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Diazenium Salts

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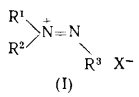
The literature on compounds of the type $[R^1R^2N=NR^3]^+X^-$ (diazenium salts) is surveyed. Their structures and properties are considered and methods for their synthesis as well as a wide variety of the chemical reactions of these reactive hydrazine derivatives are discussed.
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I. INTRODUCTION

Diazenium salts constitute a new class of nitrogen compounds having the general formula (I) containing the functional group $\rangle N^+=N$, which is not part of an aromatic system:



(I)

R^1=H, Alk, or Ar;
R^2=H, Alk, or Ar;
R^3=H, Alk, Ar, OAlk, or OAc;
X^-=Hal^-, ClO_4^-, BF_4^-, $SbCl_6^-$, etc.

The cations of diazenium salts are referred to as diazenium cations. The name of the salts is based on the nomenclature proposed for compounds containing two adjacent nitrogen atoms[1]. The complete name indicates the anion and all the substituents and their positions in the cation. For example, $[Me_2N^+=NH]Br^-$ is 1,1-dimethyldiazenium bromide, $[(PhCH_2)_2N^+=NOEt]BF_4^-$ is 1,1-dibenzyl-2-ethoxydiazenium tetrafluoroborate, and $[Ph_2N^+=NPh]ClO_4^-$ is triphenyldiazenium perchlorate.

The closest analogues of diazenium salts are, on the one hand, the well known diazonium salts and, on the other hand, the immonium salts $[R_2N^+=CR'_2]X^-$; one may therefore expect some similarity between the structures and properties of these compounds, which, as will be shown below, is indeed the case. The behaviour of diazenium salts is fully determined by the structure of the cation; the nature of the anion is not very important. Diazenium salts can be divided into several groups on the basis of the number and nature of substituents in the cation, differing appreciably in stability, properties, and the extent to which they have been investigated.

1,1-Disubstituted salts (I, R^3 = H), which have attracted the attention of investigators for a number of reasons, have been studied in greatest detail. Firstly, they are of interest in connection with the study of the mechanism of the oxidation of 1,1-disubstituted hydrazines, which is of practical importance; in acidic media this process proceeds via a stage involving the formation of the corresponding diazenium cations and the properties of the latter in many respects determine further reactions. Secondly, 1,1-disubstituted diazenium cations can be regarded as the conjugate acids of 1,1-diazenes or aminonitrenes $[R_2N^+=\bar{N} \rightleftharpoons R_2N-\ddot{N}:]$, which are unstable sextet species playing an important role in the chemistry of hydrazine derivatives[2-4]. The relation between aminonitrenes and 1,1-disubstituted diazenium cations, their interconversions in the reactions of hydrazine derivatives, and the possibility of regenerating aminonitrenes from 1,1-disubstituted diazenium salts are therefore of interest. Finally, many reactions of these salts are of independent synthetic value.

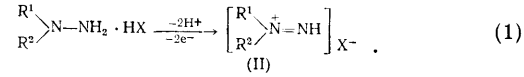
On the other hand, the properties of the isomeric 1,2-disubstituted diazenium salts have been scarcely investigated. There is also little information about the trisubstituted salts, with the exception of the so-called alkoxydiazenium salts (I, R^3 = OAlk). Fully unsubstituted and monosubstituted diazenium salts are so far unknown. The corresponding cations are apparently extremely unstable and, even if they can be generated in some reactions, so far no one has been able to detect their formation.

The literature dealing with diazenium salts is extensive, but hitherto has not been treated systematically to any great extent. Previously the syntheses and properties of diazenium salts were partly dealt with in reviews of aminonitrenes[2,3] and also in a review of reactive nitrogen-containing intermediates[5], but, in our opinion, their treatment has been inadequate. Furthermore, in recent years many new important studies have been published in this field. It therefore appears necessary to describe the present state of the chemistry of diazenium salts.

II. METHODS OF PREPARATION

1. Oxidation of Hydrazine Derivatives

In 1957 McBride[6] established that, whereas the oxidation of the simplest 1,1-dialkylhydrazines in an alkaline or neutral medium (a reaction known since the time of E. Fischer) leads to 2-tetrazenes, in an acidic medium in the cold the products obtained after the consumption of two equivalents of the oxidants are previously unknown compounds whose spectroscopic and chemical properties correspond to the structure of "diazo-like substances" (II):



(1)

(II)

McBride regarded the cations in (II) as protonated aminonitrenes (1,1-diazenes)[2-5] and therefore subsequently proposed[7] that they be called 1,1-disubstituted diazenium cations and that the salts (II) be referred to as diazenium salts.

Since then the oxidation of asymmetric disubstituted hydrazines in an acid medium [Eqn.(1)] became the usual and virtually the only method of synthesising 1,1-disubstituted diazenium salts. The oxidants used for 1,1-dialkylhydrazines have usually been halogens and alkali metal halogenates.[6-25] In addition, use was made of transition metal salts [Ce(IV) [25], Hg(II),[26] Cu(II) [27]] and peracids.[28] Hünig postulated the formation of diazenium cations in the oxidation of a number of 1,1-diarylhydrazines by $FeCl_3$ and $K_3[Fe(CN)_6]$.[29,30] However, in the latter case the oxidation was carried out in a weakly acidic (CH_3COOH) and even alkaline (pyridine, ammonia) media; under these conditions, 1,1-disubstituted diazenium salts cannot exist for any long period (see below); Hünig's claim therefore appears doubtful. It has been reported[14] that the oxidation of arylhydrazines with bromine yielded only decomposition products. However, it is more likely that this process involves the usual bromination of the aromatic ring, analogous to the bromination of analines, rather than oxidation, and that diazenium salts are not formed at all. Chemical oxidation has usually been carried out in aqueous solutions and only once in acetonitrile.[14]

Diazenium salts have been obtained by the electrochemical oxidation of 1,1-diaryl- and 1-alkyl-1-arylhydrazines at platinum electrodes in acetonitrile[14,31-37] and also of 1,1-dimethylhydrazine in aqueous H_2SO_4.[25,38] However, the attempt at an anodic oxidation of 1,1-dimethylhydrazine to a diazenium salt in acetonitrile under conditions completely identical with those in the oxidation of arylhydrazines was unsuccessful: oxidation does not occur in the presence of acid and in neutral and alkaline media other products are formed[39]. Nor was it possible to oxidise 1,1-dibenzylhydrazine under these conditions[14].

It follows from coulometric data[31-34,36-38,40,41] and from the results of potentiometric titration of 1,1-disubstituted hydrazines with KIO_3 in acid solutions[42] that two-electron oxidation takes place in conformity with Eqn.(1), the products being comparatively stable species which are not oxidised further. The EPR spectrum recorded in the oxidation of 1,1-dimethylhydrazine by Ge(IV) in H_2SO_4 showed the presence of the signal of the 1,1-dimethylhydrazinium radical-cation $[(CH_3)_2NNH_2]^{\cdot+}$, which led to the conclusion that the oxidation of 1,1-disubstituted hydrazines in acid solutions (at least by one-electron oxidants) proceeds in two stages and that the diazenium cation is preceded by the hydrazinium radical-cation[25]. On the other hand, in the electrochemical oxidation of the same hydrazine there are no EPR signals. In this case hydrazine apparently loses both electrons almost simultaneously at the anode surface[25].

The 1,1-disubstituted diazenium salts formed in the oxidation process in almost quantitative yields are most stable in strongly acidic solutions below 5°C, but even under these conditions they decompose slowly, the rate of decomposition increasing with temperature[6]. Salts with aryl substituents are stable only in non-aqueous solutions.

A salt of type (II) has been synthesised in a dry form in only one instance—McBride obtained crystalline 1,1-dimethyldiazenium perchlorate[6]:

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

It is noteworthy that the fully stable hydrazides of sulphonic acids (III) can be regarded formally as diazenium salts. It is claimed that in both acid[17] and neutral and alkaline polar solutions[43] they can dissociate reversibly into diazenium cations and sulphinate anions:

$$\underset{\text{(III)}}{R^1R^2N{-}NHSO_2R^3} \rightleftharpoons \left[R^1R^2\overset{+}{N}{=}NH\right] + R^3SO_2^- \ . \qquad (2)$$

The occurrence of this equilibrium has been confirmed by a number of experiments on the exchange of sulphonic acid residues in hydrazides[43] (see Section V in this review), from which it follows, in particular, that 1,1-dialkylhydrazides dissociate most readily. However, even for these substances the position of equilibrium (2) is apparently strongly displaced to the left, since signals corresponding to diazenium cations could not be detected in the ^1H NMR spectra of their solutions[43]. The dissociation itself can be regarded as an intramolecular oxidation-reduction process: here the hydrazinium residue is oxidised to the diazenium cation and the sulphonyl group is reduced to the sulphinate ion.

Trisubstituted salts (I, R^3 = Ar or t-Bu) can be obtained by the chemical (Ag^+)[44] and electrochemical[34,37,44-46] oxidation of the corresponding trisubstituted hydrazines, which is in many ways analogous to the formation of 1,1-disubstituted diazenium salts:

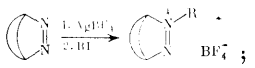
$$R^1R^2N{-}NHR^3 \xrightarrow[-H^+,-2e^-]{X^-} R^1R^2\overset{+}{N}{=}NR^3\ X^- . \qquad (3)$$

However, the anodic oxidation of trimethylhydrazine in acetonitrile does not occur in the presence of acid, while in neutral and alkaline media formaldehyde dimethylhydrazone is formed[39]. At the same time, it is believed that the chemical oxidation of trimethylhydrazine in aqueous acid solutions and the dissociation of 1,1,2-trimethyl-2-tosylhydrazine,[17] analogous to the reaction (2), proceed via the formation of the trimethyldiazenium cation. Other trisubstituted hydrazines, which have no dissociable protons at the α-carbon atoms of the substituents, can be oxidised electrochemically in neutral and alkaline media to the corresponding diazenium cation; however, on being protonated, they are not oxidised even in aqueous solutions[44].

2. The Alkylation of Azo-Compounds and *N*-Nitrosamines

Apart from the anodic oxidation of trisubstituted hydrazines, treatment of azo-compounds with strong alkylating agents constitutes an effective method for the synthesis of trisubstituted diazenium salts. Dry crystalline salts, which are fairly stable in air, are obtained in 60–90% yield.

Thus 2,3-diazabicyclo[2,2,1]heptane and a number of azo-compounds with a symmetrical environment around the azo-group have been alkylated[44,47,48]:



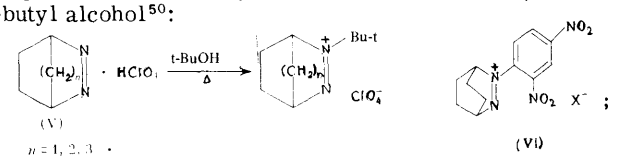
R = Me, Et, or t-Bu;

a series of 1,2-diaryl-1-methyldiazenium salts have been obtained[49]:

$$\underset{\substack{\text{(IV)}\\ R = F \text{ or } CF_3.}}{ArN{=}NAr'} \xrightarrow{MeOSO_2R} \underset{RSO_3^-}{\overset{Ar}{\underset{Me}{\overset{+}{N}}}{=}NAr'} + \underset{RSO_3^-}{ArN{=}\overset{+}{N}\overset{Ar'}{\underset{Me}{\diagup}}} \ ;$$

If Ar = Ar′ in (IV), then alkylation proceeds preferentially and sometimes exclusively at the nitrogen atom linked to the more electron-donating substituent. When the ring contains an electron-accepting substituent, the nitrogen atom linked to it is not alkylated[49].

Trisubstituted diazenium salts are obtained unexpectedly readily and smoothly (85–90% yield) by refluxing the perchlorates of bicyclic azo-compounds (IV), in t-butyl alcohol[50]:

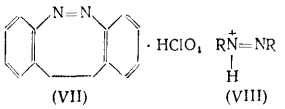


(V) (VI)

$n = 1, 2, 3$ ·

It is remarkable that in all the instances described the introduction of the t-butyl group into the molecule does not entail the liberation of isobutene.[44] Under still milder conditions (25°C, ether), the salt (VI, X = Br) can be obtained in 83% yield from 2,3-diazabicyclo[2,2,2]octene and 1-bromo-2,4-dinitrobenzene.[50]

The alkylation of protonated azo-compounds proceeds similarly[50–52]. It follows from the ^{1}H NMR spectra of certain azo-compounds in strongly acid media at a low temperature[51,52] and also from electronic spectroscopy for chemical analysis (ESCA) that the protonation of both the *cis*- and *trans*-forms of azobenzene, pyridazine, and *o*,*o*′-azobibenzyl (VII) [52] gives rise to asymmetric classical ions (VIII):



(VII) (VIII)

i.e. 1,2-disubstituted diazenium cations are produced and not a bridge ion with the proton located symmetrically relative to both nitrogen atoms. Many facts, previously treated as evidence for the formation of non-classical ions and which have aroused a prolonged discussion concerning the structure of protonated azo-compounds (see Refs. 51 and 52 and the literature quoted therein), can apparently be accounted for by very rapid proton transfer between two nitrogen atoms under the usual conditions, for example, in solutions. The classical structure of protonated azo-compounds is supported by the fact that, according to calculations in terms of CNDO/2 and MINDO/2 approximations for protonated azomethane and azobenzene, the ion (VIII) is more stable than any of the possible bridge ions[52]. Thus the salts of azo-compounds can be regarded as 1,2-disubstituted diazenium salts.

In 1962 Hünig and coworkers obtained alkoxydiazenium salts for the first time by the reaction of aliphatic *N*-nitrosamines with triethyloxonium tetrafluoroborate [53]:

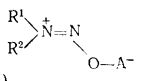
$$R_2N{-}NO + Et_3\overset{+}{O}BF_4^- \xrightarrow[-Et_2O]{CH_2Cl_2} R_2\overset{+}{N}{=}NOEt\ BF_4^-$$

Since then alkoxydiazenium salts have been obtained by the alkylation of purely aliphatic and alkylaryl-substituted *N*-nitrosamines with trialkyloxonium tetrafluoroborates,[53–57] trialkyloxonium hexachloroantimonates,[58] and alkyl halides in the presence of $SbCl_5$,[55,57] $AgClO_4$,[54,55] dimethyl sulphate,[58–60] and benzoyl chloride[61] (strictly speaking the product in the last case is not an alkoxy-salt but an acyloxydiazenium salt). The alkylation proceeds very readily and smoothly: it is sufficient to mix the reactants in a suitable solvent (CH_2Cl_2, $C_2H_4Cl_2$, etc.) with (sometimes) slight heating. Since the yields of alkoxydiazenium salts are nearly quantitative, no attempts were therefore evidently made to obtain them by other means.

In a dry form alkoxydiazenium salts are crystalline substances; only some of the lowest homologues are oily liquids at room temperature. In the absence of moisture, they can be stored for months without decomposition; they dissolve without decomposition in many solvents, including water, but decompose when the solutions are made alkaline [55]. Their toxicity is lower than that of the initial nitrosamines and is directly proportional to the electrophilicity of the cation. When administered subcutaneously to rats, many alkoxydiazenium salts induce extensive sarcomas[62].

3. Other Sources of Diazenium Salts

N-Nitrosamines form complexes with Lewis acids to which structure (IX), analogous to that of alkoxydiazenium salts, was attributed on the basis of infrared and ^{1}H NMR spectra[63,64]:

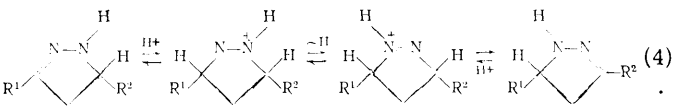


(IX)

A = BF_3, $AgCl_3$, $SbCl_5$, etc.

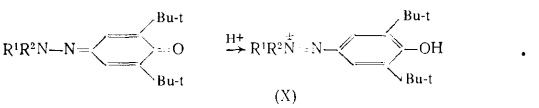
On the basis of the ultraviolet spectra of solutions of dialkylnitrosamines in a trichloroacetic acid-cyclohexane mixture, it has been concluded that nitrosamines are at least partly protonated at the oxygen atom, i.e. that hydroxydiazenium salts are formed[65].

C-Analogues of nitrosamines (hydrazones) are usually protonated and alkylated at nitrogen atoms. Nevertheless, in order to explain the isomeric transformations of 2-pyrazolines in an acid medium, their *C*-protonation with formation of a diazenium fragment has been postulated[66]:



(4)

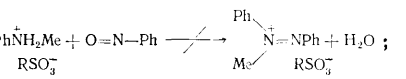
It has also been reported[67] that, when 2,6-di-t-butylbenzoquinone monohydrazones are dissolved in a 1 : 1 CF_3COOH–C_3F_7COOH mixture, trisubstituted diazenium cations (X) are formed:



(X)

However, in this case the closest analogous process is *O*-protonation of *N*-nitrosamines and the cation (X) is a phenylogue of the hydroxydiazenium cation.

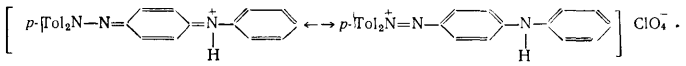
The only attempt hitherto to obtain a diazenium salt by condensing a nitroso-compound with a secondary ammonium salt was unsuccessful[49]:



R = F, or CF_3.

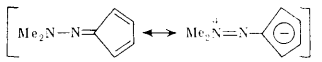
The fragment $\rangle N^+{=}N\langle$ is sometimes present in only one of several limiting structures possible for the given compound. However, if the contribution to the structure is large, the properties of such compounds can be similar to those of the usual diazenium salts. Thus, the dyes of type (XI) isolated by Hünig[5,29,30,68] following the oxidation of 1,1-diarylhydrazines in the presence of aromatic

amines can be assigned to the class of trisubstituted diazenium salts:



(XI)

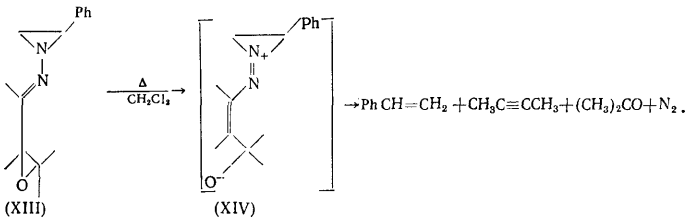
Compounds which can be regarded as a kind of intramolecular diazenium salt are also of interest. An example is the cyclopentadienone dimethylhydrazone (**XII**) [59,60]:



(XIIa) (XIIb)

The appreciable contribution of structure (**XIIb**) is confirmed by the large dipole moment of this compound (3.3 D), which greatly exceeds the dipole moments of the usual hydrazones [69] and can probably be accounted for by the ease of formation of the aromatic cyclopentadienyl anion.

The formation of another intramolecular trisubstituted diazenium salt (**XIV**) is postulated as an intermediate stage in the decomposition of the hydrazone (**XIII**) [70]:



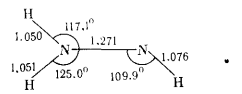
(XIII) (XIV)

Finally, up to 70% of the ions corresponding to the most intense $(M-H)^+$ line in the mass spectrum of the surface ionisation of 1,1-dimethyl-2,2-dideuterohydrazine were formed as a result of the abstraction of a deuterium atom, i.e. had a mass $M-2$, which led to the claim that this ion has the structure of a 1,1-disubstituted diazenium cation [71].

By analogy with the involvement of di- and tri-substituted diazenium cations in a number of reactions of di- and tri-substituted hydrazines, it is suggested that monosubstituted diazenium cations can be formed at intermediate stages of the corresponding reactions of monosubstituted hydrazines. For example, the formation of the methyldiazenium cation has been postulated in the oxidation of methylhydrazine and the decomposition of its tosylate in an acid medium [17]. However, in contrast to di- and tri-substituted diazenium cations, the monosubstituted cations are extremely unstable (if they are formed at all) and there are so far no reliable data concerning their existence.

III. STRUCTURE AND SPECTROSCOPIC CHARACTERISTICS

Almost all the available literature information about the structure of diazenium salts has been obtained by quantum-chemical calculations on their cations. For the simplest diazenium cation $N_2H_3^+$, it has been found by the *ab initio* method on the STO-3G basis as a result of the complete optimisation of the geometry [72] that such species can exist (an energy minimum corresponds to it), is planar, and has the following structure (the bond lengths are quoted in angstroms):



The nitrogen–nitrogen bond length in $N_2H_3^+$ has been determined by the semiempirical CNDO/2 method as 1.23 Å, [73] i.e. somewhat smaller than in the previous case [72]. Apart from the difference between the methods of calculation, the discrepancy may be caused by the fact that Bespalov and Kuznetsov [73] did not carry out a complete optimisation of the geometry and the trigonal hybridisation of both nitrogen atoms adopted in calculations on $N_2H_3^+$ and equal lengths of all the N–H bonds (1.01 Å) constitute a fairly rough simulation of the optimum geometry. The same semiempirical method yielded a structure for the hydroxydiazenium cation with an N=N bond length of 1.24 Å and the preferential transoid conformation with respect to the N–O bond [73]. Despite certain differences, it is seen from the data presented that the N=N bond length in diazenium cations is close to the usual value for the N=N bond in uncharged species (1.238 Å in *trans*-diazene HN=NH). [74]

The electronic structures of a number of simplest substituted diazenium cations have also been calculated by the CNDO/2 method [73]. It has been found that the order of the N=Nπ bond in alkyl- and aryl-substituted cations is very high (0.95–0.96), i.e., in conformity with the canonical structure (I), this is virtually a double bond. In alkoxydiazenium ions the order of the bond is somewhat lower (0.86–0.89) and the multiplicity of the N–O bond is increased, which indicates $p-\pi$ conjugation in these species [73].

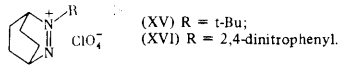
According to the canonical structure (I), the double bond between the nitrogen atoms arises as a result of the "delocalisation" of the lone electron pair of the $N_{(1)}$ atom. However, despite the high order of the π bond, the populations of the p_Z orbitals of the two nitrogen atoms are by no means equal: the population of the p_Z orbital of the $N_{(1)}$ atom remains significantly greater (1.15–1.20 for alkyldiazenium cations and 1.30–1.37 for alkoxydiazenium cations†), while the p_Z orbitals of the $N_{(2)}$ atom are less than unity [73]. The usual formula (I) reflects even less satisfactorily the distribution of the charges on the atoms: it follows from the calculations for a number of cations that the positive charge, formally wholly located at $N_{(1)}$, is to a large extent distributed over the nearest atoms. Such "smearing" of the charge is extremely typical of charged species (see, for example, Haselbach et al. [52]), the charge being distributed mainly in conformity with the electronegativities of the atoms, and ultimately an appreciable proportion of the positive charge is located at hydrogen atoms. For example, according to calculations for azobenzene and the 1,2-diphenyldiazenium cation by the CNDO/2 and MINDO/2 methods, the changes in the charges on two nitrogen atoms on protonation of azobenzene are very similar in magnitude and amount to only 0.13–0.17. [52] These conclusions have been confirmed experimentally: it has been shown by the ESCA method that, when azobenzene is converted into its perchlorate (actually into 1,2-diphenyldiazenium perchlorate), the binding energy of the 1s electrons of the nitrogen atom E_b(N 1 s) increases slightly. E_b(N 1 s) = 404.5 eV for

†Calculations by the Hückel method on 1-aryl-2-methoxy-1-methyldiazenium cations gave a still greater population of the p_Z orbital of $N_{(1)}$—about 1.49. [55]

azobenzene, and the X-ray electronic spectrum of the perchlorate has a broadened band with its centre at 406.7 eV, which is formed as a result of the superposition of two bands separated by approximately 2 eV. The splitting of the band indicates the non-equivalence of the two nitrogen atoms in the perchlorate and the experimental splitting agrees satisfactorily with the value obtained from the calculated charge distribution in the *trans*-1,2-diphenyldiazenium cation[52]. A similar picture is observed in the X-ray electronic spectra of the perchlorates of pyridazine and *o*,*o'*-azobibenzyl (VII).[52]

As a result of the delocalisation of the positive charge in diazenium cations, only a small proportion of it (0.1 to 0.2) remains at the $N_{(1)}$ atom. On the other hand, there is a fairly significant charge on the neighbouring $N_{(2)}$ atom, which is comparable (0.2–0.25) in alkoxydiazenium salts to the charge on the terminal nitrogen atom in the phenyldiazonium cation (0.20) and the carbon atom in immonium ions (approximately 0.2).[73] This apparently determines the ability of alkoxydiazenium salts, like that of diazonium and immonium salts,[75] to undergo coupling reactions (see Section V). At the same time, the comparatively small charge on the $N_{(2)}$ atom in alkyl-substituted diazenium cations (0.03–0.10) suggests a lower reactivity of the corresponding salt in reactions of this type.

The ultraviolet spectrum of 1,1-dimethyldiazenium perchlorate exhibits an absorption at 280 nm ($\epsilon = 150$),[7] while the spectrum of the perchlorate (XV) has λ_{max} 311 nm ($\epsilon \simeq 100$)[50]:



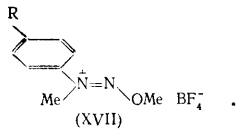
(XV) R = t-Bu;
(XVI) R = 2,4-dinitrophenyl.

The spectrum of 1-methyl-1-phenyldiazenium perchlorate has λ_{max} = 313 nm (ϵ = 6700)[37] and that of 1,1-diphenyldiazenium perchlorate has λ_{max} = 330 nm (ϵ = 9600).[31,37] The bathochromic shift and the hyperchromic effect are exhibited to an even greater extent on passing to salts with three aromatic substituents: the spectra of triphenyldiazenium perchlorate, 1,1-di-*p*-tolyl-2-(*p*-dimethylaminophenyl)diazenium perchlorate, and 1,1-di-*p*-tolyl-2-(*p*-anilinophenyl)diazenium perchlorate (XI) have λ_{max} = 430 nm (ϵ = 15 400),[37,45] 535 nm (ϵ = 55 000), and 556 nm.[29,68] λ_{max} = 232 nm (ϵ = 22 400) has been observed for 1,1-dimethyl-2-(2',4'-dinitrophenyl)diazenium perchlorate[46] and λ_{max} = 286 nm (ϵ = 7400) has been found for the salt (XVI) in acetonitrile.[50]

The nature of the long-wavelength band in the ultraviolet spectra of alkyldiazenium salts (more precisely their cations) is analogous to that of the long-wavelength absorption of aliphatic azomethines, but not to that of the seemingly similar $n-\pi^*$ transition in saturated azo-compounds[76,77]. In both $\overset{+}{N}{=}N$ and $C{=}N$ groups only one lone electron pair adjoins the π bond and the ultraviolet spectra of compounds of both classes therefore contain bands associated with the $n-\pi^*$-transition having similar energies and extinction coefficients. The appearance in azocompounds of a second lone electron pair at the neighbouring nitrogen atom leads to a qualitatively different picture, since the interaction of the non-bonding orbitals results in the formation of hybrid ψ_+ and ψ_- orbitals. The energy of one of these orbitals is smaller and that of the other approximately just as much greater than the energy of the "pure" *n*-orbital; under these conditions, for example, in *trans*-azomethane, photoelectron spectroscopic data[78] show that the splitting of the non-bonding levels reaches 3 eV. The longest-wavelength transition $\psi_+-\pi^*$ in *trans*-azo-compounds (or the $\psi_--\pi^*$ transition in *cis*-azo-compounds)[78] therefore requires a lower energy than the usual $n-\pi^*$ transition in diazenium cations, while the difference between the symmetries of the ψ_+ or ψ_- orbital, on the one hand, and the virtually localised orbital of the lone electron pair, on the other, leads to a difference in the selection rules and hence in the intensities of the corresponding absorption bands in the ultraviolet spectra of diazenium salts and azo-compounds.

An absorption maximum in the region of 217–226 nm with $\epsilon \simeq (7–9) \times 10^3$ [55] is characteristic of alkoxydiazenium salts with alkyl substituents; it corresponds to the $\psi_2-\psi_3$ transition in the fragment $\overset{+}{N}{=}N{-}O$, whose π-electron system is isoelectronic with that of the allyl anion by virtue of $p-\pi$ conjugation [73]. The ultraviolet spectra of aliphatic alkoxydiazenium salts therefore differ appreciably from those of other diazenium salts, but are similar to the spectra of alkylhydrazones [76,79] and enamines,[80] for which the existence of $p-\pi$ conjugation has been demonstrated[81]. The latter compounds are also isoelectronic with the allyl anion.

If R^1 = Ar in alkoxydiazenium salts, then a bathochromic shift is observed, but the extinction hardly changes. The shift of λ_{max} in the ultraviolet spectra of 1-aryl-2-methoxy-1-methyldiazenium salts (XVII) relative to the absorption band of the compound adopted as the standard is consistent with the results of calculations by the Hückel method[82] and is described satisfactorily by the Hammett equation[55]:



(XVII)

According to ultraviolet spectroscopic data, only diazenium salts with anions exhibiting weak electron-donating properties (I, $X^- = BF_4^-$, ClO_4^-, etc.) are purely ionic. Diazenium cations form ion pairs with more electron-donating anions[7] and a long-wavelength charge-transfer band appears in the ultraviolet spectra of the salts (I, $X^- = Br^-$ or I^-).[50,82] With decrease of the polarity of the solvent, the intensity of this band increases[82]. The absorption maximum shifts towards lower energies as the electron-donating properties of the anion and the electron-accepting properties of the cation are enhanced[50,82].

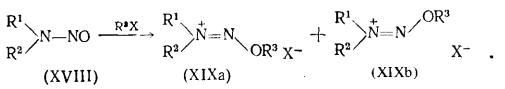
Infrared spectra have been obtained only for alkoxydiazenium salts. Purely aliphatic salts have an intense band at 1540–1575 cm^{-1} in the infrared spectrum[53–55], due to the stretching vibrations of the $\overset{+}{N}{=}N$ bond. For the compound (XVII), this band is weakened and shifts to 1510 cm^{-1}, so that its presence is masked in certain cases by the strong absorption of the aromatic ring at approximately 1500 cm^{-1}. Furthermore, if the anion is BPh_4^- or $SbCl_6^-$, then an intense band, which has been attributed to the stretching vibrations of the N–O bond, is seen in the range 1000–1200 cm^{-1}, usually obscured by the absorption due to the BF_4^- or ClO_4^- anions[55]. On average, the frequency of the stretching vibrations of the $\overset{+}{N}{-}N$ bond in alkoxydiazenium salts proved to be somewhat lower than the stretching vibration frequency of the N=N

bond in aliphatic azo-compounds (1574 cm^{-1} for azomethane[83]), which confirms the conclusion that there is $p-\pi$ conjugation in the $\rangle\overset{+}{N}{=}N{-}O\langle$ system.

The ^1H NMR spectra of diazenium salts have characteristic signals due to protons at the α-carbon atoms of the substituents, but the chemical shifts of the signals to the groups at the neighbouring nitrogen atoms in 1,2-di- and tri-substituted diazenium salts differ very little (0.1 to 0.3 p.p.m.). When $R^3 \neq$ OAlk, the typical range of δ values for α-methyl groups is 4.3–5.1 p.p.m.,[11,15,19,44,49,67] while the signals due to α-methylene (δ = 4.7 to 5.4 p.p.m. for ethyl groups[19,44], and δ = 5.5–6.0 p.p.m. for allyl[44] and benzyl[14] protons) and α-methylidyne protons (δ = 5.6–6.2 p.p.m.[19,44,47]) are located in a weaker field. The same dependence of the chemical shift on the type of α-protons is observed for alkoxydiazenium salts, but the corresponding signals are displaced upfield by approximately 0.5–0.8 p.p.m.[55] On the other hand, the signals of the α-protons of the alkoxy-group in these salts are in the range δ = 4.5–5.2 p.p.m., i.e. in weaker fields than the signals of α-protons in alcohols and ethers (δ = 3.2–4.1 p.p.m.)[84].

The t-butyl substituents at the nitrogen atoms in all the diazenium salts absorb in the region δ = 1.47–1.75 p.p.m.[44,47,51,55] The proton of the N–H group in disubstituted diazenium salts usually gives rise to a common signal with the solvent protons owing to rapid (on the ^1H NMR time scale) exchange. On the other hand, if the exchange can be retarded, then the absorption of the N–H proton is observed in a very weak field (δ = 12.9–16.6 p.p.m.[24,51,52]).

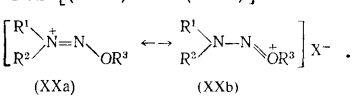
Owing to the high nitrogen–nitrogen bond order, *syn–anti* isomerism is possible for diazenium salts. The ^1H NMR spectra of salts (XIX) therefore contain two signals even for $R^1 = R^2$, corresponding to the protons at the α-carbon atoms of the groups in the *syn*- and *anti*-positions relative to the alkoxy-group[55,58]. The alkylation of nitrosamines (XVIII, $R^1 \neq R^2$), which are themselves usually a mixture of *syn*- and *anti*-isomers, yields, both isomeric alkoxydiazenium salts [(XIXa) and (XIXb)]. An exception is provided by nitrosamines with R^1 = t-Bu where only the *anti*-isomer (XIXa) is formed even for R^3 = Me[55,57]:



(XVIII) (XIXa) (XIXb)

In 1,1-disubstituted diazenium salts, *syn-anti* isomerism has not so far been observed. Under the usual conditions of the recording of the ^1H NMR spectra (HBr/H_2O, 25–30°C), there is a rapid exchange of N–H protons with the solvent and the two substituents R^1 and R^2 give rise to a common signal in the ^1H NMR spectrum. When HBr/H_2O is replaced by DBr/D_2O, the form of the spectrum changes: the lines are broadened and the fine structure of the multiplets is smeared, which can be regarded as a consequence of the slow exchange of protons at the α-carbon atoms of the substituents for deuterium.[19] However, the integral intensity of the signal due to α-protons hardly decreases and in addition it is found that the ^1H NMR spectra in HBr/H_2O assume the same form when the temperature is reduced to 0°C; here too a diffuse signal due to the N–H proton is observed in weak fields ($\delta \simeq$ 16.6 p.p.m.)[24]. Thus the changes in the spectra most probably are not due to the deuterium exchange involving α-protons, but are caused by the retardation of the exchange of the N–H proton with decrease of temperature, or following its replacement by deuterium, which leads to the non-equivalence of the *syn*- and *anti*-substituents. In DBr/D_2O at 0°C the exchange becomes so slow that the signals of the *syn*- and *anti*-substituents in the ^1H NMR spectra of 1,1-diethyl- and 1,1-di-isopropyldiazenium bromides are clearly different. However, for 1,1-dimethyldiazenium bromide, an appreciable signal separation has not been observed even under these conditions[24].

Summarising the calculated and experimental data concerning the diazenium salt structure described above, one may say that, in conformity with the canonical structure (I), the N=N bond in these compounds is virtually a double bond. Owing to the appreciable $p-\pi$ conjugation in the $\overset{+}{N}{=}N{-}O$ fragment, in alkoxydiazenium salts the order of this bond is somewhat lower, so that the structure of such salts should be described, in the language of valence bond schemes, not by one but by a superposition of at least two structures [(XXa) and (XXb)]:



(XXa) (XXb)

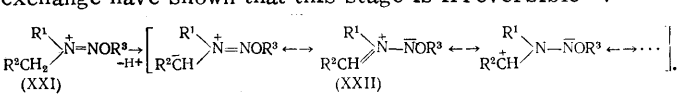
Finally the distribution of charges in diazenium cations is described quite unsatisfactorily by the canonical formula—instead of being located at the $N_{(1)}$ atom, part of the positive charge is "smeared" over neighbouring atoms, which conflicts with the formula.

IV. THE ACID PROPERTIES OF DIAZENIUM CATIONS

The presence of a positive charge in diazenium cations determines in many respects their acid properties. On the one hand, diazenium cations can be regarded as Lewis acids, which accounts for their electrophilic properties and tendency towards the formation of charge-transfer complexes. On the other hand, they can behave as H-acids (Brønsted acids) and the ability to split off a proton also plays an important role in the chemistry of diazenium salts.

The α-protons of the substituents in the $\rangle\overset{+}{N}{=}N\langle$ fragment are extremely acidic. The proton is split off particularly readily from a substituent at the second nitrogen atom. For example, in all reactions which could lead to the trimethyldiazenium cation, only formaldehyde dimethylhydrazone was obtained[17,38]; furthermore, the formation of a 1,2-disubstituted diazenium cation, which readily tautomerises, and the rapid loss of a proton by the latter from the α-carbon atom at $N_{(2)}$ were suggested by Elguero et al.[66] to account for the isomerisation of 2-pyrazolines in an acid medium [reaction (4)]. This is why, among diazenium salts having a proton at the α-carbon atom in the substituent at $N_{(2)}$, only those in which the carbon atom is of a bridge type have been obtained hitherto. The removal of a proton from it is then forbidden by the Bredt rule[47,48,50].

The abstraction of a proton by a nucleophile from an α-carbon atom at $N_{(1)}$ via scheme (5) has been proposed as the first stage in the majority of reactions of alkoxydiazenium salts (XXI),[5] and experiments on deuterium exchange have shown that this stage is irreversible[85]:

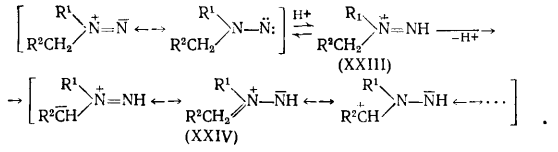


(XXI) (XXII)

(5)

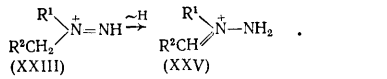
The methyl group in 1,1-dimethyl-2-(2′,4′-dinitrophenyl)-diazenium cations, which have a strong electron-accepting substituent at the second nitrogen atom, is lost very readily [46].

An analogous abstraction of a proton from the α-carbon atom with formation of dipolar azomethineimines (**XXIV**) is believed to be possible for 1,1-disubstituted diazenium cations (**XXIII**) and it is postulated [43,86] as an intermediate stage in the isomerisation of aminonitrenes to azomethine-imines:



(XXIII) (XXIV)

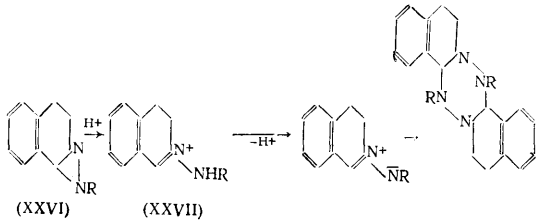
Apart from this, another similar process has also been considered, namely the transfer of an α-proton to the terminal nitrogen atom [15,17-19,24,26,27,46,87]:



(XXIII) (XXV) (6)

The virtually complete absence of the deuterium exchange of α-protons in 1,1-dialkyldiazenium cations in DBr/D_2O [24] is consistent with the results obtained for alkoxydiazenium salts [85] and permits the conclusion that the abstraction of an α-proton from the cation (**XXIII**) is irreversible and the previously postulated [15,18,19,26,27] tautomeric equilibrium (**XXIII**) ⇄ (**XXV**) does not occur in solutions of diazenium salts. The changes in the ^1H NMR spectra of 1,1-dialkyldiazenium salts on passing from HBr/H_2O to DBr/D_2O, which had been treated as a possible consequence of deuterium exchange [19], are induced by the retardation of the exchange of the N–H proton, as stated above‡.

Structures of type (**XXV**), isomeric in relation to the diazenium cations, had already been considered earlier by Schmitz [88-90], who suggested the formation of (**XXVII**) as a result of the opening of the diaziridine ring in (**XXVI**) and also on treatment of *o*-(β-chloroethyl)-benzaldehyde with hydrazine hydrate:

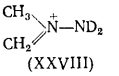


(XXVI) (XXVII)

Under the influence of bases, the cation (**XVII**) splits off a proton to give the corresponding azomethineimine and then dimerisation products, but the salts (**XXVII**) are stable and Schmitz was able to isolate the chloride (**XXVII**, R = Me) [89] and the picrate (**XXVII**, R = H). [90]

‡However, it is claimed [15] that evidence has been obtained for deuterium exchange involving 1,1-dimethyldiazenium bromide in DBr/D_2O and CF_3COOD, although experimental facts are not quoted. It is quite possible that this claim is due to a similar error in the interpretation of the results.

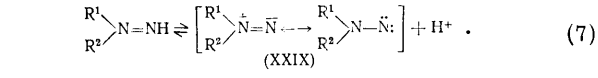
When 1,1-dimethyl-2,2-dideuterohydrazine is ionised by electron impact, more than 95% of the peaks of the $(M-H)^+$ ions are obtained as a result of the abstraction of hydrogen from the methyl group; these ions can be represented as:



(XXVIII)

Their proportion in the surface ionisation spectra is 30%, and the remaining ions of this type arise by the abstraction of deuterium from a nitrogen atom [71].

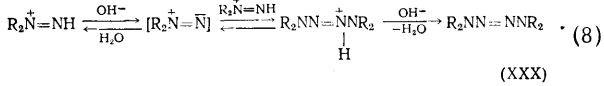
In disubstituted diazenium cations, the loss of the N–H proton is an alternative to the abstraction of protons from the α-carbon atom and the former process is probably reversible and fairly rapid. In the first study on diazenium salts [6] it was already noted that 1,1-disubstituted diazenium cations are N–H acids conjugated with respect to the corresponding aminonitrenes (**XXIX**) and the occurrence of the following acid–base equilibrium in solutions was postulated:



(XXIX) (7)

The position of equilibrium (7) is determined to a first approximation by two factors—the acidity of the medium and the basicity of the aminonitrene (**XXIX**), which depends in its turn on the substituents R^1 and R^2.

The influence of the acidity of the medium can be readily followed. Whereas acid solutions of diazenium salts (I, $R^3 = H$) are fairly stable in the cold, when they are made alkaline equilibrium (7) shifts to the right with formation of products typical for reactions involving aminonitrenes. Thus, when acid solutions of these salts are neutralised by the addition of a solution of alkali, the corresponding 2-tetrazenes (**XXX**) are formed in high yields [6-10,13,15,20,23,27,28,91], their formation being regarded as a result of the reaction of intermediate aminonitrenes with the surrounding diazenium cations [2,7]:



(XXX) (8)

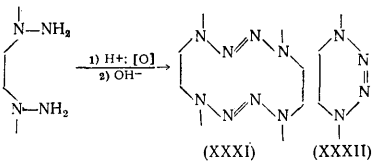
Reaction (8) has been patented as a method for the synthesis of 2-tetrazenes [9], which had been believed hitherto to be its sole products.

However, when the opposite method of neutralisation is used, involving the addition of a solution of the salt (I, $R^3 = H$) to a solution of alkali, and at a low salt concentration, the yield of the tetrazene is low [7,20], since in this version the aminonitrenes formed virtually lack an environment made up of electrophilic diazenium cations. At the same time, these conditions favour intramolecular transformations of aminonitrenes, as a result of which it is possible to detect virtually the entire set of products typical for reactions involving aminonitrenes: mono- and disubstituted hydrazones, tetrazenes, and geminal azohydrazines [20]. This result constitutes important evidence confirming the formation of aminonitrenes when 1,1-disubstituted diazenium salts are treated with bases and suggests that the neutralisation reactions of acid solutions of these salts can serve as a convenient source of aminonitrenes under extremely mild conditions [20].

The neutralisation of solutions of two different diazenium salts (I, $R^3 = H$), prepared separately and then mixed, leads to a mixture of all three tetrazenes (symmetrical and asymmetrical) in the statistically expected proportions [6-8,27]. The joint neutralisation of a large number of

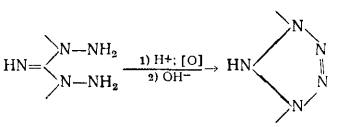
salts leads to a corresponding increase of the number of tetrazenes, and their number is also similar to that expected on statistical grounds [7].

When an attempt was made to synthesise tetrahydrotetrazine (**XXXII**) by the intramolecular closure of the tetrazene chain, only the twelve-membered bistetrazene (**XXXI**) was isolated [91]:



(XXXI) (XXXII)

although, according to McBride's report, the tetrazene fragment was incorporated in the five-membered ring under completely analogous conditions [6]:



The formation of tetrazenes in concentrated solutions of 1,1-dialkyldiazenium salts begins already at pH 0.5–1,[7] so that tetrazenes or the products of other reactions of aminonitrenes, but not diazenium salts, are formed immediately in the oxidation of the corresponding hydrazines in a weakly acid medium.

On passing from 1,1-dialkyl to 1,1-diaryl-diazenium salts, the basicity of the corresponding aminonitrenes should decrease and equilibrium (7) should shift to the right. It may be that, precisely because of this, 1,1-diphenyldiazenium perchlorate is significantly less stable than 1-methyl-1-phenyldiazenium perchlorate [37], since the former should be converted more rapidly into a tetrazene, which readily decomposes further in an acid medium.

The N–H proton of 1,1-disubstituted diazenium cations is also very mobile. Under the influence of nucleophiles, it is readily split off with the regeneration of the initial azo-compound and in the cation it is involved in a rapid exchange between neighbouring nitrogen atoms [51,52].

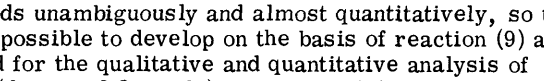
By comparing the tendencies towards the elimination of N–H and α-C–H protons from disubstituted diazenium cations, one may reach the purely qualitative conclusion that in the majority of cases the N–H proton is more acid and mobile. However, virtually no one has made a quantitative comparison of the acidities of these hydrogen atoms and, as shown above, in certain cases one must assume that, even in the presence of the N–H group, a proton may be abstracted preferentially from α-carbon atoms.

V. REACTIONS OF DIAZENIUM SALTS

1. Decomposition Reactions

Information about the decomposition pathways of diazenium salts is fairly contradictory and confused§, probably owing to the large number of secondary reactions in which the primary decomposition products can be involved. It is therefore not surprising that sometimes it is merely concluded that the decomposition of the salts takes place and no attempt is made to establish the structure of the products, let alone the decomposition mechanism [6,13,46].

On the basis of literature data, one can conclude that the first stage in the decomposition of diazenium salts is usually the abstraction of a proton by a nucleophile from the α-carbon atom in the substituent at $N_{(1)}$, already considered, or the transfer of this proton to $N_{(2)}$. The subsequent attack by the nucleophile leads to the dissociation of the highly polarised carbon–nitrogen bond and the decomposition of the diazenium cation. The hydrolysis of 1,1-disubstituted diazenium cations [reaction (9)] apparently proceeds in this way [17,18,26,27], its last stage being analogous to the ready hydrolysis of immonium cations [75,92]:



(XXIII) (XXV) (9)

In the cold reaction (9) is virtually negligible but, with increase of temperature, its rate increases rapidly and on boiling hydrolysis terminates in several minutes. 1,1-Diisopropyldiazenium bromide hydrolyses with greater difficulty than salts having primary substituents; if R^1 in (**XXIII**) is a primary group and $R^1 \neq R^2CH_2$, then hydrolysis takes place via both possible pathways, but if R^1 is a secondary group, then R^2CHO and R^1NHNH_2 are formed exclusively [18,26]. In dilute solutions the decomposition proceeds unambiguously and almost quantitatively, so that it was possible to develop on the basis of reaction (9) a method for the qualitative and quantitative analysis of small (down to 0.2 μmole) amounts of 1,1-dialkylhydrazines by determining the carbonyl compounds formed [26].

The hydrolysis products—monoalkylhydrazines and (usually) an aldehyde—can react subsequently with one another, which may be the cause of the appearance of the corresponding monoalkylhydrazones in certain reactions involving 1,1-dialkyldiazenium cations [27,38]. Incidentally, there are no grounds for ruling out other possible pathways leading to the formation of hydrazones, for example, the conversion of the cation (**XXIII**) into the azomethineimine (**XXIV**) with the rearrangement of the latter into a hydrazone, i.e. the reaction can be regarded tentatively as the concluding stage of the so-called "diazene–hydrazone" rearrangement of aminonitrenes [2,86], or the true diazene–hydrazone rearrangement of aminonitrenes, which are involved in equilibrium (7) with 1,1-disubstituted diazenium cations. Then the formation of a monoalkylhydrazone must be regarded as the primary reaction and the monoalkylhydrazine and the aldehyde must be regarded as secondary products of the hydrolysis of the monoalkylhydrazone. If in addition account is taken of the fact that the protonation of the aminonitrene to give a diazenium cation is postulated as one of the intermediate stages in the diazene–hydrazone rearrangement [2] and that there is as yet no satisfactory mechanism for the rearrangement itself [2,5,93], then evidently it would be premature to reach final conclusions about the mechanism of the hydrolysis of 1,1-dialkyldiazenium cations.

When 2,4-dinitrophenylhydrazine (2,4-DNPH) is added to solutions of 1,1-dialkyldiazenium salts, a precipitate of the 2,4-dinitrophenylhydrazone is formed even in the cold, albeit fairly slowly [18,24]:



(10)

§ For example, according to one set of data [6], the decomposition of 1,1-dialkyldiazenium salts in acid solutions is a first-order reaction with respect to the diazenium salt, while in a later study [15] it is mentioned casually that the decomposition of 1,1-dimethyldiazenium bromide in HBr obeys the equation for a second-order reaction with respect to the diazenium salt.

When $R^1 \neq R^2CH_2$, reaction (10) resembles the hydrolytic reaction (9), but the interaction of 1,1-di-isopropyldiazenium bromide with 2,4-DNPH in the cold does not give a precipitate at all[18,24]. One can also postulate at least two mechanisms for the interaction with 2,4-DNPH: preliminary hydrolysis or the direct reaction of 2,4-DNPH with the species (XXV) isomeric with the diazenium cation; a more definite choice cannot as yet be made[24].

The decomposition reactions of alkoxydiazenium[55] and in certain cases trisubstituted diazenium salts[46] in the presence of water are apparently similar to the hydrolysis of 1,1-dialkyldiazenium salts. The preliminary elimination of an α-proton is indicated, for example, by the fact that, with increase of its acidity, the stability of alkoxydiazenium salts diminishes[55]. A mechanism in many respects analogous to reaction (9) has been proposed by Norman et al.[87] for the formation of benzylhydrazine and benzaldehyde in the oxidation of 1,1-dibenzylhydrazine with lead tetra-acetate, which involves the isomerisation of the diazenium cation to a species of type (XXV) and its acetolysis.

Another decomposition pathway, which is usual for 1,1-disubstituted diazenium salts, is the formation of tetrazenes and their subsequent decomposition. This yields primary and secondary amines, aldehydes, and nitrogen[94]. This process plays a notable role in weakly acid or highly concentrated solutions and also for very acidic diazenium cations[6,7,37]. It has also been observed that, after stirring a solution of 1,1-di-isopropyldiazenium bromide at 0°C for 4 h, neutralisation leads to the formation of 60% of di-isopropylamine and only 23% of 1,1,4,4-tetrapropyl-2-tetrazene.[13] The cause and mechanism of such extensive decomposition are obscure.

The decomposition of diazenium cations can result from attack on them by halide ions. Thus it is claimed[17] that 1,1-dialkyldiazenium cations react with Cl^- or Br^- anions in concentrated HCl or HBr with formation of alkyl halides and ultimately of a di-imide which rapidly decomposes under these conditions, reducing some of the reactants:

$$Me_2\overset{+}{N}{=}NH\ \overset{-HX}{\longrightarrow}\ MeX + \underset{X^-}{\overset{+}{Me}NH} \rightarrow MeX + HN{=}NH \quad . \qquad (11)$$

The reaction is rapid on boiling but, if a solution of 1,1-dimethyldiazenium bromide in HCl is allowed to stand at room temperature, CH_3Cl, CH_3Br, and N_2 are liberated. However, one should note that the total volume of the evolved gases does not exceed 10% of the amount calculated by Eqn.(11) and that the role of such processes is apparently small.

Whereas attack on alkoxydiazenium salts by strong nucleophiles usually begins with the abstraction of a proton from the α-carbon atom of the substituent at $N_{(1)}$, weak nucleophiles remove the substituent at the oxygen atom. Thus the salts (XIX) are readily dealkylated by sulphides to give the initial nitrosamines[58]:

$$\underset{X^-}{\overset{R^1}{\underset{R^2}{\overset{+}{N}{=}NOR^3}}}\ \xrightarrow{R^4_2S}\ \overset{R^1}{\underset{R^2}{\rangle}}N{-}NO + R^3\overset{+}{S}R^4_2\,X^-$$

(XIX)

while dealkylation by iodide ions proceeds as follows[55,82]:

$$(XIX)\ \xrightarrow{I^-}\ \overset{R^1}{\underset{R^2}{\rangle}}N{-}NO + R^3I - X^- \quad . \qquad (12)$$

Reaction (12) is almost instantaneous at room temperature.

Other diazenium salts are also unstable in the presence of iodide ions, because the latter can reduce diazenium cations[15,50]. Furthermore, diazenium cations can be reduced by the primary products of their decomposition or other reactions (examples will be examined below), which also leads to their disappearance.

2. The Reduction of Diazenium Salts

1,1-Disubstituted diazenium salts can be reduced to the initial hydrazinium salts both chemically (with $SnCl_2$[6,28] or HI[15]) and electrochemically[31-33,37,38] with nearly quantitative yields:

$$\underset{X^-}{\overset{R^1}{\underset{R^2}{\overset{+}{N}{=}NH}}}\ \xrightarrow[+2H^+]{+2e^-}\ \overset{R^1}{\underset{R^2}{\rangle}}N{-}NH_2{\cdot}HX \quad . \qquad (13)$$

The electrochemical reduction of trisubstituted diazenium salts takes place similarly, yielding trisubstituted hydrazines[37,45,46], but the hydrogenation of alkoxydiazenium salts gives rise to disubstituted hydrazines[53,54]. For example:

$$\underset{BF_4^-}{\overset{+}{N}{=}NOEt}\ \xrightarrow[MeOH]{H_2/Pt}\ N{-}NH_2{\cdot}HBF_4 + EtOH \quad . \qquad 97\%$$

In an aprotic medium the electrochemical reduction of trisubstituted diazenium salts is a one-electron process[44,45,48,82,85] and stops at the stage involving the formation of hydrazyl radicals (XXXIII):

$$\underset{R^2}{\overset{R^1}{\rangle}}\overset{+}{N}{=}N{-}R^3\ \xrightarrow{+e^-}\ \underset{R^2}{\overset{R^1}{\rangle}}N{-}\dot{N}{-}R^3$$

(XXXIII) .

Furthermore, reversible one-electron reduction can be observed also in highly alkaline aqueous solutions but, with decrease of pH, the protonation of the radical (XXXIII) is accelerated and the resulting radical-action is readily reduced to hydrazine—the overall process requires a two-electron mechanism[44].

According to polarographic data, typical half-wave potentials $E_{1/2}$ for the one-electron reduction of alkyldiazenium salts are in the range between −0.5 and −0.8 V,[44,48] the values for salts with phenyl substituents are in the vicinity of 0 V,[31,37,45] and the introduction of the 2,4-dinitrophenyl group into the diazenium cation shifts the half-wave potential to 0.2 V.[46,50] $E_{1/2}$ for 1-aryl-2-methoxy-1-methyldiazenium salts (XVII) varies from −0.35 to −0.04 V, and it has been shown that the dependence of $E_{1/2}$ on the substituent in the aromatic ring is described satisfactorily by the Hammett equation[82]. In one-electron reduction $E_{1/2}$ can be regarded as a quantity characterising the energy of the lowest unoccupied orbital (LUMO) of the diazenium cation to which an electron is in fact transferred. When electron-accepting substituents as well as substituents capable of conjugation, for example, aryl groups, are introduced into the ion, the above energy level is lowered and reduction is correspondingly facilitated; electron-donating substituents have the opposite effect. It is therefore not surprising that the changes in $E_{1/2}$ for the salts (XVII) are also satisfactorily correlated with the LUMO energy differences calculated by the Hückel method[82].

Reduction is a side reaction in many reactions of diazenium salts, other components of the reaction mixture behaving as reductants. For example, it has been found that 1,1-dimethyldiazenium bromide is reduced to the initial hydrazine by acetaldehyde[11]. The primary products of the reaction of 1,1-diphenyl-[33,34] and 1-methyl-1-phenyldiazenium perchlorates[34] with *trans*-stilbene are tetra

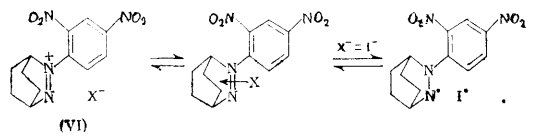
hydrocinnolines; the triazolidines obtained in the reaction with alkoxydiazenium salts with Schiff bases[53,96-98] reduce diazenium salts under the reaction conditions, i.e. diazenium salts can behave as oxidants.

Finally, diazenium cations can be reduced by the counterions, possibly via the formation of donor–acceptor complexes, which we shall now consider.

3. Donor–Acceptor Interactions in Solutions of Diazenium Salts

Depending on the structure of the substituents and the nature of the counter-ion, the group $\overset{+}{N}{=}N$ can behave partially or even completely as an electron acceptor. It has already been stated that, according to ultraviolet spectroscopic data, diazenium cations exist only in solutions of diazenium salts in combination with anions which are poor electron donors in polar solvents. On the other hand, in other cases the diazenium cations form ion pairs and donor–acceptor complexes with the counterions[7,50]. The stability of the complexes and the degree of charge transfer increase with enhancement of the electron-donating properties of the anion, for example, in the sequence $Cl^- < Br^- < I^-$, after the introduction of electron-accepting substituents into the cation, i.e. when the difference between energies of the LUMO of the acceptor (diazenium cation) and the highest occupied orbital (HOMO) of the donor (the counterion) is reduced, and after a decrease of the polarity of the solvent. In the limiting case the electron is fully transferred—one-electron reduction of the diazenium cation takes place and a radical pair is formed.

It has been established[50] that the ultraviolet spectrum of the perchlorate (VI, $X^- = ClO_4^-$) changes little in solvents of different polarities; an intense long-wavelength charge-transfer band appears in the spectrum of the bromide on passing from an aqueous solution to one in acetonitrile and methylene chloride, while the iodide, which is still a salt in water, gives rise to green paramagnetic solutions in non-polar solvents—the ion pair is converted into a radical pair:

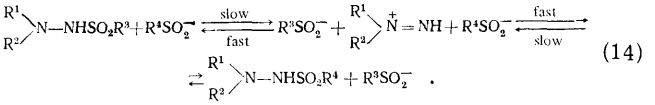


(VI)

On the other hand the replacement of the 2,4-dinitrophenol group in (VI, $X^- = I^-$) by the t-butyl group weakens the electron-accepting properties of the cation and complete electron transfer does not take place even in solvents of low polarity[50].

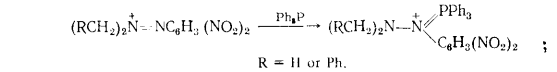
Another example is the interaction of a number of alkoxydiazenium salts (XVII) with NaI.[82] At room temperature rapid dealkylation takes place in accordance with reaction (12), but at −46°C in acetonitrile it is possible to detect the formation of donor–acceptor complexes of alkoxydiazenium cations with I^- ions. Since the HOMO energy of the donor (the iodide ion) is constant in the entire series of complexes, the energy of the charge-transfer band in the ultraviolet spectra changes in parallel with the calculated LUMO energy of the corresponding diazenium cations, and their $E_{1/2}$, as expected[82].

Apparently the same rules hold for exchange processes involving the 1,1-di-alkylhydrazides of sulphonic acids, which have been investigated in detail by Lemal[2,43], who observed that the sulphonic acid residue in hydrazides can be exchanged [reaction (14)] in polar solvents in the presence of sulphinate salts. It has been shown by ^1H NMR that, when solutions of the hydrazide and a sulphinate salt are mixed, the initial rate of exchange is independent of the concentration of the metal sulphinate, which led to the conclusion that the rate-determining stage is the dissociation of the hydrazide into a diazenium cation and a sulphinate anion, i.e. that an S_N1 mechanism operates[43]:



(14)

As a result of exchange with bisulphites, sulphonic acid, 1,1-dialkylhydrazides form little-dissociated sulphuric acid hydrazides, but there is no sign of interaction with effective nucleophiles such as the N_3^-, OCN^-, SCN^-, and $S_2O_3^{2-}$ ions[2,43]. The hypothesis was put forward that the selectivity of the diazenium cations and the stability of the hydrazides obtained are due to the ease of the interaction of the lone electron pair of the $N_{(2)}$ atom with the vacant *d* orbital of sulphur, as a result of which the multiplicity of the N–S bond in hydrazides should be increased. The fact that phosphines, where the phosphorus atom also has vacant *d* orbitals with a suitable energy and could therefore form a partial double bond with a nitrogen atom, give rise to adducts with 1,1-disubstituted[2,43] and trisubstituted[46] diazenium cations was explained from the same standpoints. For example:



However, in the light of what was said at the beginning of this section, it appears more correct to treat all the instances discussed here as the usual donor–acceptor interaction. Evidently diazenium cations form stable complexes with reducing ions which have a high HOMO and readily give up an electron, reducing the diazenium ion to a hydrazyl residue; on the other hand, the nucleophilic properties of the anion do not in fact play an appreciable role in this instance. Adducts with phosphines are also formed as a result of electron transfer from phosphorus to nitrogen and not conversely; according to the results of Lemal himself, the hydrolysis of these adducts yields the corresponding hydrazines and phosphine oxide[2,43]. The decrease of the tendency of sulphonic acid hydrazides towards dissociation on passing from 1,1-dialkylhydrazides to aryl-substituted compounds and its increase when more electronegative groups are introduced into the sulphonic acid residue[43] is also consistent with the general characteristics of donor–acceptor interactions.

Finally, one may note that, according to some data[34,45] the triphenyldiazenium cation forms a stable complex with pyridine—a compound in which there are no low-lying vacant orbitals capable of interacting effectively with the lone electron pair of $N_{(2)}$ in the diazenium cation. We believe that the existence of the complex, which is fully analogous to the adducts of diazenium cations with phosphines, is ensured by the interaction of the LUMO of the triphenyldiazenium cation with the lone electron pair of the nitrogen atom in pyridine. This is also supported by

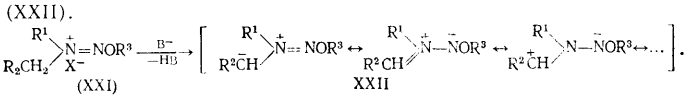
the absence of complex formation with 2,6-lutidine, where the nitrogen atom is sterically shielded[34,45].

It may be that the reduction of 1,1-dimethyldiazenium cations in the KI/HCl system proceeds via a stage involving the formation of donor–acceptor complexes with iodide ions[15] and that in an acid medium two-electron reduction to a hydrazinium salt takes place.

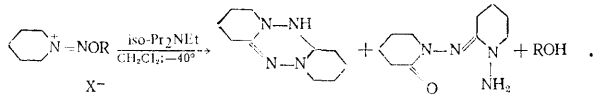
4. Reactions of Diazenium Salts Via 1,3-Dipolar Species

It was already noted above (Section IV) that treatment of diazenium salts with bases can lead to the irreversible abstraction of an α-proton from the substituents at the first nitrogen atom and the formation of 1,3-dipolar species (azomethineimines). Reactions beginning at this stage have been observed for various types of diazenium salts; they are most characteristic of alkoxydiazenium salts (XXI) whose properties are in many respects determined by the subsequent reactions of the corresponding 1,3-dipoles (XXII):

(XXII).

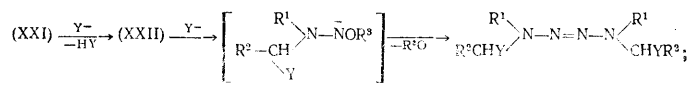


When azomethineimines are generated by weakly nucleophilic bases, dimeric products are obtained, in particular derivatives of 1,2,4,5-tetrazine[5].



For reactions in which the involvement of azomethineimines is postulated, the formation of a fully or partly saturated (most probably as a result of oxidation) tetrazine ring is extremely typical[2,5,99,100]. It was believed previously that perhydrotetrazines are produced by the concerted "head to tail" dimerisation of the azomethineimines themselves, but, firstly, the interaction of two such unstable intermediate species is unlikely for statistical reasons, and, secondly, it has been noted recently[100] that the concerted process is in this instance forbidden. It is therefore most probable that the dimers are the products of the interaction of azomethineimines with the initial compounds.

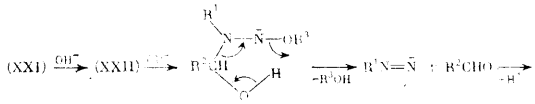
The more nucleophilic bases themselves react with the zwitterions formed initially. Thus treatment of alkoxydiazenium salts in alcoholic solution with alkoxide or azide ions leads to α-substituted tetrazenes[5,101]:

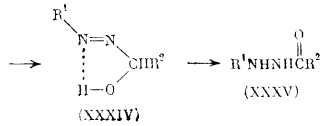


Y = OAlk or N_3.

The mechanism of the last stage is still obscure, but it may be that the reaction proceeds via the corresponding aminonitrene or the 1,1-disubstituted diazenium cation[101].

The products of the interaction of alkoxydiazenium salts and OH^- ions are extremely unexpected[53,57,85,102-104]. Only salts with aliphatic groups undergo this reaction and in the case of acyclic compounds[57,85,103] it leads to *trans*-azoalcohols (XXXIV), for the formation of which the following mechanism has been proposed:



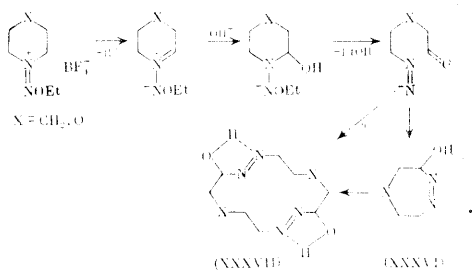


(15)

The intermolecular mechanism of reaction (15) has been demonstrated by kinetic data, by the formation of cross-products following the addition to the reaction mixture of both an extraneous monosubstituted diazene and an aldehyde, and also by the independent synthesis of a number of azoalcohols from aldehydes and monosubstituted diazenes[84,103]. It is remarkable that the decomposition into a diazene and an aldehyde strongly resembles the hydrolysis of 1,1-dialkyldiazenium cations examined above, and it can be treated (at least formally) as the hydrolysis of an alkoxydiazenium cation to an aldehyde and an alkoxyhydrazine $R^1NHNHOR^3$ accompanied by the elimination of R^3OH. It is noteworthy that, although 1,1-di-isopropyl-substituted alkoxydiazenium salts are decomposed by aqueous alkali, azoalcohols are not formed in this process[57¶].

Azoalcohols (XXXIV) readily isomerise and only the hydrazide (XXXV) can sometimes be isolated as a result of reaction (15).[84]

All the azoalcohols obtained in this way had the *trans*-configuration, which was additionally stabilised by an intramolecular hydrogen bond. Treatment of the alkoxydiazenium salts obtained from *N*-nitrosopyrrolidines and *N*-nitroso-4,4-dimethylpiperidine with bases should lead (and apparently does so) to cyclic *cis*-azoalcohols, but the latter decompose when an attempt is made to isolate them[103,104]. On the other hand, when derivatives of piperidine itself and morpholine were introduced into reaction (15), the products were not the seven-membered *cis*-azoalcohols (XXXVI), as had been suggested earlier[53], but their dimers—14-membered rings (XXXVII) containing only the $\backslash N{=}N/$ *trans*-bonds[102,104]:

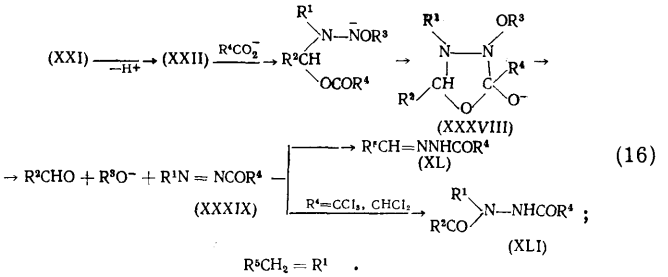


The ultraviolet spectra recorded in the course of the reaction show that the first stage involves the formation of the *cis*-azoalcohol (XXXVI), which is then rapidly converted into compound (XXXVII).[102-104]

The interaction of alkoxydiazenium salts with carboxylate ions gives high yields of acyldiazenes (XXXIX).[106-108] The proposed reaction mechanism involves the formation

¶ The attempts by Hünig to obtain an azoalcohol with a quaternary alcoholic carbon atom from acetone and t-BuN=NH were also unsuccessful[35]. However, it has been recently reported that this reaction has been successfully carried out in the synthesis of MeEtC(OH)N=NPh.[105]

of a five-membered cyclic intermediate complex (XXXVIII) and its decomposition[5,108]:

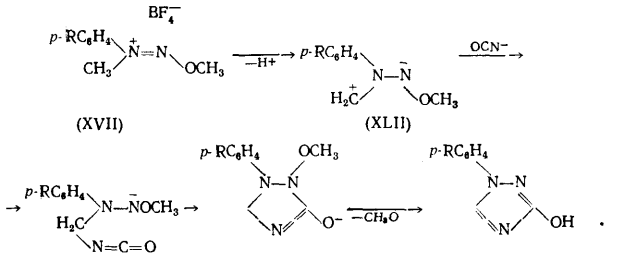


(16)

Reaction (16) depends little on the solvent and on the nature of the substituents R^1, but acyldiazenes can be isolated only when there are no hydrogen atoms at the α-carbon atom in R^1. Otherwise, (XXXIX) immediately isomerises to the acylhydrazone (XL).[107,108] If the primary group R^2CH_2 in (XXI) is replaced by the isopropyl group, the yield of the corresponding acyldiazene falls almost by a factor of two. The anions of both aromatic and aliphatic carboxylic acids readily undergo reaction (16), but for the acetate ion the yield is somewhat lower. According to Hünig the reaction of di- and tri-chloroacetate ions yields initially acyldiazenes, which are apparently capable of recombining with the aldehyde to form the hydrazides (XLI).[108] The interaction of (XXI) with formate ions proceeds quite differently and will be discussed below.

Aryl- and alkyl-acyldiazenes (XXXIX) obtained in this way can serve as a source of monosubstituted diazenes[108,109] and as effective acylating agents. It is therefore significant that reaction (16) takes place to an extent of 80–90% with the anions of *N*-protected aminoacids and can therefore be used to activate them in the synthesis of peptides[108].

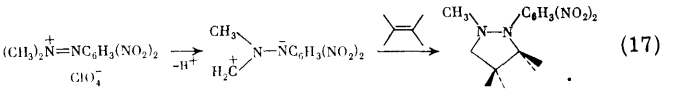
The reaction of 1-aryl-2-methoxy-1-methyldiazenium salts (XVII) with cyanate ions proceeds very similarly to reaction (16).[108] It results in a 40–70% yield of 1-aryl-3-hydroxy-1,2,4-triazoles:



The anomalous behaviour of alkoxydiazenium salts with isopropyl groups in the above reactions is noteworthy. Similar phenomena are observed in the hydrolysis and hydrazinolysis of 1,1-dialkyldiazenium salts—it is also found that salts with secondary groups react much less effectively. The common stage in both cases is usually the initial abstraction of an α-proton, so that one can postulate that the process involving secondary groups is hindered compared with the process involving primary groups. It is still not clear what causes this.

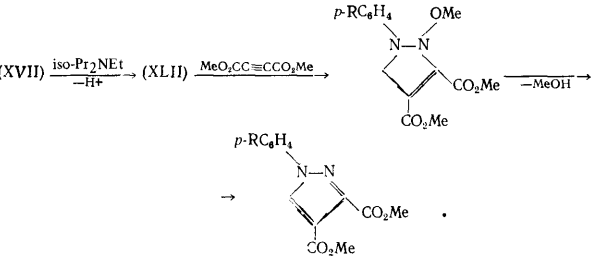
A common property of the azomethineimines obtained from diazenium salts, like that of other 1,3-dipoles, is their ability to undergo 1,3-dipolar addition to multiple bonds, with formation of five-membered heterocycles[99].

The interaction of 1,1-dimethyl-2-(2′,4′-dinitro)phenyldiazenium perchlorate with olefins is of this type[46]:



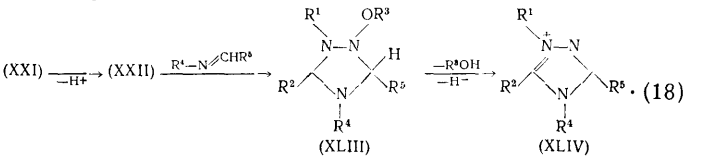
(17)

This is also true of the reactions of alkoxydiazenium salts (XVII) with dimethyl acetylenedicarboxylate[108]:



Reaction (17), involving *cis*- and *trans*-but-2-enes, proceeds with retention of configuration, which supports the operation of a concerted mechanism.

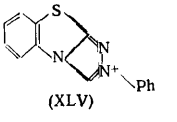
The 1,3-dipolar addition in the interaction of alkoxydiazenium salts with a C=N bond[56,96-98], the final products of which are *s*-triazolium salts (XLIV), has been studied on the greatest scale:



(18)

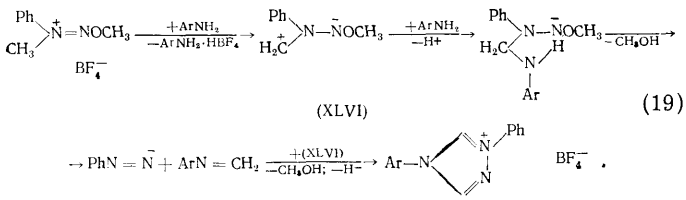
It is believed that a hydride ion is abstracted by the second cation of the diazenium salt in the transition (XLIII) → (XLIV),[56,98] but the yields relative to the initial diazenium salt frequently exceed 50%, so that it is assumed that the cation of the salt (XXI) can combine with more than one hydride ion.

Reaction (18) proceeds best in CH_2Cl_2 at 0–20°C; a proton is abstracted from (XXI) by the imine component itself, for which various nitrogen-containing heterocycles[56,96,97], Schiff bases[96-98], azines and hydrazones[98] have been used. It has been established that any alkoxydiazenium salts (XXI, R^1 = Alk, or Ar, R^2 = Alk) can react with Schiff bases and heterocycles, but only the more reactive 1-aryl-substituted salts (XXI, R^1 = Ar) react with azines and hydrazones[56,98]. Among six-membered heterocycles, pyridine, quinoline, isoquinoline, and phenanthridine have been used; isoquinoline is the most reactive. Five-membered heterocycles (benzoxazole, indole, imidazole, etc.) could not be made to undergo this reaction with one exception: the adduct (XLV) has been obtained in 27% yield from benzothiazole[56]:



Schiff bases can be obtained directly in the reaction mixture from the amine and the aldehyde and the yield does not diminish under these conditions. It has been found possible to obtain *s*-triazolium salt (XLIV) when only the amine was introduced into the reaction. The second component (the aldehyde) is obtained from the

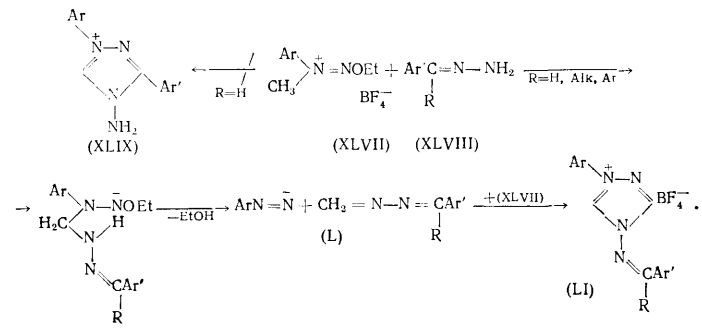
alkoxydiazenium salt by a reaction analogous to reaction (16). For example[56]:



(19)

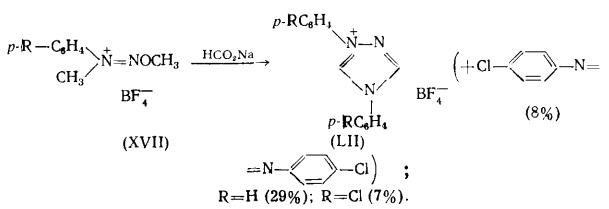
Only one C=N bond of the azines of aromatic aldehydes is involves in reaction (18).[98] The positive charge on the resulting triazolium ring (XLIV) apparently deactivates the remaining imino-group under these conditions. The presence of electron-donating substituents in the azine facilitates the interaction; on the other hand, the azines of nitrobenzaldehydes are inert in relation to alkoxydiazenium salts. Purely aliphatic azines and the azines of aromatic ketones also could not be made to undergo this reaction[98].

It was thought possible to synthesise *N*-aminotriazolium salts (XLIX) from unsubstituted hydrazones (XLVIII). However, contrary to expectation, the mixed azine (L) is formed initially by a process fully analogous to reaction (19) and only then the triazolium salt (LI) can be obtained only from the azine[98]:



The hydrazones of aliphatic carbonyl compounds do not undergo this reaction. Nor was it possible to isolate the products of the interaction of alkoxydiazenium salts with oximes and amidines[98], CS_2, and Ph–N=C=S.[108] It may be that the absence of cycloaddition products in the reactions of certain types of compounds can be accounted for by their low basicity and inability to abstract a proton from the salt (XXI) and to generate the dipole (XXII), rather than their inertness to dipolarophiles. One cannot therefore rule out the possibility that, when a non-nucleophilic base (for example iso-Pr_2NEt) is introduced into the reaction mixture, it is still possible to isolate the corresponding adducts.

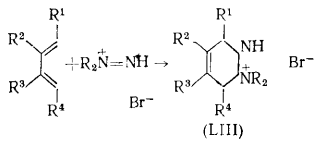
Finally, yet another example of a reaction apparently proceeding via a 1,3-dipolar cycloaddition stage is the interaction of alkoxydiazenium salts (XVII) with formate ions in which it was possible to isolate only small amounts of triazolium salts (LII) containing two aryl residues, instead of the expected formyldiazenes (XXXIX, R^4=H)[56]:



If R = Cl in the salt (XVII), 4,4′-dichloroazobenzene is obtained in addition. The mechanism of this reaction is obscure; it has only been established that, when sodium formate labelled with ^{14}C is used, the triazolium ring does not contain the label[56].

5. Diazenium Cations as Dienophiles

1,1-Dialkyldiazenium cations proved to be very active dienophiles, capable of undergoing the Diels–Alder reaction with many dienes in the cold. This gave satisfactory yields of Δ_4-tetrahydropyridazinium salts (LIII):



(20)

Reaction (20) was discovered by Urry and coworkers[10,11], and was then investigated in detail by other workers[12–14,110] for various dienes and diazenium salts. The yield of (LIII) exceeds 70% in almost all cases and even cyclohexa-1,3-diene, whose reactivity is reduced owing to the incomplete coplanarity of the double bonds in the six-membered ring and which therefore reacts only with very active azodienophiles, gives an adduct with 1,1-dimethyldiazenium bromide in 80% yield. However, reaction (20) does not take place at all with the still less reactive *trans*, *trans*-1,4-diphenylbuta-1,3-diene.[13] The structural specificity of the reaction is usual for diene synthesis: the *ortho*-isomers of the adducts (LIII) are obtained from 1-substituted dienes (piperylene), while the *para*-isomers are obtained from the 2-substituted dienes (isoprene, chloroprene).[10,12–14]

The branching of the alkyl groups in the diazenium cation is apparently important, because 1,1-di-isopropyldiazenium bromide could not be introduced into the synthesis, evidently owing to steric hindrance[13]. The 1,1-dibenzyldiazenium cation reacts in the usual way, but the reaction pathway for aryldiazenium cations changes: instead of diene synthesis, addition to one of the double bonds of the diene, which will be discussed below, takes place instead of diene synthesis[14]. The change in the nature of the interaction is evidently due to the conjugation of the N=N bond with the aryl substituents[14], but it is at present not clear which specific consequences of conjugation are of decisive importance under these conditions.

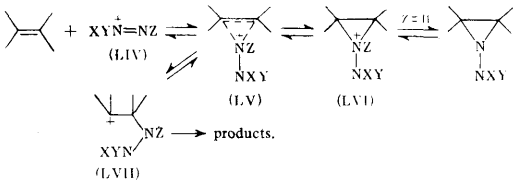
It is known that the diene usually behaves as the donor in the Fiels–Alder reaction, while the dienophile behaves as the electron acceptor. The high reactivity of diazenium cations as well as their analogues—immonium [111] and even diazonium [112] cations—in the Diels–Alder reaction is therefore not surprising.

On another occasion a small amount (12%) of tiglaldehyde dimethylhydrazone was isolated when 1,1-dimethyldiazenium bromide was allowed to react with isoprene [10], but since then nobody has observed the formation of such hydrazones simultaneously with reaction (20).

6. Reactions with Olefins

Formally, the interaction of diazenium salts with olefins can be regarded as the usual reaction of an electrophile (diazenium cation) with a multiple bond. It is therefore not surprising that mechanism (21), proposed to

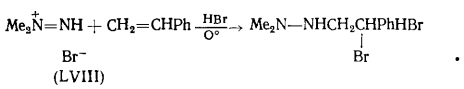
account for such interaction [33,34], is merely a special case of the general mechanism of the addition of electrophiles to unsaturated systems [113] (see also Dolbier [114]):



(21)

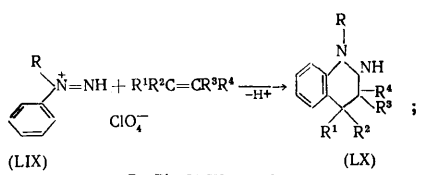
According to mechanism (21), the reaction begins with the attack by the diazenium cation (LIV) on the olefin and the formation of the π-complex (LV), which is in equilibrium with the azidirinium cation (LVI) (in actual fact a σ-complex) and with the carbonium ion (LVII). The positions of all these equilibria and hence the products of reaction (21) are in many respects determined by the structures of the diazenium salts and the olefin [33,34].

In conjugated olefins the substituents are capable of effectively stabilising the positive charge and the equilibrium position shifts in the direction of the ion (LVII). Urry et al. showed [11] that 1,1-dimethyldiazenium bromide (LVIII) reacts with styrene, indene, and 2-phenylpropene to form products, which can be regarded, on the basis of Eqn. (21), as a result of the addition of a bromide ion or water to an intermediate cation of type (LVII). For example:



It has been shown that this reaction is reversible and that the degree of conversion of the olefin and the equilibrium position depend strongly on the solubility of the product and the structure of the olefin. Thus 1-phenylpropene and *trans*-stilbene do not react with compound (LVIII) at all [11].

1,1-Diphenyl-, 1-methyl-1-phenyl-, and 1-benzyl-1-phenyl-diazenium perchlorates react quite differently with these olefins in acetonitrile [14,32-36], forming tetrahydrocinnolines (LX):

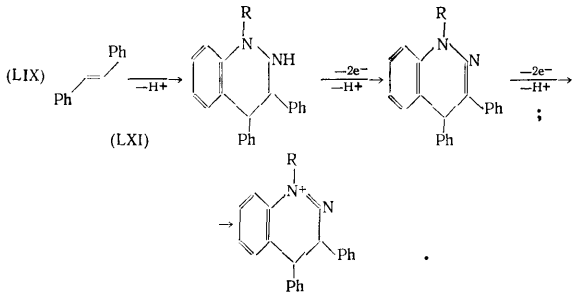


R=Ph, $PhCH_2$, or Me.

(22)

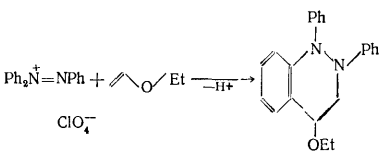
The yields are nearly quantitative when R = Ph and are somewhat lower than R = $PhCH_2$ or Me. Furthermore, the reaction is much slower in the latter case, probably owing to the weaker electrophilic properties of such diazenium cations.

Styrene, indene, 1,1-diphenylethylene, acenaphthalyne, 2-phenylnorbor-2-ene, and tetracyclone (tetraphenylcyclopentadienone) have been introduced into reaction (22). *cis*-Stilbene is inert under these conditions, which is believed [33,34] to be due to steric hindrance, and, although *trans*-stilbene does react, the resulting tetrahydrocinnolines (LXI) are oxidised by diazenium cations to cinnolinium salts:

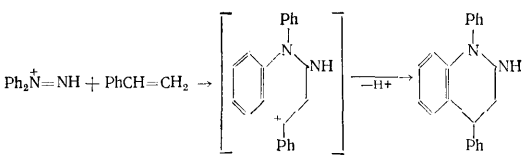


Tetrahydrocinnoline (LXI) was isolated only for R = Me (33%). [34]

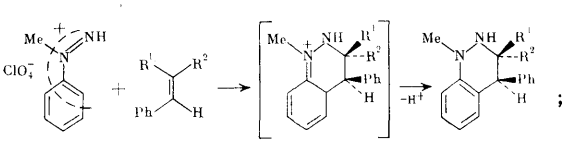
Triphenyldiazenium perchlorate is less reactive than compound (LIX) and does not react with the above olefins; however, its reaction with the more reactive vinyl ether gives the corresponding tetrahydrocinnoline in 95% yield [34,45]:



The formation of tetrahydrocinnolines has been considered, on the basis of mechanism (20), as a result of intramolecular coupling in the intermediate carbonium ion (LVII). [33,34] For example:

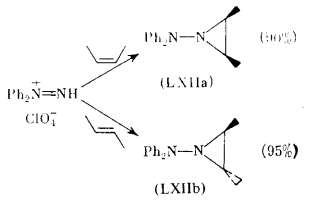


However, according to Zelenin [35], reaction (22) takes place differently and is a concerted [4 + 2] cycloaddition process with the reactants having inverse electronic properties (the so-called "reversed" diene synthesis [115]). Strong evidence in support of this treatment is provided by the complete retention of the configuration of the initial olefin in the tetrahydrocinnoline, which has been demonstrated by the reaction of 1-methyl-1-phenyldiazenium perchlorate with *cis*- and *trans*-β-deuterostyrenes [35]:



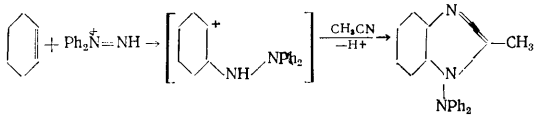
(a) R¹ = D, R² = H; (b) R¹ = H, R² = D.

Only the most electrophilic diazenium cations react with non-conjugated olefins. Thus the reaction of compounds (LIX, R = Ph) with *cis*- and *trans*-but-2-enes in acetonitrile led to the isolation of the aziridines (LXII):



(23)

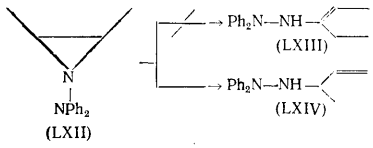
but the reaction with cyclohexane unexpectedly gives an 80% yield of 2-methyl-1-diphenylaminohexahydrobenzimidazole [33,34]:



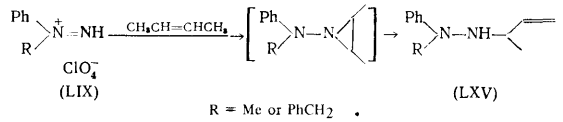
(24)

The difference between the products of reactions (23) and (24) is attributed to steric strain, which reduces in the latter case the stability of the bicyclic aziridinium ion (LVI) [reaction (21)], and to the steric hindrance of the formation of aziridine from cyclohexene. [33,34]

In an acid medium both *cis*- and *trans*-aziridines (LXII) decompose in an extremely non-trivial manner, giving, instead of compound (LXIII), the isomeric hydrazine (LXIV); *trans*-aziridine is much less stable than its *cis*-isomer [33,34]:



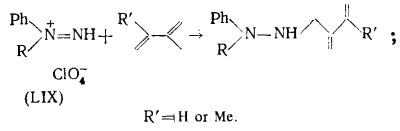
1-Methyl-1-phenyldiazenium perchlorate (LIX, R = Me) does not react with cyclohexene at all and its reaction with *cis*- and *trans*-but-2-enes is much slower than that of (LIX, R = Ph). The corresponding aziridines (LXII) are apparently unstable under these conditions and only the product of their decomposition—a hydrazine (LXV)—can be isolated in approximately 35% yield [34]. 1-Benzyl-1-phenyldiazenium perchlorate reacts similarly with but-2-enes, but the yield of the hydrazine is somewhat higher [14]:



; (25)

R = Me or $PhCH_2$.

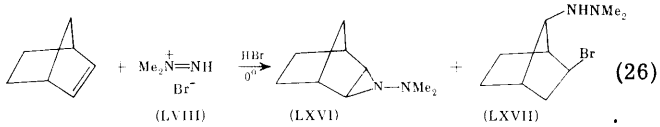
The interaction of aryldiazenium salts (LIX) with 1,3-dienes is apparently analogous to reaction (25). This reaction also leads to the formation of unsaturated hydrazines [14]:



;

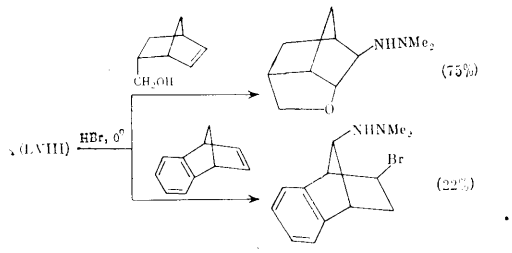
R' = H or Me.

1,1-Dialkyldiazenium salts are evidently less electrophilic than aryldiazenium salts and do not react with the usual olefins. However, the reaction does nevertheless occur with the more reactive double bonds of compounds of the norbornene series. Thus, 1,1-dimethyldiazenium bromide (LVIII) reacts with norbornene to form *exo*-*N*-dimethylaminoaziridine (LXVI) (in 59% yield), and also the bromohydrazine (LXVII) or the corresponding hydrazinoalcohol [15]:

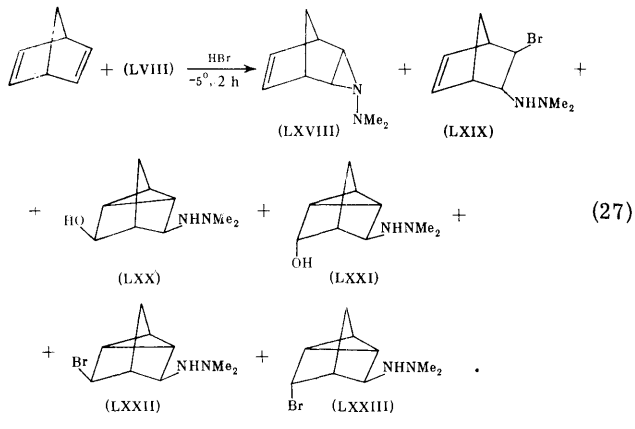


(26)

If account is taken of the possible rearrangements of the norbornyl cations, reaction (26) can be readily accounted for in terms of mechanism (21). The interaction of (LVIII) with *endo*-2-hydroxymethylnorborn-5-ene and benzonorbornadiene also fits satisfactorily within the framework of this mechanism [15]:



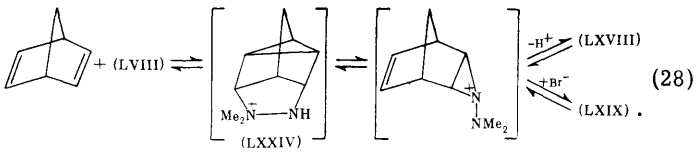
It is noteworthy that in the above examples the first reaction stage is *exo*-attack by the diazenium cation on the norbornene double bond, which is typical for electrophilic addition to such systems. However, the reaction of (LVIII) with norbornadiene yielded the *endo*-aziridine (LXVIII) as well as a series of products of both *endo*-addition [compound (LXIX)] and *exo*-addition [compounds (LXX)–(LXXIII)] with an overall yield in excess of 95% [15]:



(27)

The authors [15] explained the formation of the *endo*-products by the fact that the 1,1-dimethyldiazenium cation can react with norbornadiene not only as an electrophile but also as a dienophile, and that certain reactions of conjugated dienes are characteristic of norbornadiene. It is suggested that the initial [2 + 2 + 2]-cycloaddition product

(LXXIV) is subsequently converted into an *endo*-aziridinium ion, which is then transferred into compounds (LXVIII) and (LXIX):



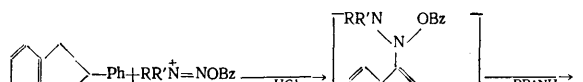
(28)

With increase of the HBr concentration, the yield of the *endo*-aziridine (LXVIII) falls sharply (from 52% to 0) and, although the amount of (LXIX) increases, the *endo*:*exo* ratio in the reaction products diminishes. To explain this, it has been suggested[15] that the dication $Me_2\overset{+}{N}=\overset{+}{N}H_2$ is involved in the reaction; its addition to norbornadiene takes place with formation of an *exo*-adduct, from which all the *exo*-products (LXX)–(LXXIII) are subsequently obtained.

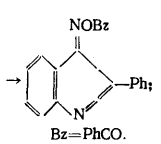
However, the existence of this dication is extremely unlikely even in a very strongly acid medium and the *exo*-products are most probably formed via a less exotic route. It appears that, when compound (LVIII) interacts with norbornadiene cycloaddition [reaction (28)] leading to *endo*-products is accompanied by the usual electrophilic attack at a comparable rate via reaction (26) with formation of an *exo*-π-complex and possibly the corresponding *exo*-aziridine. *exo*-Derivatives of norbornene are known to react with nucleophiles at a rate higher by several orders of magnitude than their *endo*-isomers[116,117], so that *exo*-aziridine should be converted into the decomposition products (LXX)–(LXXIII) much faster than the *endo*-isomer (LXVIII) and its absence from the reaction mixture is quite understandable. It is also possible that the attack by the nucleophile takes place at the stage of the *exo*-π-complex. With increase of HBr concentration, the main role in the alteration of the composition of the products of reaction (27) is apparently played by the increase of the concentration in solution of the extremely nucleophilic bromide ions rather than a change in the pH of the medium.

7. Diazenium Cations in Coupling Reactions

Although coupling reactions are typical for the closest analogues of diazenium salts (diazonium and also immonium salts[75]), there are comparatively few examples of such processes involving diazenium cations. Only the most electrophilic diazenium cations undergo coupling reactions with aromatic compounds. Thus the coupling of benzoyloxydiazenium chlorides (LXXV) with 2-phenylindole leads to 3-benzoyloxyimino-2-phenylindolenine[61]:



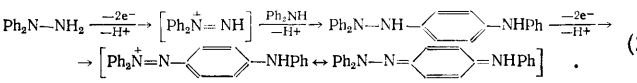
(LXXV)



Cyclopentadienone dimethylhydrazone has been obtained from 2-methoxy-1,1-dimethyldiazenium methyl sulphate and cyclopentadienylsodium[59,60]:



Hünig postulated the involvement of 1,1-diaryl-substituted diazenium cations in the oxidative coupling of 1,1-diarylhydrazines wtth aromatic amines, phenols, etc.[5,29,30,68,118]. For example:

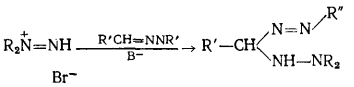


(29)

However, it was already noted above (Section II) that the involvement of diazenium cations in these coupling reactions is fairly controversial, since the oxidation was carried out only in a weakly acid and even in an alkaline medium. The formation of tetrazenes, the typical products of the oxidation of asymmetric hydrazines, competes with the coupling reaction[2-5] and in certain cases only the tetrazene is obtained. The yield of coupling products has amounted to between 10 and 50%.[29,30,68]

When 1,1-dialkyl- and 1-alkyl-1-arylhydrazines, except 1-methyl-1-*p*-nitrophenylhydrazine, are used instead of 1,1-diarylhydrazines, the coupling reaction does not occur at all[29,30]. The attempt to couple 1,1-dimethyldiazenium bromide (LVIII) with aniline and phenol in an acid medium was also unsuccessful[11].

Despite the relatively low reactivity of diazenium salts in relation to aromatic compounds, their interaction with hydrazines takes place smoothly. The coupling of diazonium salts with hydrazones leads to formazans and the corresponding reaction involving diazenium salts was found to lead to the formation of various compounds with the dihydroformazan group. Thus the addition of acid solutions of 1,1-dialkyldiazenium bromides to aldehyde monoalkylhydrazones in the presence of bases led to the synthesis of a series of 3,4-dihydroformazans (LXXVI)[20-22,24]:

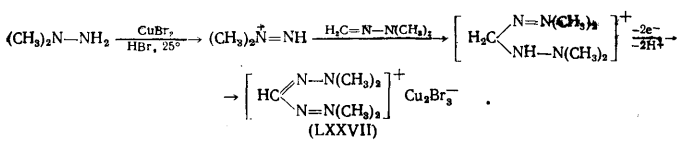


(LXXVI)

(30)

The formation of compound (LXXVI) can be treated as a result of the coupling of the hydrazone either directly with the diazenium cation or with the aminonitrene formed from the latter under the influence of the base. It is so far difficult to reach a final conclusion, although the second mechanism is apparently more probable, since compounds (LXXVI) have been isolated also following the reaction of hydrazones with aminonitrenes generated in other ways[22].

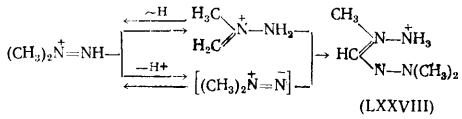
On the other hand, coupling of the diazenium cation with the hydrazone has been postulated as one of the intermediate stages in the formation of the copper complex of 1,1,5,5-tetramethylformazanium cation (LXXVII), which is very similar to reaction (30)[27]:



(LXXVII)

The structure proposed for (LXXVII) is consistent with the infrared and ^1H NMR spectra as well as X-ray diffraction data. Furthermore, when the complex is decomposed in an alkaline medium, the product is 1,5,5-trimethylformazan—the simplest formazan obtained hitherto[27].

Finally, yet another version of this type of coupling has been put forward by Urry[15]. He believes that the following reactions are possible in a solution of 1,1-dimethyldiazenium bromide [cf. Eqns. (6) and (7)]:



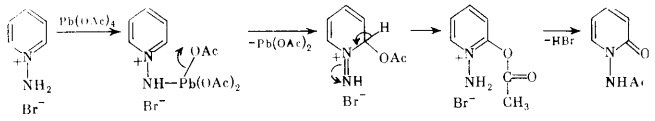
(LXXVIII)

There is no evidence for the structure of the dihydroformazanium ion (LXXVIII) in his paper[15]. It is merely stated that the ion can be hydrolysed to 1,1-dimethylhydrazine, methylhydrazine, and formic acid or can react further to give 1-methyl-1,2,4-triazole and dimethylamine.[15]

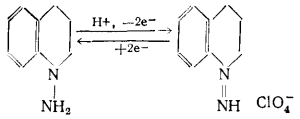
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Several studies on the methods of synthesis and properties of diazenium salts were published in 1977.

The formation of diazenium cations was suggested to account for the oxidation of *N*-aminopyridinium bromide by lead tetra-acetate [119]:



The perchlorate (LXXIX) (λ_{max} = 319 nm, ϵ = 9900),[120] whose properties are in many respects similar to those of 1-alkyl-1-aryldiazenium salts investigated previously, was obtained by the electrochemical oxidation of *N*-amino-1,2,3,4-tetrahydroquinoline in acetonitrile ($E_{1/2}$ = 0.87 V):



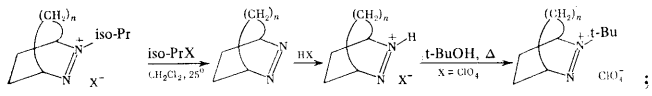
(LXXIX)

Its reduction ($E_{1/2}$ = −0.18 V) regenerates the initial hydrazine in 80% yield and its reaction of type (22) with acenaphthylene, 1,1-diphenylethylene, and indene leads to the corresponding tetrahydrocinnolines (LX) in 54 to 67% yield.

In their study of the mass spectra, generated by electron impact, of various hydrazines, tetrahydrocinnolines (LX), and pyrazolidines, prepared by the condensation of diazenium salts with olefins [reactions (25), (22), and (17) respectively], Cauquis et al.[121] concluded that the main pathway in the fragmentation of the molecular radical-anion is in all cases the retroreaction—the decomposition to the olefin of the diazenium cation or the protonated azomethineimine.

A number of bicyclic trisubstituted diazenium salts (LXXX) were obtained in 90–100% yield by the alkylation of the corresponding azoalkanes with isopropyl bromide in an atmosphere of nitrogen in the presence of $AgClO_4$.

Isopropyl iodide alkylates (LXXXIb) even on simple mixing of the reactants without the addition of a silver salt (yield 86%) [122]:

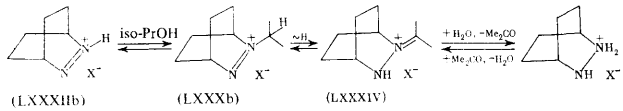


(LXXX, a and b) (LXXXI, a–d) (LXXXII, a–d) (LXXXIII, a–c)

(a) n = 1, (b) 2, (c) 3, (d) 4; X = Cl, Br, I or ClO_4.

When a gaseous hydrogen halide was passed through an ethereal solution of (LXXXI) or the latter was treated with 70% $HClO_4$, the corresponding 1,2-disubstituted diazenium salts (LXXXII) were obtained in 70–100% yield. The trisubstituted salts (LXXXIII) were then synthesised from the perchlorates (LXXXII) in 80–85% yield on refluxing in t-butyl alcohol[122].

The attempt to use the last reaction for the introduction of groups other than t-butyl were unsuccessful: when methyl, ethyl, and isopropyl alcohols were used, (LXXXII) was reduced to hydrazine instead of being alkylated. It has been shown for (LXXXIIb) that the reduction is a reversible process proceeding via stages involving alkylation, isomerisation, to (LXXXIV), and hydrolysis, the rate of equilibration depending on the nature of the anion[122]:



(LXXXIIb) (LXXXb) (LXXXIV)

It is important to note that Snyder et al.[122] were able to isolate a number of salts of the type (LXXXIV) (cf. Section IV).

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