by LTA, i.e. under the "standard" conditions for the generation of amino- and alkoxy-nitrenes, affords almost quantitatively the *N*-acetoxy-derivative (X), which is stable in solution up to ~0 °C.[35] However, even at –40 °C the addition of styrene (1.5 equiv.) to this solution leads to the rapid disappearance of compound (X) and the formation of the *syn*-invertometer of the aziridine (XII) in 76% yield, which has always been regarded as typical for the corresponding aminonitrene (XI):



Furthermore, the involvement of the nitrene (XI) or the nitrenium ion, which are intermediates in equilibrium with compound (X), in the reaction is ruled out because neither the NH proton nor the acetoxy-group are exchanged in CF_3COOD, while the hypothesis of the non-equilibrium generation of the nitrene (XI) with its subsequent addition to the double bond conflicts with the observed dependence of the rate of disappearance of the acetoxy-derivative (X) on the alkene concentration.[35]

Hitherto the oxidation of amino-compounds by LTA was regarded as one of the most reliable methods for the generation of most varied nitrenes and the principal piece of evidence was in fact the stereospecific formation of the corresponding aziridine derivatives in the presence of alkenes. An alternative interpretation has now appeared: since the acetoxy-derivative of type (X) is in essence the nitrogen analogue of peracetic acid, the formation of aziridines can be treated similarly to the epoxidation of alkenes by peracids, which is incidentally also stereospecific. Evidently the non-trivial results of Atkinson and Kelly[35] require a critical analysis of the mechanism of not only the formation of aziridines but also of a whole series of seemingly typical "nitrenes" reactions.

It is remarkable that intermediates of the non-nitrene type in the oxidation of hydrazine by LTA had already been sought earlier[36] but it had been assumed that they must be compounds of the type $X{-}NH{-}Pb(OAc)_3$. For the oxidation of *N*-aminopyrrole derivatives by LTA and lead tetrabenzoate, on the one hand, or by $PhI(OAc)_2$ and $PhI(OCOCHCl_2)_2$, on the other, it was then shown that the results are almost independent of the type of oxidant and hence the involvement of a lead-containing compound in the rate-determining state of the reaction is unlikely.[36] An *N*-acetoxy-compound of type (X) also occurred more than 10 years ago in the mechanism of the oxidation of *N*-aminophthalimide by LTA [37] but it was assumed that it is obtained as a transient formation as a result of a side process—the interaction of phthalimidonitrene with acetic acid, and that it does not play a significant role in this reaction.

In conclusion of the discussion of the study of Atkinson and Kelly,[35] one must state that its results by no means rule out the possibility of the formation of nitrenes of type (XI) in the oxidation of the corresponding amino-compounds—in fact acylaminonitrenes (VII) are obtained by precisely this procedure. However, they indicate that the acetoxy-group leaves the molecule of the nitrene precursor (VIII) extremely unwillingly and, in order to direct the reaction precisely along the aminonitrene pathway, it is best to use not LTA but another oxidant, for example t-butyl hypochlorite.

Apart from studies using the traditional range of oxidants, a number of communications have appeared in recent years concerning the oxidative generation of aminonitrenes under new conditions, in particular, in the electrochemical oxidation of certain hydrazines.[38,39] The formation of aminonitrenes has been postulated in the oxidation

of 1,1-disubstituted hydrazines by oxygen,[40] nitrogen dioxide,[41] and nitrobenzene[42] and also in the pyrolysis of 2,2-dimethyltriazanium chloride,[43] the result of which can be regarded as an intramolecular oxidation-reduction reaction. However, in all these cases one is dealing merely with hypotheses while reliable evidence for the intermediate formation of *N*-nitrenes in the above investigations[40–43] is lacking.

2. Decomposition of sulphonic acid derivatives and other methods

A second general method for the generation of amino- and oxy-nitrenes is the alkaline decomposition of the corresponding sulphonamides:[3–7]

$$XNHSO_2R' \xrightarrow[\Delta]{B^-} \underset{(I)}{X-\ddot{N}:} + BH + R'SO_2^-;$$

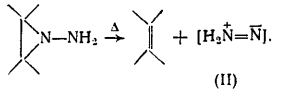
$$X = R_2N,\ RO;\quad R' = Me,\ Ph,\ p\text{-}MeC_6H_4.$$

This procedure is especially suitable for the generation of the nitrenes (I) at a high temperature.[3–7,32,44] The high-temperature decomposition of the sulphonic acid hydrazides themselves[45] as well as the thermolysis of dry salts of the type R_2NNMSO_2R', where M is an alkali metal,[46,47] are variants of this method. It has been claimed that the last reaction is one of the "cleanest" methods of generating aminonitrenes.[47]

The reactions discussed above exhaust the known methods for the preparation of *O*-nitrenes. The approaches used to obtain *N*-nitrenes are significantly more varied[3,7] but the applicability of many of them is extremely limited. Thus the formation of aminonitrenes in the reduction of nitrosamines[3] is evidently an exception rather than the rule: typical "aminonitrene" reactions are observed in this instance mainly when sodium hydrogen sulphite is used as the reductant but even then not always:[3,32]

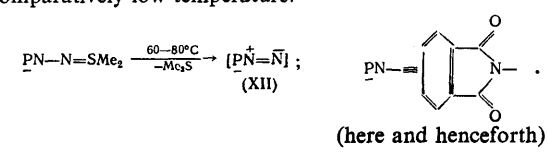
$$R_2N-NO \xrightarrow[OH^-]{Na_2S_2O_4} R_2N-\ddot{N}:$$

In the remaining cases the participation of aminonitrenes in the reaction must be postulated with much caution[48] and their presence in complex mechanisms of the reactions of a wide variety of nitrosamines[49–51] bears in our view a formal character in many respects. The possibility of the formation of the simplest amino-nitrene (II) in the thermolysis of a number of *N*-aminoaziridines is purely tentative,[52] although here one may note that the generation of acylaminonitrenes by the thermolysis and photolysis of the corresponding substituted derivatives has already been described in the literature:[3]



(II)

Few new methods for the generation of aminonitrenes have appeared during the last decade. In 1979 it was suggested that phthalimidonitrene (XII), perhaps the most thoroughly investigated aminonitrene, be generated by decomposing its adduct with Me_2S at a comparatively low temperature:[53]

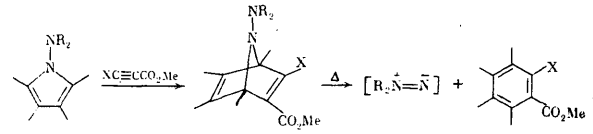


(XII)

(here and henceforth)

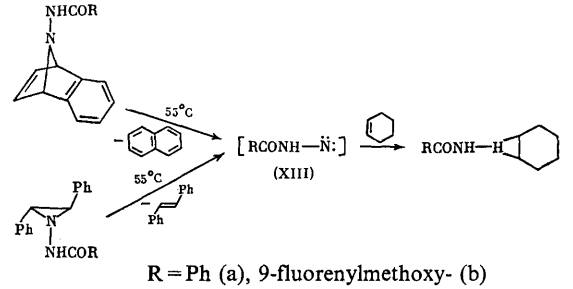
This method of generation makes it possible to obtain adducts of the nitrene (XII), which are sensitive to strong heating, oxidants, or acids. In particular, it has been possible to obtain aziridine in the reaction with *p*-methoxystyrene by this procedure.[54]

The intermediate formation of *N*-nitrenes in the reactions of various *N*-aminopyrroles with electron-deficient acetylenes has been postulated:[55–57]



R = H, Me, $PhCH_2$; R_2N = $NHCO_2Me$, $N(CH_2CH_2)_2O$; X = CO_2Me, SO_2Ph.

Subsequently a similar reaction was used to obtain acylamino-nitrenes (XIII) [58] and here it proved possible to observe for the first time an intermolecular reaction of monosubstituted nitrenes:



(XIII)

R = Ph (a), 9-fluorenylmethoxy- (b)

In addition, the nitrene (XIIIb) has been obtained also by a more traditional method—the decomposition of the corresponding 2,3-diphenylaziridine.[58]

IV. Reactions of amino- and oxy-nitrenes

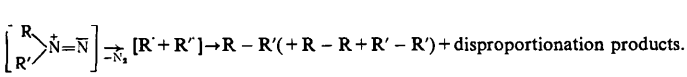
The known reactions of amino- and oxy-nitrenes can be divided into three large groups: decomposition, isomerisation, and addition to double bonds or unshared electron pairs. The occurrence of the reaction via a particular pathway is determined in the first place by the structure of the nitrene. Decomposition has been observed so far only for aminonitrenes and its driving force is evidently the formation of the stable nitrogen molecule. The presence of substituents of the benzyl or allyl type at the amino-nitrogen atom makes decomposition the principal reaction pathway. The tendency of amino- and oxy-nitrenes to undergo rearrangements with migration of groups to an atom with an incomplete electron shell is determined in many respects by the migrating capacity of the substituents. Finally, if the nitrene is relatively stable in relation to intermolecular reactions, then, in the presence of a suitable reagent in the reaction mixture, it can add to multiple bonds or can attack an unshared electron pair with formation of the corresponding adducts.

All these processes usually occur simultaneously and the contribution of each is determined additionally by the reaction conditions and the comparative reactivities of the components of the reaction mixture. An increase in temperature usually increases the contribution by fragmentation and rearrangement processes. On the other hand, the addition of a large excess of active nitrene "trapping" agents, such as dimethyl sulphoxide (DMSO), makes it

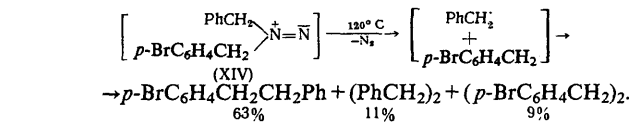
possible to obtain adducts even for nitrenes which usually tend to undergo rearrangements or decomposition.

1. Decomposition of aminonitrenes

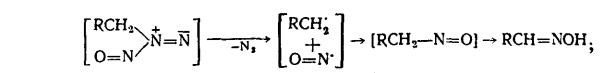
Decomposition with evolution of nitrogen is one of the most general reactions of aminonitrenes for the most varied methods of their generation. The ease of their decomposition and its mechanism depend significantly on the structure of the nitrene, but in most cases the available data fit satisfactorily within the framework of the biradical mechanism with a strong cage effect, which increases the stereospecificity of the reaction:[3,46,47]



The decomposition with the recombination of the radicals formed is most typical for dibenzylaminonitrene derivatives. It is, on the one hand, a convenient method of synthesis of bibenzyl derivatives[3] and, on the other hand, it is a kind of diagnostic test for the aminonitrene reaction mechanism.[32,39,42,46,47,55] The radical decomposition of dibenzylaminonitrene has been demonstrated reliably by EPR methods using "spin trapping agents"[46] and CINP [47] and it has been established that dibenzylaminonitrene produces a singlet radical pair and therefore decomposes in the singlet state, which is apparently the ground state[47] (cf. the calculations of Davis and Goddard[9]). The decomposition of the asymmetrically substituted nitrene (XIV) confirmed the major role of the cage effect, but, in contrast to the earlier study,[3] the cross-products,[47] obtained when the radicals emerge from the cage into the solution, were isolated in an appreciable yield:

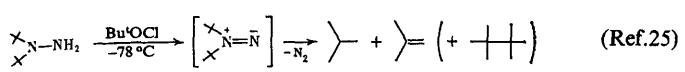


Ready decomposition with recombination of the species formed is characteristic of many other aminonitrenes having substituents at the amino-nitrogen atom which give rise to fairly stable radicals.[3] For example, the decomposition of nitrosaminonitrenes proceeds via this mechanism:[59]

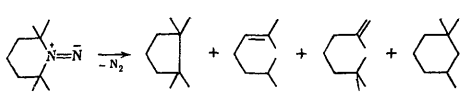


R = Ph, Pr^i.

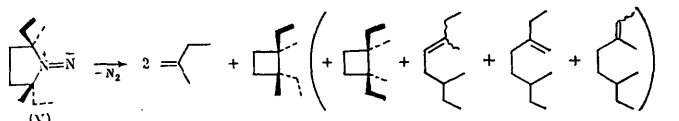
On passing to alkyl-substituted aminonitrenes, the main pathway becomes the disproportionation of their radicals,[25] while the decomposition of cyclic *N*-nitrenes[19–21,23,24,26–28,45] usually leads to a mixture of products of these two processes:



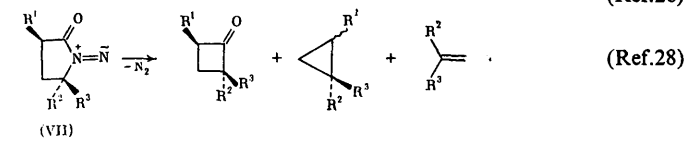
(Ref.25)



(Refs.24, 26)

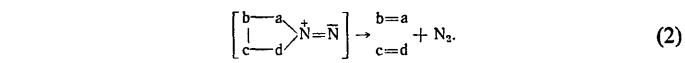


(Ref.26)



(Ref.28)

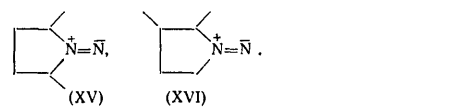
An additional possibility of concerted fragmentation into three parts (β-decomposition) via Scheme 2, symmetry-allowed as a $[\sigma_s^2 + \sigma_s^2 + \sigma_s^2]$ process, appears for five-membered aminonitrenes under these conditions:



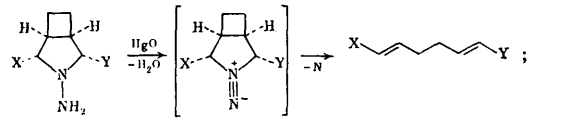
(2)

On the other hand, such decomposition can be treated also as a result of the cleavage of the central bond in the intermediate 1,4-biradical.

The study of the thermal and photochemical decomposition of a large series of five-membered *N*-nitrenes,[21,24,27,28] including the "stereochemically labelled" nitrenes (V) and (VIIc, d) and the *cis*- and *trans*-isomers of the nitrenes (XV) and (XVI),[45] showed that the main reaction pathways usually involve the formation of cyclobutane derivatives and β-elimination, both processes occurring highly stereospecifically with preferential retention of the relative disposition of the substituents:

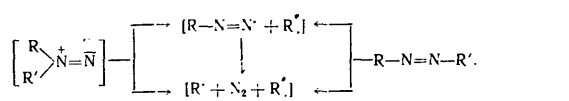


The stereospecificity of the β-decomposition is especially high (> 96%),[45] which has been used in the synthesis of a series of long-chain (*E*,*E*)-1,5-dienes:[60]



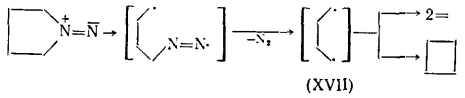
X, Y = Bu, CH_2CH_2Ph, $(CH_2)_6OH$ etc.

The composition and stereochemistry of the products of the thermolysis and direct photolysis of aminonitrenes are extremely similar and also resemble the outcome of the decomposition of the corresponding azo-compounds, which suggests the involvement in these reactions of common intermediate species of a radical type. A general question also arises: how are these radicals formed—synchronously, with the simultaneous cleavage of both C–N bonds, or in stages?



Computational assessment of both possibilities for the aminonitrene (II) itself,[10] diethylaminonitrene,[61] and the corresponding azo-compounds[10,61,62] has indicated in all cases that the multistage process with the intermediate formation of diazenyl radicals is preferred. This pathway agrees with experimental data for the fragmentation of azo-compounds[61,62] and in principle does not conflict with the results of studies of the decomposition of many aminonitrenes.[19-21,23-28,45] However, according to Savin,[47] the benzyldiazenyl radical is not formed as a kinetically independent species in the decomposition of dibenzylaminonitrene and both C–N bonds are therefore cleaved synchronously. This is apparently associated with the high stability of the benzyl radicals obtained, which is responsible for the sharp decrease in the strength of the C–N bonds in the aminonitrene which are weak in any case.

In any case, the decomposition of the five-membered aminonitrenes (and the corresponding azo-compounds) via the radical-mechanism should proceed via a derivative of the biradical (XVII) (tetramethylene):



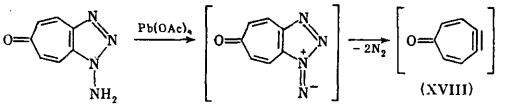
(XVII) (3)

However, a non-empirical calculation for tetramethylene yielded remarkable results: it was found that, instead of a minimum a kind of "plateau" on the energy surface corresponds to this 1,4-biradical.[63] Consequently, if one disregards entropy factors, this is not an intermediate compound but a transition state and processes with its participation can be regarded as "quasi-concerted". According to calculated data, the fate of tetramethylene depends on its geometry: the *gauche*-conformer cyclises while the *anti*-conformer undergoes non-activated decomposition into two ethylene molecules.[63]

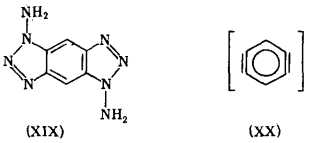
Taking into account the foregoing as well as kinetic and stereochemical data,[20,21,23,24,26-28,45] the decomposition of five-membered cyclic aminonitrenes presumably proceeds via two parallel channels:[45] as concerted β-decomposition via Scheme 2, with complete retention of the configuration of the substituents in the reaction products, and as a multistage process of type (3), which begins with the formation of the diazenyl biradical. In the absence of substituents capable of stabilising the biradical of the tetramethylene type, the subsequent cyclisation or decomposition of the latter should take place almost simultaneously with the elimination of the nitrogen molecule. The contribution of each pathway is determined by the nature of the substituents. Thus unsubstituted pyrrolidinonitrene apparently decomposes wholly via the concerted pathway into nitrogen and ethylene (although, contrary to old data, approximately 2% of cyclobutane was detected in the products[45]), while the introduction of alkyl and even more so aryl substituents in the 2- and 5-positions favours the radical process.

The usual consequence of the radical mechanism is a low stereospecificity of the reaction, but the fragmentation of aminonitrenes and of the corresponding azo-compounds represents a clear exception. The cyclisation and β-decomposition of the biradical intermediates (whatever their structure) is apparently appreciably faster in this instance than the rotation around the C–C single bonds. As was to be expected, with increase in temperature there is an increase in the fraction of the β-elimination products and the stereospecificity of the decomposition is reduced.[45] Similar changes occur on passing from the direct photolysis of stable aminonitrenes and azo-compounds to the sensitised photolysis,[26] which can be naturally accounted for by the involvement of triplet biradical species in the process.

The fragmentation of unsaturated 1-(1,2,3-triazolyl)nitrenes via Scheme 2 has found wide scale application for the generation of aromatic dehydrohydrocarbons and other unstable acetylene derivatives.[3] It has been used in recent years to obtain 4,5-dehydrotropone (XVIII) and its adducts with dienes[64,69] or enamines.[70]

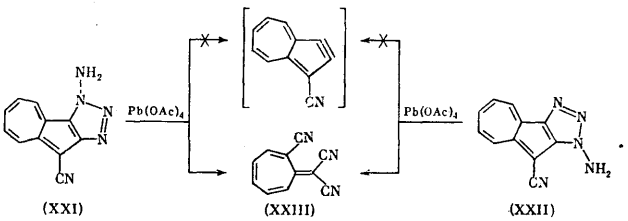


(XVIII)



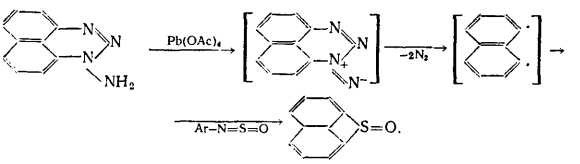
(XIX) (XX)

Similarly, 1,5-diaminobenzobistriazole (XIX) (and its 1,7-isomer) is an excellent synthetic equivalent of "1,4-dibenzyne" (XX) in 1,3- and 1,4-cycloaddition reactions (the yields of the diadducts are 40–93%);[71-73] however, when an attempt is made to obtain the corresponding dehydroazulene from the aminoazulenotriazoles (XXI) or (XXII) via the same scheme, only the rearrangement product (see below—the heptafulvene (XXIII)—is isolated:[74]

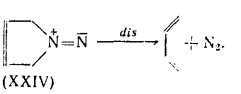


(XXI) (XXIII) (XXII)

A similar reaction has been used to generate 1,8-dehydronaphthalene:[75]



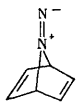
A concerted cheletropic decomposition is allowed for 3-pyrroline derivatives of type (XXIV) and it has been shown for a whole series of examples that, in conformity with the Woodward–Hoffmann rules, this process is indeed disrotatory and is fully stereospecific:[3]



(XXIV)

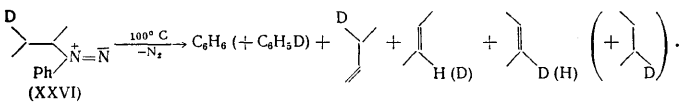
The results of recent calculations[76] have confirmed the possibility of the concerted decomposition of the nitrene (XXIV), but they predict a highly asymmetric transition state for this reaction (the process is concerted but not synchronous). The calculations permit a synchronous or almost synchronous fragmentation only for the

nitrene (XXV),[77] but, in Dewar's view, this exception merely confirmed the general conclusion that the transition state in cheletropic reactions is asymmetric:[76,77]



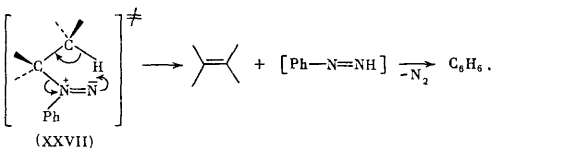
(XXV)

The study of the decomposition of the diastereoisomeric (*threo-* and *erythro-*) deuterio-substituted aminonitrenes (XXVI)[44] showed that this process proceeds highly stereospecifically as *cis*-1,2-elimination:



(XXVI)

In each case deuterium remains in only one of the two-isomeric but-2-enes, which can be explained by proton transfer to the nitrene nitrogen atom in the transition state (XXVII). This resembles the mechanism of the fragmentation of amine oxides:[44]

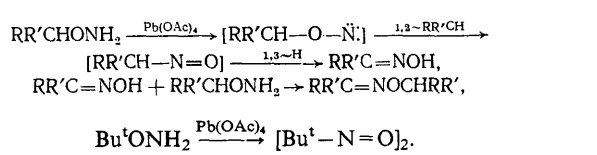


(XXVII)

Thus the concerted (but not biradical) decomposition of amino-nitrenes is possible also in the acyclic series.

2. Rearrangements

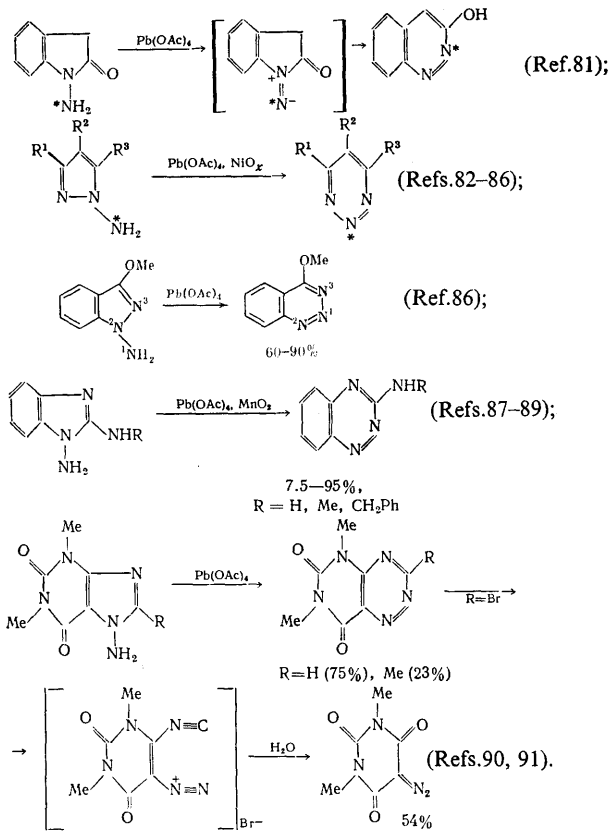
Rearrangements, including the 1,2-migration of substituents to the atom with an incomplete electron shell, are characteristic of all the sextet species, including amino- and oxy-nitrenes. For alkoxy-nitrenes, this is the cause of the permanent presence in the reaction mixtures of oximes, their ethers, and nitroso-compounds:[78,79]



The yields of the oxime ethers are 16–32% and that of the dimer of the tertiary nitroso-compound is up to 57%.

The corresponding conversion of the simplest aminonitrene (II) to the significantly more stable (by 123 kJ mol^{-1} [9]) *trans*-diazene HN=NH is symmetry-prohibited[80] but nevertheless the *trans*-diazene is one of the nitrene(II) reaction products already at 90 K.[29] On the other hand, the 1,2-migration of the alkyl group with inversion at the migrating centre is already an allowed process for dialkylaminonitrenes, but unambiguous examples of the rearrangement of dialkylaminonitrenes to aliphatic azo-compounds are not as yet available in the literature. On the other hand, a whole series of conversion of *N*-heteroarylnitrenes to the corresponding azo-compounds with ring expansion are known; many of them are of preparative value.[3] Here an additional driving force is the formation of a stable aromatic system.

Thus, cinnolinol has been obtained by oxidising *N*-amino-oxindole,[3,81] compounds of the 1,2,3-triazine series have been synthesised from *N*-aminopyrazoles[82–86] and indazoles,[86] while substituted 1,2-diaminobenzimidazoles[87–89] and theophylline derivatives[90,91] can be converted into the corresponding 1,2,4-tri-azines:

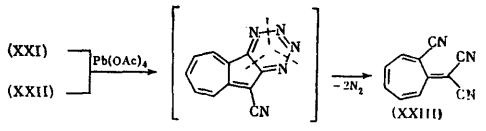


(Ref.81); (Refs.82–86); (Ref.86); (Refs.87–89); (Refs.90, 91).

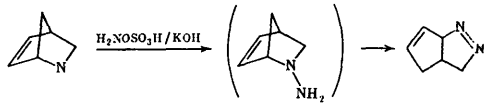
Best results are achieved as a rule by oxidising amino-compounds with LTA—the yields of 1,2,3-triazines are then usually 40–80%. However, 1-aminopyrazole itself affords only about 2% of 1,2,3-triazine when LTA is used,[85] although the yield increases to 20% on oxidation with nickel peroxide.[83–85] Such dependence of the yield on the nature of the oxidant, particularly when account is taken of the possible role of *N*-acetoxy-compounds in the oxidation of amino-compounds by LTA,[35] clearly requires a revision of the degree of involvement of aminonitrenes in the reactions described above.

Substituents have a significant and not always understood influence on the course of rearrangements. The unsubstituted 1,2,3-triazine is obtained in a low yield, while the 4,5,6-triphenyl-substituted derivative is not obtained at all.[86] Among different 2-substituted 1-aminobenzimidazoles, ring expansion is observed only for the 1,2-diamino-derivatives.[87,88] The results of studies of the mechanisms of the first three reactions with the aid of isotope substitution have also contributed little to the foregoing[81,86] (they are illustrated in the corresponding schemes).

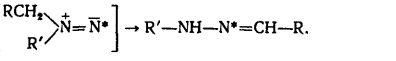
A related rearrangement but one involving the formation of the 1,2,3,4-tetrazine ring may occur on oxidation of the aminotriazoloazulenes (XXI) and (XXIII) with LTA (see above),[174] whose final product is the heptafulvene (XXIII):



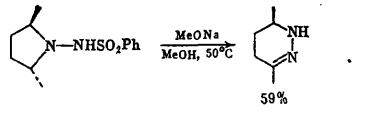
Finally, one cannot rule out the possibility that aminonitrenes participate in rearrangements of the allyl type on oxidation or reduction of certain derivatives of 2-azabicyclo[2.2.1]hept-5-ene,[48] for example:



Another variant of the isomerisation of aminonitrenes is their conversion into monosubstituted hydrazones, the so called "diazene–hydrazone" rearrangement:



Mono- and also di-substituted hydrazones (see below concerning the possible pathway leading to their formation) are the usual products of the oxidation of hydrazines,[3,39,42,43,92] the cleavage of sulphonic acid hydrazides, and other reactions in which the intermediate involvement of aminonitrene is postulated. In the heterocyclic series, the rearrangement results in ring expansion,[27,45,93] for example:[45]



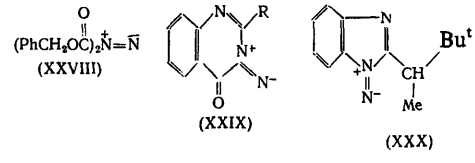
The reaction appears to be entirely similar to the rearrangement of alkoxynitrenes to oximes already considered, especially bearing in mind that aliphatic azo-compounds also isomerise comparatively readily to the more stable hydrazones.[33] However, here the similarity is mainly formal. This is demonstrated most convincingly by the results of the alkaline decomposition of 1,1-diethyl- and 1-benzyl-1-phenyl-2-arenesulphonyl[2-^{15}N]hydrazines,[3] as well as the present authors' experiments on the neutralisation of solutions of 1,1-diethyldiazenium bromide, similarly labelled with ^{15}N. In all cases hydrazones are obtained with the label present preferentially and (frequently exclusively) in the imine nitrogen atom. Furthermore, it is evident that, if the reaction occurred in accordance with the "nitrene → azo-compound → hydrazone" mechanism, both nitrogen atoms would have been labelled to equal extents. In order to explain the rearrangement, other mechanisms have also been proposed (with the intermediate formation of diaziridines, azomethine imines, etc.[3]).

3. Addition to carbon–carbon multiple bonds

The addition of amino- and alkoxy-nitrenes to the C=C bond constitutes a general method of synthesis of a wide variety of *N*-amino- and *N*-alkoxyaziridines.[1–7,94] It has been shown in numerous instances that the reaction proceeds entirely stereospecifically with retention of configuration and that the yields of products depends strongly on the nature of the substituents at the double bond and on the type of nitrene.

Calculation for the simplest model reaction of the aminonitrene $H_2N\dot{N}$: (II) with ethylene[80,95,96] has shown that it can proceed via two pathways—as the reduction of ethylene to ethane with formation of a N_2 molecule[80] (without the rearrangement of $H_2N\dot{N}$: to the *cis*-diimide HN=NH—cf. Lahti[52]) and as a linear cheletropic formation reaction of *N*-aminoaziridine[95,96] with retention of the symmetry plane as the reactants approach one another.[96] The results of *ab initio* calculations[96] and calculations by the MNDO method[95] agree that the addition is electrophilic in character. The degree of charge transfer from ethylene to the nitrene in the transition state is ~0.1–0.16 e, the excess negative charge being concentrated mainly on the central nitrogen atom. The heat of the reaction is extremely low and the activation barrier is estimated as 90–100 kJ mol^{-1}.

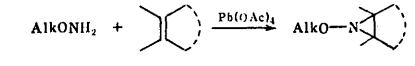
It follows from the data presented that the addition of aminonitrenes to the C=C bond is not unduly favourable from the energetic standpoint but it should be facilitated when the aminonitrene molecule contains substituents capable of stabilising the additional negative charge in the transition state. Accordingly, only aminonitrenes which have at least one or better two electron-accepting substituents enter into reactions via multiple bonds: phthalimidonitrene (PIN) (XII), the acylnitrenes (XIII) and (XXVIII), the heteroaromatic nitrenes (XXIX) and (XXX), and similar compounds:



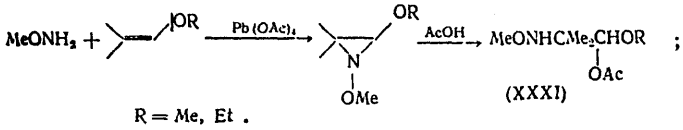
It may be that the presence of the electronegative oxygen atom in fact accounts for the ability of the alkoxynitrenes to enter into addition reactions.

N- and *O*-nitrenes are usually generated in reactions with multiple bonds by oxidising the corresponding amino-compounds with LTA. However, as already stated, at least in the oxidation of aminoquinazolinone (IX) the corresponding *N*-acetoxy-derivative (X) assumes the role of the nitrene (XI)[35] (see above). It is extremely likely (although not in fact obligatory) that in many other instances similar nitrenoids are in fact the real intermediates and instead of alkoxynitrenes we may be dealing with derivatives of *N*-acetoxyhydroxylamine. This alternative must be always borne in mind, although for the sale of brevity we shall henceforth no longer make this stipulation.

The oxidation of alkoxyamines by LTA in the presence of various alkenes affords the corresonding *N*-alkoxyaziridines:[2,5,6,94,97–99]



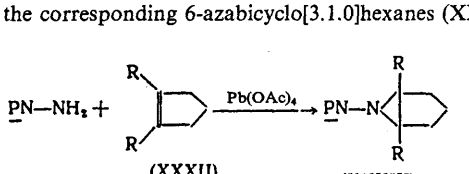
The yields of the adducts vary within wide limits (7–45%) and are apparently determined not only by the reactivity of the double bond in the alkenes but also by the ease of the corresponding rearrangements (see above). It has been shown for the stereoisomeric but-2-enes that the addition is entirely stereospecific[97] (the earlier opposite conclusion apparently arose because of errors in the determination of the structures of the products). In the reactions with vinyl ethers, the acetates (XXXI), which can be regarded as the products of the opening of the ring in the intermediate 1,2-dialkoxaziridines by acetic acid, were isolated:[101]



R = Me, Et .

The set of aminonitrenes involved in the reactions with C=C bonds in studies carried out during the last decade is fairly traditional. These are in the first place PIN (XII)[35,53,54,102–114] and nitrenes of the quinazolinone (XXIX)[35,105,115–117] and benzimidazole (XXX)[118] series. The yields of the aminoaziridines are in this instance usually 50–70% but can also approach 95% in the presence of a very slight excess of the alkene. It has recently been suggested that the diacylaminonitrene (XXVIII) be used in the synthesis of aminoaziridines,[119] but, in order to obtain even fairly moderate yields of the aziridines (30–70%), an almost hundredfold excess of the substrate is required in this case. At the same time, aziridines are formed in fair yields on addition of monosubstituted acylaminonitrenes (XIII) to cyclohexene and (*Z*)-4-methylpent-2-ene,[58] this being in general the first example of intermolecular reactions of monosubstituted nitrenes. Hitherto it has been assumed that they are too unstable and decompose instantaneously with liberation of nitrogen. At the same time the stable acylaminonitrene (VIIb) does not interact with cyclohexene, or dihydropyran, or methyl acrylate.[27]

Phthalimidonitrene (XII) and other heteroarylnitrenes react smoothly with most varied multiple bonds. The corresponding aminoaziridines have been obtained in satisfactory yields from indenes[105,108,113] and indoles[110] (cf. Meyer et al.[105]), derivatives of cyclopentadiene[108,109] and vinyl phosphonate esters,[103,117] norbornadiene and its analogues,[104,107,114] propelladiene,[102] etc. The reactions of PIN (XII) with cyclopentene derivatives (XXII) afford the corresponding 6-azabicyclo[3.1.0]hexanes (XXXIII):[105,120]

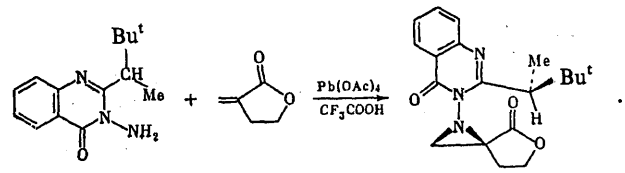


(XXXII) (XXXIII)

R = H (a), Co_2Me (b).

The nitrene (XXIX, R = Me) reacts with cyclopentene (XXXIIa) itself but not with the diester (XXXIIb).[105] Nor has it been possible to obtain its adduct with 1,2-di(methoxycarbonyl)cyclobutene,[105] whereas PIN affords the aziridine (XXXIIIb)[105] and adds even to 1,2-dichlorocyclobutene, forming the strained 1,4-dichloro-5-azabicyclo[2.1.0]pentane.[120]

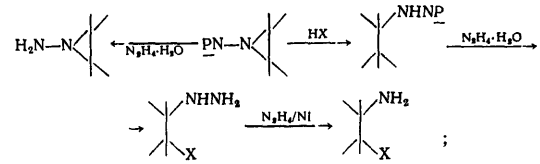
The addition of the chiral nitrenes [XXIX, R = Bu^t(Me)CH][115,116] and (XXX)[118] to prochiral alkenes leads to mixtures of diastereoisomeric aziridines in various proportions. After the addition to the reaction mixture of several equivalents of trifluoroacetic acid (TFAA), the reaction can be carried out at –60 °C, which sharply increases its stereoselectivity.[115,116] For example, in the presence of TFAA only one aziridine is formed from methylenebutyrolactone instead of approximately equal amounts of diastereoisomers:[115,116]



The addition of up to 10 equiv. of TFAA greatly facilitates the conversion of relatively unreactive substrates into aziridines by quinazolinone derivatives.[117] Thus the yield of the adduct of allyl chloride (1.5 equiv.) with the nitrene (XXIX, R = Et) increases from 10 to 90% in the presence of 6 equiv. of TFAA. Furthermore, according to data obtained by means of competing reactions, the selectivity of the reacting species increases. The protonation of the intermediate aminonitrene (XXIX) at the N(1) atom of the quinazolinone ring is believed to be a possible explanation of all these changes.[115–117]

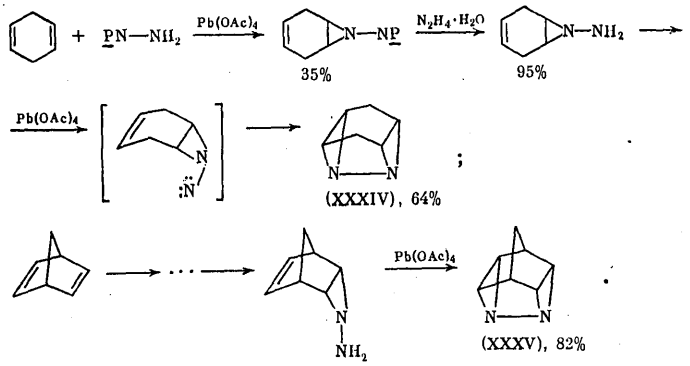
Although, as already mentioned, *N*-heteroarylnitrenes react with the most varied substrates, the view has been established that they are nucleophilic in nature (see, for example, Meyer et al.[105]). However, we have shown recently for a typical and perhaps most thoroughly investigated nitrene of this kind, namely PIN (XII), by the method of competing reactions that its addition to a series of ring-substituted styrenes is electrophilic in character.[111,113] Secondary orbital interactions of the heterocyclic ring of the *N*-nitrene with unsaturated substituents at the bond attacked (aromatic ring, double bond, carbonyl group, etc.) play a major role in the reaction.[3,112–118] For their occurrence, it is necessary that the aminonitrene and the substrate are arranged in parallel planes in the transition state, the *syn*-orientation of the unsaturated substituent and the heterocyclic residue being essential. The suitability of this structure of the transition state is clearly manifested in the preferential formation of the thermodynamically less stable *syn*-invertomers of aziridines[3,112–118] and it may be one of the causes of the asymmetric induction in the reactions of chiral nitrenes.[115,116,118]

The adducts of *N*-nitrenes with C=C bonds, which consist of a wide variety of aminoaziridines, are not only of intrinsic interest but are also of interest as possible intermediates in the synthesis of numerous derivatives of hydrazines, amines, etc. with functional group substituents.[121] *N*-Phthalimidoaziridines are especially convenient in this respect, because the phthaloyl group can be easily removed:[102,104,121]



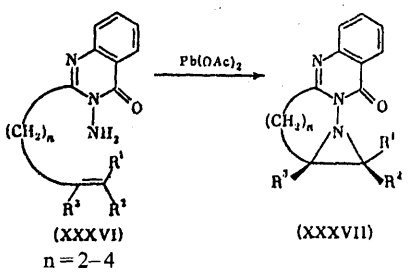
X = PhO, PhS, PhNH, TsO, OH, OAc, etc.

This possibility has been used in the synthesis of polycyclic hydrazines (XXXIV) and (XXXV):[104]



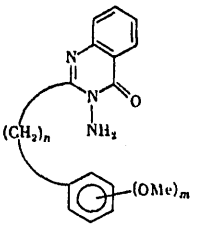
Admittedly, it is essential to note that the addition of PIN to norbornene and norbornadiene derivatives affords mainly the *exo*-adducts[104,107,114] and that the *endo*-aziridine required for the synthesis of compound (XXXV) constitutes only about 10% of the mixture of isomers.[104]

Apart from the intramolecular reactions quoted, other instances of the addition of dialkylaminonitrenes to the C=C bond are unknown. Evidently the success in this instance can be explained by the steric proximity of the interacting groups[104] (cf. Rüttimann and Ginsburg[102]). The influence of electronic and steric factors on the intramolecular addition of typical acylaminonitrenes has been investigated in detail in relation to aminoquinazolinone derivatives.[122–133] It has been shown for a large series of alkenylaminoquinazolinones (XXXVI), frequently containing two different double bonds in the branched side chain, that the reaction proceeds in all cases via a concerted mechanism and leads to the corresponding polycyclic aminoaziridines (XXXVII):[122–126]



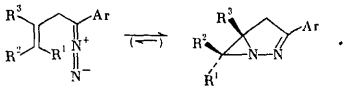
However, for a short side chain (n = 2), the symmetrical transition state must be greatly strained. The two C–N bonds are therefore formed non-synchronously and a polar seven-membered transition state is formed with the localisation of an appreciable positive charge on the β-carbon atom of the double bond.[126]

Similar conclusions follow the results of the oxidation by LTA of aminoquinazolinones (XXXVIII) containing an activated aromatic ring in the side chain.[127–133] Similarly to intermolecular reactions,[134] when n = 2–4, the products of the insertion of the nitrene in aromatic C–H bonds and also of the expansion of the aromatic ring to the azepine ring are formally produced,[127–133] but the short connecting bridge (n = 1) rules out the involvement of the aryl substituent in the reaction:[127]

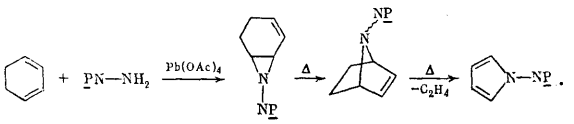


An increase in chain length by one unit (n = 2) leads to a highly polar seven-membered transition state and the process proceeds in essence via an S_E mechanism. The reaction of the long-chain compounds (n = 3, 4) includes, as usual,[1,4] stages involving the formation and cleavage of 7-azanorcaradienes.[127–133] It is important to note that in all the reactions considered[122–133] the quinazolinonylnitrene exhibits electrophilic properties.

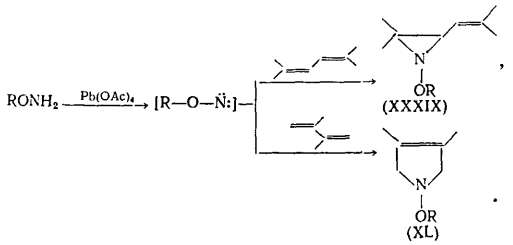
The remarkable analogy between aminonitrenes and diazocompounds can be seen from the intramolecular cyclisation of allyl-substituted aryldiazomethanes:[135]



The interaction of aminonitrenes with 1,3-dienes and cyclooctatetraene produced the corresponding aziridines in 30–70% yields. Asymmetric dienes (isoprene, penta-1,3-diene) afford a mixture of comparable amounts of two isomeric vinylaziridines. Neither diadducts nor 1,4-addition products are then formed.[3] Vinylaziridines are extremely unstable and undergo ready ring opening on treatment with nucleophiles, isomerising on heating to 3-pyrroline derivatives,[136,137] for example:[137]

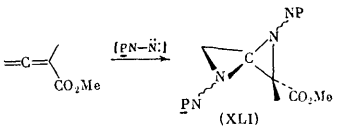


Alkoxynitrenes react with conjugated dienes in different ways:[99] their addition to 2,5-dimethylhexa-2,4-diene affords the alkoxyaziridines (XXXIX), apart from the analogous unsaturated aziridine, the isomeric 3-pyrrolines are formed from 2,4-dimethylpenta-1,3-diene, while in the reactions with 2,3-dimethylbuta-1,3-diene the main products are 1-alkoxypyrrolines (XL):[99,100]



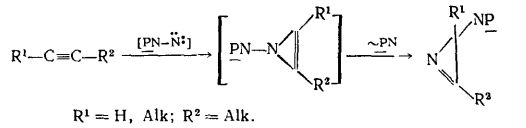
Formally 3-pyrrolines can be regarded as the products of the 1,4-addition of alkoxynitrenes but it may be that they are formed simply as a result of the ready isomerisation of the intermediate unsaturated alkoxyaziridines.[94]

The addition of PIN (XII) to the methyl ester of 2-methylbutadienoic acid leads, in contrast to 1,3-dienes, to a diadduct, to which the spiro-structure (XLI) has been attributed:[138]



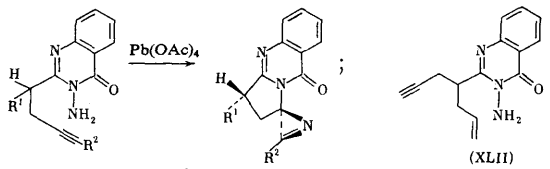
(XLI)

The interaction of the same nitrene with alkylacetylenes leads to 2*H*-azirines in low yields (2–15%).[139] The antiaromatic 1*H*-azirines are probably formed in the first stage:



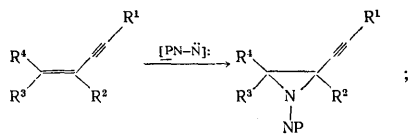
R^1 = H, Alk; R^2 = Alk.

Acetylenes with electron-accepting substituents, tolane, and phenyl-t-butylacetylene do not enter into this reaction at all.[139] The intramolecular addition to the C≡C bond proceeds readily, affording azirines in 80–100% yields:[140–142]



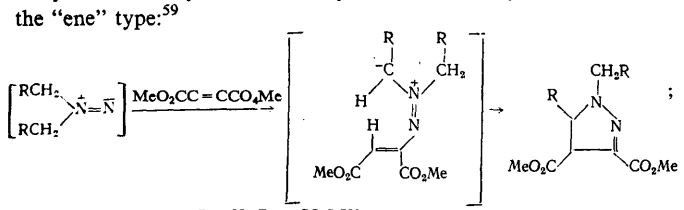
R^1 = H, $CH_2C{\equiv}CR^2$; R^2 = H, Me.

At the same time, oxidation of aminoquinazolinone (XLII) by LTA results in the formation of only the adduct involving the C=C bond in 84% yield.[142] The reaction of PIN (XII) with conjugated enynes also proceeds fully regio-selectively[139,143] § and may serve as a convenient method of synthesis of 2-alkynyl-1-aminoaziridines having different structures:



R^1–R^4=H, Alk, Ph.

Addition to multiple bonds is characteristic almost exclusively of acylaminonitrenes. However, a reaction has been described recently which is treated as the interaction of the triple bond in dimethylacetylenedicarboxylate with dialkylaminonitrenes by a mechanism of the "ene" type:[59]

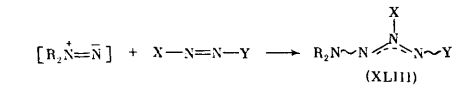


R = H; $R_2 = CO_2OCH_2$.

§ See also M A Kuznetsov, V V Semenovskii, V N Belov, V A Gindin *Khim. Geterotsikl. Soedin.*, 1989, 235.

4. The reactions with N=X (X = N, O, C) bonds

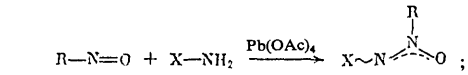
The interaction of aminonitrenes with azo-compounds leads to the formation of 1,3-dipolar compounds of a new class—aminoazimines (XLIII):



(XLIII)

Since this reaction has been described in detail in a recent review,[144] here we should like merely to note the general rule of the "mutual complementarity" of substituents in the nitrene and the azo-compounds. It has been found that PIN (XII) adds smoothly to azoalkanes, 1-pyrazolines, and azoarenes, while, conversely, diphenyl- and dialkyl-aminonitrenes react satisfactorily with derivatives of azodicarboxylic acid, but all attempts to carry out "cross reactions" have so far been unsuccessful.

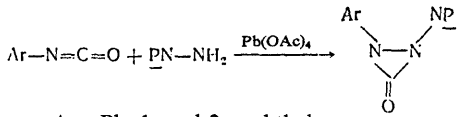
PIN (XII)[145–147] as well as a series of alkoxynitrenes[148,149] add similarly (at the LEP of the nitrogen atom) to various *C*-nitroso-compounds[145,148] and nitrosamines:[146,149]



X = PN, OAlk; R = Bu^t, t-C_5H_{11}, cyclo-C_6H_{11}, Ar, $R_2'N$. (4)

Phthalimidodiazene oxides (XLIV, X = PN) can be obtained from *C*-nitroso-compounds in 80–94% yield (with the exception of nitrosocyclohexane for which the yield is 18%[145]). The yield of the adducts of PIN with nitrosamines are 70–80%.[146] The yields of the alkoxydiazene oxides (XLIV, X = OAlk) are usually lower but they too can reach up to 60–70%.[148,149] It is important to note that, in the generation of PIN by the thermolysis of its adduct with acetylbenzofuran in the presence of nitrosocyclohexane, the corresponding diazene oxide (XLIV, X = PN, R = cyclo-C_6H_{11}) was obtained in 23% yield[145] (which is even higher than in the case where LTA is used). The attempt to extend reaction (4) to *O*-nitroso-compounds was unsuccessful: when aminophthalimide was oxidised by LTA in the presence of isopentyl nitrite, the formation of adducts was not detected.[146]

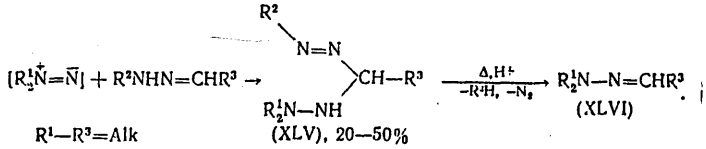
There are no reliable examples in the literature of the addition of acylaminonitrenes and alkoxynitrenes to the C=N bond. In fact it has been reported that possible adducts were not detected in the reaction mixtures after the oxidation of alkoxyamines by LTA in the presence of a large series of compounds: azomethines, azines, hydrazones, and oximes and their ethers.[98] However, it has been claimed that PIN is capable of adding to the C=N bond of aryl isocyanates, affording phthalimidodiazirinones:[150]



Ar = Ph, 1- and 2-naphthyl.

However, here one should note that aryl isocyanates react readily with primary amines, affording urea derivatives. Therefore, when they are mixed with aminophthalimide, the corresponding semicarbazide should be formed rapidly and the latter apparently is in fact oxidised further by LTA.

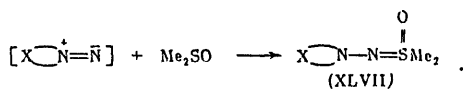
At the same time, dialkylaminonitrenes react with aldehyde monoalkylhydrazones, affording the so called geminal azohydrazines (XLV):[151]



On heating, on treatment with acids, and simply on standing, azohydrazines (XLV) decompose to the disubstituted hydrazones (XLVI).[151] Since monosubstituted hydrazones are readily obtained in the diazene–hydrazone rearrangement, it may be that the invariable presence of disubstituted hydrazones among the products of the reactions of dialkylaminonitrenes can be accounted for by this sequence of reactions.

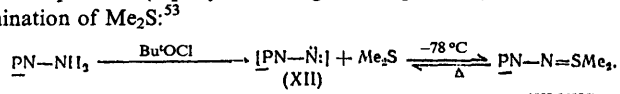
5. Reactions with dimethyl sulphide and sulphoxides. The formation of tetrazenes

The reactions listed in the heading have a common feature, namely they all reduce to the attack by the nitrene on the LEP of some kind of heteroatom. We have already seen examples of such interaction in the previous subsection—the addition of nitrenes to azo- and nitroso-compounds does actually occur at the LEP of the nitrogen atom. *N*-Heteroarylnitrenes, capable of adding to multiple bonds, react similarly with the classical "trapping agent" for sextet species—dimethyl sulphoxide, and other sulphoxides:[3,27,28,85,119]

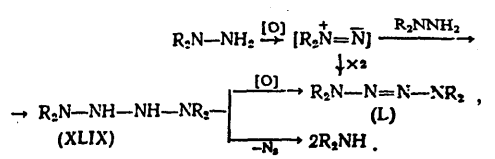


The extremely stable sulpoximines (XLVII) are then formed in a nearly quantitative yield. The attack on the LEP of the sulphur atom is so fast that vinyl-substituted sulphoxides are converted into unsaturated sulphoximines without any traces of addition to the double bond.[152] The stable nitrene (VIIb) does not react with DMSO,[27] although the sulphoximines (XLVII) corresponding to the nitrenes (VIIa, b) can be obtained by oxidising the initial acylhydrazines by LTA in DMSO.[28] Here they are clearly formed from "precursors" of the free nitrenes. Contrary to expectations, after the oxidation of alkoxyamines by LTA in DMSO, the adduct of alkoxynitrenes with the solvent could not be detected.[98]

The addition of PIN (XII) to dimethyl sulphide gives rise to a fairly labile sulphimide (XLVIII), which dissociates slowly even at room temperature (rapidly on raising the temperature) with elimination of Me_2S:[53]



The interaction of aminonitrenes with the starting materials used in their synthesis, usually hydrazine derivatives, is of a general character.[3] Here the intermediates are the extremely unstable tetrazans (XLVI), which can decompose, affording deamination products, or can be converted into 2-tetrazenes (L), which are the usual products of the oxidation of 1,1-disubstituted hydrazines:[3,85,119]



The tetrazenes (L) give rise to stable aminonitrenes simply as a result of dimerisation.[20–26]

By analogy with tetrazenes, one would expect the formation of 1,2-dialkoxydiazene RON=NOR in the oxidation of alkoxyamines but these compounds are extremely unstable and so far they have never been detected in any reactions of alkoxynitrenes.

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The last decade has provided extensive data illustrating the wide variety of the reactions of amino- and oxy-nitrenes. Although the range of reactions and methods for the generation of oxynitrenes investigated is appreciably narrower, the data obtained demonstrate their similarity to aminonitrenes. The general problem of the separation of the reactions of nitrenes proper and "nitroenoids" is associated directly with further progress in this field of the chemistry of sextet nitrogen intermediates. The properties and reactions of stable nitrenes can serve as a kind of standard. From the standpoint of theoretical organic chemistry as a whole, the study of the mechanism of the decomposition and rearrangements of amino- and oxy-nitrenes is of interest. There are good prospects that their reactions with a wide variety of unsaturated compounds will prove useful in syntheses. Evidently in the immediate future the search for new types of amino- and oxy-nitrenes, new methods for their generation, and new reactions of these species will becomes of current interest.

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