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The Formation of the Azoxy-group in Reactions Involving Anions with Nitrogen - Nitrogen Bonds

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The methods for the formation of azoxy-compounds by substitution reactions with participation of anions having nitrogen - nitrogen bonds are examined. Attention is concentrated on the alkylation reactions of alkanediazotates, nitrosohydroxylamines, and nitroamines as well as substitution reactions involving the distal nitrogen atom in azoxy-compounds. The literature up to 1976 inclusive is covered.
The bibliography includes 194 references.

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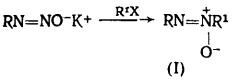
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I. INTRODUCTION

The chemistry of azoxy-compounds is now attracting considerable interest as shown by the publication of several monographs and reviews in the last ten years[1-9]. The vigorous growth of research in this field has led to the discovery of new methods for the introduction of the azoxy-group into organic compounds and has imparted a new significance to the studies by Bamberger, Hantzsch, Angeli, and others carried out at the beginning of the XXth century. In a previous review[10] we examined the methods for the formation of the azoxy-group by the oxidation of compounds with nitrogen–nitrogen bonds[10]. This review deals with the formation of the azoxy-group in substitution reactions with participation of ambident anions having nitrogen–nigrogen bonds.

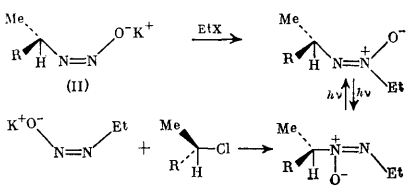
II. ALKYLATION OF ALKANEDIAZOTATES

A convenient method for the synthesis of azoxyalkanes, consisting in the alkylation of alkanediazotates, has been developed by Moss and coworkers[11-16]:



(I)

Azoxyalkanes, particularly those containing asymmetric substituents (I, $R \neq R^1$) were previously described in isolated instances only, but have now become more available. The method of synthesis described is unsuitable for compounds (I) where R and (or) R^1 = aryl or t-alkyl, but it does have many advantages, as noted by Moss et al.[12], and makes it possible to vary the groups R and R^1, which can be primary and (or) secondary alkyl or arylalkyl groups. The synthesis by this method is specific, and it leads to a single structural iosmer. The method makes it possible to obtain optically active azoxyalkanes, since the alkylation stage is not accompanied by the loss of chirality in the R and R^1 groups[12,13,15,16] (see also McGahren and Kunstmann[17]):



(II)

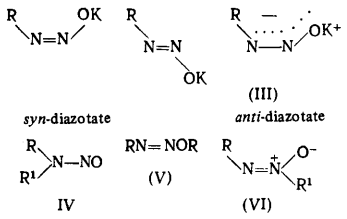
Evidently the configuration of the centre in the distal position remains unchanged, but there is a complete inversion at the carbon atom of the reagent[13,15,16].

The retention of the chiral centre in the diazotate (II) in the alkylation reaction has been used in a 12-stage synthesis of the dihydro-derivative of elaiomycin—an antiobiotic and carcinogen, which is encountered in nature and which contains the azoxy-group[15]. The photochemical interconversions of the distal and proximal isomers into their equilibrium mixture without loss of asymmetry at C* constitute an additional confirmation of the possibilities of the new method of synthesis of azoxyalkanes, which makes it possible to obtain a chiral centre in R and (or) R^1.[13]

The possibility of using allyl halides for the alkylation of diazotates indicates yet another interesting aspect of their practical application, since "functional" alkylating agents can be introduced into the reaction[14].

Alkanediazotates, which are the key compounds in the new synthesis, usually occur merely as intermediates in the nitrosative deamination of alkylamines and alkylhydrazines[16,18,19], in the alkaline cleavage of *N*-alkyl-*N*-nitroso-urethanes[20-30], etc. but can also be isolated in a pure state[20-27]. Moss[31] modified somewhat the procedure for the decomposition of urethanes, usually employed for the synthesis of diazoalkanes, and carried out the reaction with potassium t-butoxide in an inert solvent. Diazotates are then obtained in the form of solid salts and are believed to have the *syn*-configuration[16]. Other methods, for example, the alkaline nitrosation of hydrazines, give rise to the more stable *anti*-diazotates, but the *syn* → *anti* conversion is greatly hindered[16,27]. The N–N (1.32 Å) and N–O (1.29 Å) bond lengths in *syn*-methanediazotate are intermediate between the values for single and double bonds, so that the compound is best represented by

the mesomeric anion (III).[16,32] The presence of *p* electrons at $N_{(2)}$ is responsible for the formation of nitrosoamines (IV), diazoethers (V), or ethoxy-compounds (VI) in the alkylation of the anion:



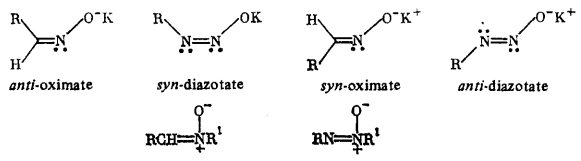
syn-diazotate (III) *anti*-diazotate

IV (V) (VI)

The yield of azoxyalkanes varies from 30 to 60% and is little affected by the solvent. In alkylation in hexamethylphosphoramide, a polar aprotic solvent which causes the dissociation of the salt, an appreciable proportion of the alkanediazotate remains in the form of the anion. The high electron density at the oxygen atom and its appreciable steric accessibility compared with the $N_{(1)}$ atom cause the yield of the nitrosoamine to be small and make the yield of the *O*-alkylation product up to 50%. In a less polar solvent (95 : 5 ether–hexamethylphosphoramide mixture) a considerable proportion of the alkanediazotate is present in the form of ion pairs, the $O_{(3)}$ atom is blocked by the counter-ion, and the nitrosoamine (IV) predominates over the diazoether (V) among the side products[16]. Arylation of the alkanediazotate (III, $R = CH_3$) gives rise exclusively to compound (IV), i.e. takes place at the $N_{(1)}$ atom[21].

It is of interest to compare all these data with the alkylation of arenediazotates. The latter are known to exist in the more stable form of isodiazotates[33–39] (equivalent to the *anti*-configuration of alkanediazotates) and calculation of the electron density in the anion shows that the site of attack is the key nitrogen atom and the oxygen atom[39]. Experimental data[39,40], indicating the predominant formation of *O*-alkylation products in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), are fully consistent with the calculations. Thus the ambident anion reacts in the usual way, at the first and third atoms[39,40], and azoxy-compounds are not formed in this case.

The unusual behaviour of alkanediazotates, manifested by the possibility of alkylation in the 2-position of the ambident anion, is associated with the presence of the electron pair at $N_{(2)}$. This situation is not unique in the series of nitrogen-containing functional groups and has a direct analogy in the alkylation of the oximate anion. In both cases the 2- and 3-positions in the ambident anion are alkylated preferentially. Whereas alkylation at $C_{(1)}$ is not observed in the oximate anion[41–43], $N_{(1)}$-alkylation does occur to a slight extent in the *syn*-alkanediazotate owing to the presence of an electron pair at the key nitrogen atom[12,16]:



anti-oximate *syn*-diazotate *syn*-oximate *anti*-diazotate

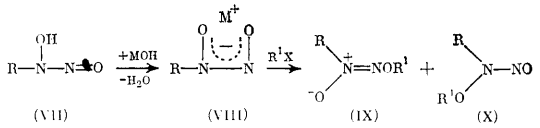
The *anti*-oximate anion, which is sterically equivalent to *syn*-diazotate†, is alkylated preferentially at the nitrogen atom[41–43,45–51], giving rise to a nitrone, i.e. the ambident anion is alkylated in both cases in the 2-position (but with different selectivities). The *syn*-oximate anion, which is sterically equivalent to the *anti*-diazotate and to the anion derived from ketoximes, gives preferentially $O_{(3)}$-alkylation products[41–43], i.e. in both cases the ambident anion is alkylated preferentially at the oxygen atom and nitrones or, correspondingly, azoxy-compounds[52] are not formed. The influence of the geometry of the diazo-bond on the regio- and stereo-specificity of the alkylation of alkanediazotates has been recently discussed[52].

The intramolecular interaction of propargyl[30,53,54], allene[55], and epoxy-groups[56,57] with the *syn*-diazotate ion, obtained by the decomposition of "functional" urethanes, proceeds in the same way as *O*-alkylation.

The formation of an azoxy-compound in the decomposition of cyclopropane-bisdiazotate, which constitutes an intramolecular *N*-cyclopropylation reaction, has been reported[58]. However, the multiplicity of pathways leading to the decomposition of the initial product hinders interpretation.

III. ALKYLATION (ACYLATION) OF *N*-NITROSOHYDROXYLAMINES

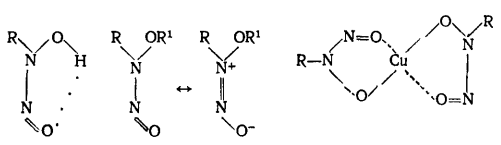
The alkylation of *N*-nitrosohydroxylamines (VII) and their salts (VIII) constitutes yet another group of reactions leading to the formation of azoxy-compounds (IX).[59–78]. The side products in this process are apparently alkoxynitrosoamines (X):



(VII) (VIII) (IX) (X)

The key compounds for this reaction—the acids (VII) and the salts (VIII)—constitute an interesting class of compounds; the problem of their structure has been discussed in earlier studies by Bamberger[62,63,79], Hantzsch[67,80,81], Traube[65,81–83], Gomberg[84], Angeli[85–87]#, and Thiele[88]. A recent review[78] is a first attempt at a systematic account of the relevant data (see also Bamberger and Baudisch[79], and Marvel, where methods for the preparation of cupferrons are summarised[89]). The acids (VII) are unstable in a free state, while their salts are more stable; for example, the ammonium salt of phenylnitrosohydroxylamine (cupferron) is a familiar analytical reagent[90,91].

O,*N*-Disubstituted nitrosohydroxylamines (X) exist preferentially and the free acids (VII) exclusively in the *trans*-configuration[92], whose additional stabilisation in the case of the acids (VII) is caused by the intramolecular hydrogen bond[92]. The salts of nitrosohydroxylamines, which are represented as the chelates (VIII) and (XI), have an analogous configuration[78,90,93]:



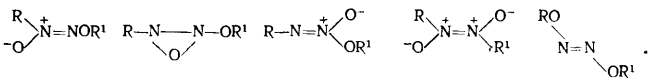
(VII) (X) (XI)

† The effective size of the free electron pair in space is even smaller than the size of bound hydrogen[44].

Angeli represented arylnitrosohydroxylamines by the formula $ArN(O)=NOH$ and regarded them as the oximes of nitro-compounds or as the oxides of diazohydrates[79,85–87].

The geometry of the salts and their stability are apparently associated with the formation of a 6-electron system, the principle of the structure of which has already been used to account for the geometry, thermal stability, and reactivity of the ketoxime dianions[94] and has been extrapolated to other "*U*-type" molecules–tosylhydrazone dianions[94,95] and *cis*-difluoro-olefins[94,96].

The salts of *N*-nitrosohydroxylamines are readily alkylated and, as shown for the first time[60,61] in relation to the benzylation of *N*-benzyl-*N*-nitrosohydroxylamines, can give rise to two reaction products—(IX) and (X) (R = $R^1 = CH_2Ph$). The structure of the latter compound was adopted immediately and was not questioned subsequently, since in the general case it can be obtained by specific synthesis—the nitrosation of alkoxyamines[61–63,77,78,97]. The structure of the first product (which is more stable), represented by formulae (IX),[63] (XII),[62] (XIII),[67] and (XIV),[70] has been the subject of a prolonged controversy. Wright and coworkers[70] seemingly demonstrated by all the available evidence that the first alkylation products exist in form (IX), but the fact that these compounds (R = alkyl or aryl; R^1 = alkyl) evolve methane on treatment with methylmagnesium chloride led them into a blind alley§. Wright and coworkers[70] then attributed formula (XIV) to the alkylation products and at the same time threw doubt on the structure of the dimers of nitroso-compounds:



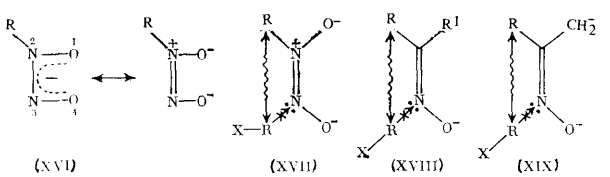
(IX) (XII) (XIII) (XIV) (XV)

Freeman[73] and Stevens[74] corrected this error and later Smith[59] and Woodward and Wintner[75,76] confirmed that the product has structure (IX). Bearing in mind that the structure of the dimers of nitroso-compounds was not immediately adopted and that the hyponitrites (XV) are isomeric with compounds (IX) and that the spectroscopic characteristics of their salts (XV, R = R^1 = Na) are close to those of nitrosohydroxylamines salts[98,99], the difficulties in the determination of the structure become understandable.

The alkoxydiazene oxides (IX) are isolated by the usual preparative methods—distillation, crystallisation, and chromatography. The products of the methylation of the Traube salt (VIII, R = $CH_2N_2O_2Na$, M = Na) as well as other alkoxydiazene oxides constitute surprising examples of stability[65,76–78]. Their high stability can be used for their purification by heating with sulphuric acid or alkali[77].

The geometry of compound (IX) has not been established, but Lamberton and Yusuf[77] clearly noted the formation of a single stereoisomer in the ethylation of *N*-nitrosomethylhydroxylamine.

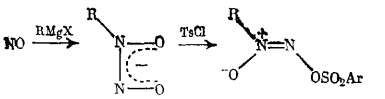
The anion (XVI) has three potential nucleophilic centres susceptible to attack—both oxygen atoms and the $N_{(3)}$ atom. In reality only the first possibility is realised:



(XVI) (XVII) (XVIII) (XIX)

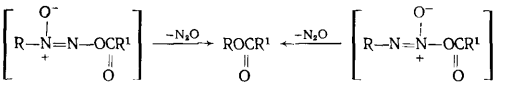
§ Subsequently Stevens[74] explained this finding.

We believe that the general considerations concerning the alkylation of the oximate and diazotate anions, described above, are applicable in this case too. As the reagent approaches the nitrogen atom of nitrosohydroxylamine, a structure, analogous to the two non-realisable structures conceivable in the alkylation of the ketoximate anion (XVIII) and the dianion (XIX), is produced. In all three cases the nitrogen atom is sterically blocked, so that the oxygen atom (see Section II above) and the carbon atom are attacked in the alkylation of compounds (XVIII) and (XIX) respectively[94]; in compound (XVI) alkylation proceeds via both oxygen atoms. It is of interest that the electron pair of the nitrogen atom of the anion (XVI) is blocked also for other electrophilic reactions. Thus its tosylation takes place at the $O_{(4)}$ atom with formation of compound (XX)[74] in which the *cis*-orientations of the oxygen atoms are retained[100]:



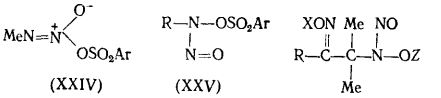
(XVI) (XX)

Compounds of type (XX) are of interest as starting materials for the synthesis of azoxy-compounds by substitution using various nucleophiles (carbanions and alkoxides) (see below) and are frequently obtained as a result of a single-stage reaction[74]. The tosyl derivatives (XX) are more stable than other acyl derivatives of *N*-nitrosohydroxylamines. For example, the alkali metal salts (VIII) evolve N_2O and give rise to the esters (XXI) on treatment with aroyl halides, since the intermediates (XXII) readily decompose[101]:



(XXII) (XXI) (XXIII)

It is of interest that both the diazene $N_{(2)}$-oxides (XXII) and the diazene $N_{(1)}$-oxides (XXIII)[101–104] behave similarly and that the position of the oxygen atom does not influence the formation of esters[101]. On the other hand, the tosyl derivatives (XX) and (XXIV) have sharply different stabilities; thus the attempt to tosylate the silver salt of methylnitroamine gives rise solely to methyl tosylate as a result of the decomposition of the intermediate (XXIV):[105]



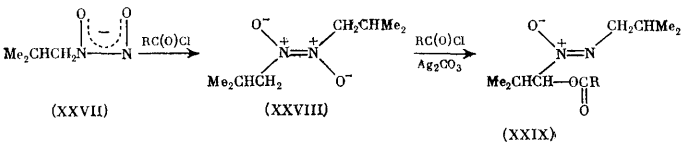
(XXIV) (XXV) (XXVI)

(a) R=Ph, X=MeCO, $Z=SO_2Ar$;
(b) R=Z=Me, X=H

Nor is it possible to obtain the tosyl derivative (XXV) by the nitrosation of the corresponding hydroxylamine[105], which confirms the validity of the choice, made for the first time by Stevens,[74], between the alternative structures (XX) and (XXV) in favour of (XX). In a recent study White et al.[100] explained some of the properties of compounds of type (XX). In contrast to these data, structure (XXVIa) has been attributed to the product of the tosylation of N-[1-acetoxymino-2-methyl-1-phenyl-(2-propyl)] hydroxylamine[106]. The anomalous course of the reaction may be due to the specific properties of the initial compound, so that the alkylation of its homologue (XXVI, R = Me, X = Z = H) with dimethyl

sulphate leads to the formation of compound (XXVIb),[106] which again conflicts with the analogous reaction of cupferron[70] or *N*-t-alkyl-*N*-nitrosohydroxylamines[105].

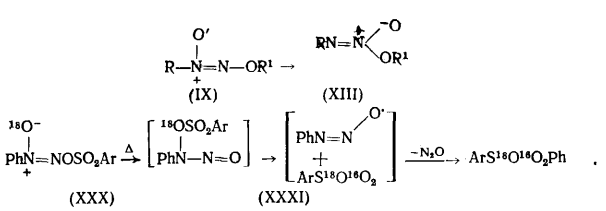
The prolonged controversies which have accompanied each new step in the development of the chemistry of nitrosohydroxylamines can be accounted for by the weak theoretical ideas concerning the state of the bonds in the initial anion (VIII) or structures of type (IX). Evidently its further development promises to have many unexpected features. For example, it has been observed quite recently that the 3,5-dinitrobenzoylation of salts of *N*-isobutyl-*N*-nitrosohydroxylamine (XXVII) gives rise to compound (XXIX),[107] whose formation is difficult to account for by the mechanism involving the acylation of the $O_{(1)}$ atom[108] or the $O_{(4)}$ atom[101] in the initial anion. It has been shown that in the general case compounds (XXIX, RCO = acetyl, 3,5-dinitrobenzoyl, or 3-nitro-1-naphthoyl) are products of the acylation of the nitroso-dimers (XXVIII), which is usually accompanied by reactions of *N*-nitrosohydroxylamines[107]:



(XXVII) (XXVIII) (XXIX)

Acylating deoxygenation of compounds (XXVIII) constitutes a new type of rearrangements, related to the generalised Polonovskii reaction[109].

The alkylation of nitrosohydroxylamines gives rise to azoxy-compounds (IX), which are isomeric with the products of the alkylation of primary nitroamines (XIII). The possibility of the migration of oxygen from $N_{(1)}$ to $N_{(2)}$ has not been investigated by the intermediates in this migration [oxadiaziridines (XII)] have been erroneously regarded by Bamberger[62] as possible products of the alkylation of nitrosohydroxylamines. We may note, incidentally, that the double bond in diazoethers is not azoxidised under the influence of peracids[70]:

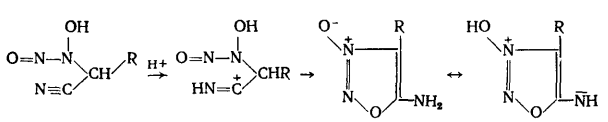


(IX) (XIII)

(XXX) (XXXI)

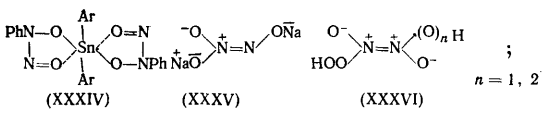
Another variety of isomeric transformations, namely in the pair of compounds (IX) and (X), has not been investigated, but it has been shown in relation to the thermal decomposition of the derivatives (XXX) labelled at the oxygen atom[110] that the tosyl group migrates to the *N*-oxide oxygen with formation of compound (XXXI). According to the mechanism presented above, its further decomposition gives rise to the phenyltosylate (Ar = *p*-tosyl) in which the label is uniformly distributed between the three oxygen atoms in the sulpho-group[110].

Nitrosohydroxylamines (XXXII) can also undergo intramolecular alkylation processes, giving rise to the sydnones (XXXIII):[141]



(XXXII) (XXXIII)

The interaction of diaryltin dichlorides with cupferron leads to chlorine-substitution products instead of the expected complexes suitable for the quantitative precipitation of the metal. According to a brief communication[112], the substance obtained has the structure (XXXIV), which has been demonstrated by infrared spectroscopy:

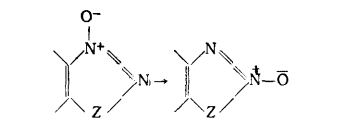


(XXXIV) (XXXV) (XXXVI) $n = 1, 2$

Organic derivatives of the Angeli salt (XXXV) and other oxyhyponitrites (XXXVI) have not been investigated at all[113]. When an attempt is made at a direct alkylation of (XXXV) by primary alkyl halides, the products are aldoximes and the reaction proceeds without the intermediate formation of the nitroxyl NOH.[114] It is also significant that in ethanol the nitrogen atom is alkylated and that the contribution of this process usually diminishes (relative to *O*-alkylation) on passing from alcohol to water[114].

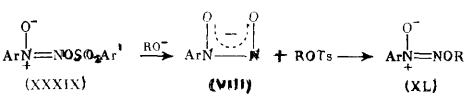
IV. SUBSTITUTION REACTIONS INVOLVING THE DISTAL NITROGEN ATOM IN AZOXY-COMPOUNDS

Numerous substitution, addition, and degradation reactions of azoxy-compounds with retention of the azoxy-group are known. In the present section we shall confine ourselves to the consideration of processes involving direct substitution at the $-N=N(O)$ group. Reactions of this type include the photochemical reactions of aliphatic and aliphatic-aromatic azoxy-compounds as a result of the migration of the oxygen atom. They were considered in our previous review[10] and have been studied only in recent years. Analogous migration of oxygen from $N_{(1)}$ to $N_{(2)}$, induced photochemically, has been observed in heterocycles: triazole oxides (XXXVII)[115–117] and thiadiazole oxides (XXXVIII)[118–120]:



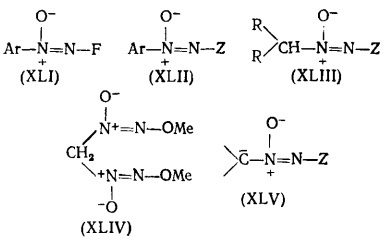
(XXXVII): Z=NR (XXXVIII): Z=S

Examples of migrations of this kind are few; reactions involving substitution at the distal nitrogen atom of the azoxy-group are more familiar. The formation of alkoxydiazene oxides (XL) in the reaction of alkoxides with tosyl derivatives (XXXIX) is fully consistent with this behaviour[74]. However, in reality the anion of nitrosohydroxylamine (VIII), liberated as a result of the substitution at the sulphur atom, is alkylated:



(XXXIX) (VIII) (XL)

The reaction of compounds (XXXIX)[74,121], (XL, R = Me),[70] and (XLI)[122] with organomagnesium reagents (Ar^1MgX, AlkMgX), which leads to the exchange of the OSO_2Ar^1, OMe, and F groups for a hydrocarbon group, giving rise to yet another possibility for the synthesis of the azoxy-compounds (XLII, Z = aryl or alkyl), takes place quite differently; however, the tosyl group in azoxysulphones (XLII, $Z = SO_2Ar^1$)[123] is not exchanged for the aryl group in Ar^1MgX:[124]

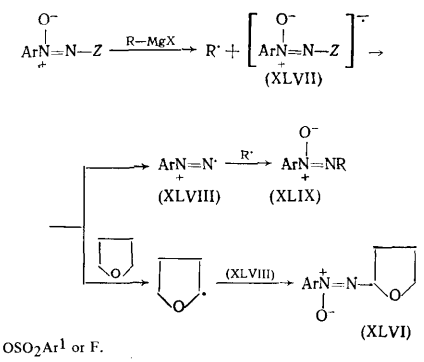


(XLI) (XLII) (XLIII) (XLIV) (XLV)

The attempt to substitute a group Z for a hydrocarbon group in aliphatic diazene oxides (XLIII, $Z = OSO_2Ar^1$ [74] or F[121,122]) was unsuccessful owing to the exchange of the proton in the α-position. For the same reason, the substitution of the alkoxy-group in bis(nitrosohydroxylamine)methane (XLIV) also fails, since the CH_2 group is metallated in the first place[70,76]. The stability of the anion having the general formula (XLV), where Z = Me, MeO, etc., has been used in a number of synthetic investigations[14,76].

Despite the fact that the distal group in the diazene oxides (XXXIX)–(XLI) can be exchanged for the alkyl (aryl) group in organomagnesium reagents, direct substitution at the nitrogen atom is not observed in reactions with other nucleophiles; for example, compounds (XLI) do not change under the influence of MeCOOH, MeONa, or Et_2NH.[121,122] Furthermore, in the reactions of compounds (XXXIX) and (XLI) with organomagnesium reagents in tetrahydrofuran (THF), compounds (XLVI) are formed as side products, evidently as a result of radical substitution[121]. (The α-position in THF is activated for radical substitutions of this kind; see, for example, Refs.125 and 126).

This finding and also the fact that, among the nucleophiles investigated, only Grignard reagents led to substitution at the nitrogen atom while other reagents proved to be inert or led to exchange at the sulphur atom or to metallation indicate the validity of the mechanism proposed by Stevens[121]:



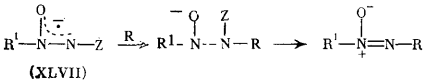
(XLVII) (XLVIII) (XLIX) (XLVI)

Z = OSO_2Ar^1 or F.

It is based on electron transfer to the azoxy-group with formation of the radical-anion (XLVII), which is converted into the azoxy-radical (XLVIII). The latter combines with the primary (R·) or secondary () radical, giving rise to compounds (XLIX) and (XLVI) respectively. Whereas the first stage, one-electron transfer from the organometallic compound to the azoxy-group, has aroused no doubts hitherto and has been adequately confirmed in the literature[127–129], the attempt to detect radical (XLVIII) by EPR has failed[121].

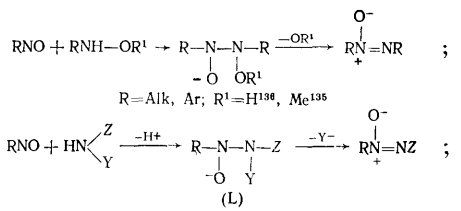
The azoxy-radical, with the unpaired electron at the nitrogen atom, is identical with the diazenyl radical, the possibility of the formation of which has been studied vigorously. Nevertheless many substitution reactions at the N–N bond can be accounted for on the basis of the addition–elimination mechanism[130–132] without resorting to ideas involving a discrete diazenyl radical.

Similar considerations are apparently applicable also to the substitution reactions with organomagnesium reagents involving the distal nitrogen atom of the azoxy-group, considered in this review. The final products of such reactions arise as a result of the pairing of the species (XLVII) with the primary or secondary radical present in the medium and subsequent elimination of the anionic fragment¶:



(XLVII)

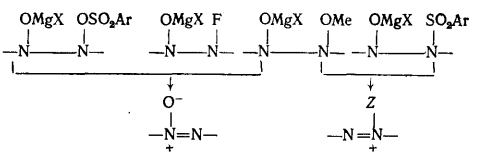
In this interpretation the substitution reaction is put in the same class with the already known processes involving the formation of the azoxy-group via the coupling of N-centred radicals†:



R = Alk or Ar; Z = Y = F[122] or Cl[137]; Y = Cl, Z = SO_2Ar[123]; Z = Y = Cl, H = Alk or Ar[138].

The formation of azoxysulphones[123] and not azoxychloro-derivatives by the condensation of nitroso-compounds with chloramine-T indicates the preferential rupture of the N–Cl bond compared with N–SO_2Ar in the intermediate (L, Y = Cl, Z = SO_2AR). It is also remarkable how much more difficult are the conditions for the elimination of the sulphinate group, for example in the Carpino reaction[139–141] compared with the analogous elimination of the sulphonate group, for example, in the amination of nitrogen-containing bases by hydroxylamine-*O*-

All the foregoing considerations illustrate the idea that the stabilisation of the intermediate (L) by the elimination of the anion (in the form of OMgX or Y) is apparently determined by the ease of dissociation of the N–O and N–Y bonds and the stability of the leaving anion:

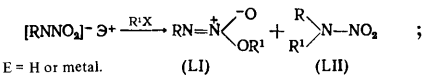


¶ The coupling of R· with the O-centred radical-anion leads to deoxygenation to a first approximation. Such a process is well known for the reaction of azoxyarens with organomagnesium reagents[70,133,134].

† Another mechanism of these reactions involves nucleophilic addition to the N = O double bond (see, for example, Taylor et al.[135]).

V. NUCLEOPHILIC SUBSTITUTION REACTIONS INVOLVING *N*-NITROAMINES AND *N*-NITROAMIDES

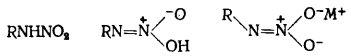
The alkylation of primary nitroamines, nitroamides, and their salts leads to the corresponding 1-alkoxydiazene 1-oxides (LI). The ratio of the *O*-alkylation [compound LI)] and *N*-alkylation [compound (LII)] products differs within very wide limits depending on the nature of the substituting group (R = alkyl, aryl, or SO_2AR), the alkylating agent, the metal cation (sodium, potassium, or silver), and the solvent:



E = H or metal. (LI) (LII)

Reactions in which primary nitroamines add to multiple bonds and many other nucleophilic substitution processes involving their anions also lead to a mixture of products (LI) and (LII). The chemistry of nitroamines has been considered in a number of reviews[144–150] and sections devoted to the alkylation of primary nitroamines are contained in a number of monographs[145,146,148,149]. However, since the publication of the last monograph, numerous experimental facts have accumulated, which have to be surveyed.

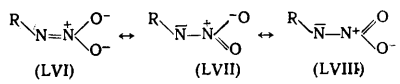
The structure of primary nitroamines and their salts has been the subject of theoretical disputes at the end of the XIXth and the beginning of the XXth century. The principal topic of these disputes has been the following question: do nitroamines exist in the form of true nitro-compounds (LIII) or do they have the structure of isonitroamines (LIV)# (for the history of the development of the relevant views, see Wright[147]):



(LIII) (LIV) (LV)

It has been shown recently that the N–N and N–O bond orders in methylnitroamine are to some extent equalised, which is accompanied by partial localisation of the negative charge at the oxygen atoms. However, primary nitroamines in the non-ionised state have the true nitroamine structure. It has been shown[152] that the ionisation of methylnitroamine entails an increase of the N–N bond force constant and a decrease of the N–O bond force constant, which corresponds to the isonitroamine structure being preferred for its salts, the metal cation being located in the *cis*-position relative to the alkyl group [structure (LV)].

Although the static distribution of charges in alkali metal salts of nitroamines is described by structure (LV), the reactivity of the corresponding anion is determined by the presence of three reaction centres—both oxygen atoms and the amino-nitrogen atom. The localisation of the electron pair at the central nitrogen atom is impossible in any of the main mesomeric structures (LVI)–(LVIII) and the central atom is consequently not susceptible to electrophilic attack:



(LVI) (LVII) (LVIII)

In a number of early studies, *N*-nitrosohydroxylamines were referred to as "isonitroamines", which introduced an additional confusion into this problem (See, for example, Traube[151]).

Nitroamines and their anions are typical examples of ambident (1,3) nucleophiles and many features of their individual behaviour can be accounted for on the basis of the general characteristics of the behaviour of such reagents. For example, it is well known that the reaction of silver salts of nitroamines gives rise to *O*-alkylation products, while alkali metal (potassium and sodium) salts give rise preferentially to *N*,*N*-dialkylnitroamines[145,146,148,149]. This conclusion is based both on studies carried out at the end of the XIXth and the beginning of the XXth century[153–159] and on more modern data[77,160–172]. Unfortunately in the majority of these investigations accurate ratios of the *O*- and *N*-alkylation products are not quoted. The available data are compiled in Table 1, which clearly illustrates the quantitative aspect of the relation.

Table 1. The ratios of the products of the *O*- and *N*-alkylation of $RNHNO_2$ and its salts.

No.	R/[$RNNO_2$]$^-$	Cation	Alkylating agent R^1/R^1X	Ratio* of products of *O*- and *N*-alkylation	Refs.
1	Isopropyl	K	MeI	0.15	162
2	Isopropyl	Ag	MeI	12.5	162
3	Neopentyl	Ag	MeI	12.5	162
4	Methyl	Na	$PhCH_2Cl$	0.25	167
5	Methyl	Na	*p*-$BrPhCH_2Cl$	0.14	167
6	Ethyl	Na	*p*-$BrPhCH_2Cl$	0.4	167
7	Methyl	Na	*p*-$CNPhCH_2Cl$	0.18	167
8	Ethyl	Na	*p*-$CNPhCH_2Cl$	0.4	167
9	Methyl	Li	$FcCH_2CH_2I$**	***	171
10	Methyl	Li	$FcCH_2X$**	***	170
11	n-Butyl	Na	n-BuI	0.75	160
12	Isopropyl	Na	iso-*o*-PrI	1.8	161
13	n-Octyl	Na	n-$C_8H_{17}I$	2.50****	161
14	Isopropyl	H	Me_2SO_4	1.2	162
15	Methyl	Na	$EtOCH_2Cl$	1.0	167

* The alkylation of alkali metal (Li, Na, K) salts was carried out in alcohol (MeOH, EtOH), that of silver salts was carried out in ether, and the alkylation with dimethylsulphate was carried out in water.

** Fc = ferrocenyl.

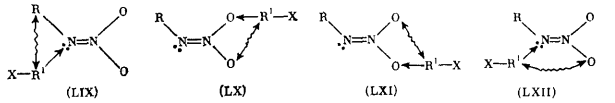
*** Only *N*-alkylation takes place.

**** The result is apparently distorted by partial decomposition on distillation.

The different modes of alkylation, depending on the metal cation, can be explained in terms of the general rule for the alkylation of ambifunctional nucleophiles; a polar electrophile combines primarily with the atom of the nucleophilic substrate having the highest electron density[173]. Such a centre in the nitroamine anion is the oxygen atom, which is attacked in the presence of a strong electrophilic catalyst (silver), which polarises the R^1–X bond[174]. Similarly other polar compounds [Me_2SO_4 and $EtOCH_2Cl$ (Nos. 14 and 15, Table 1)] give rise to a high percentage of the *O*-isomer.

Electrophiles with a small positive charge or electrically neutral electrophiles react preferentially with the atom of the ambifunctional system which is most readily polarised[173]. Such a centre in a nitroamine is the amino-nitrogen atom, which reacts preferentially, in relation to oxygen, with R^1–X (in the absence of silver ions) or adds to the multiple bond. Thus the condensation of alkylnitroamines with epoxyethane[175] and an activated double bond[146,148,168,176] as well as the aminomethylation of nitroamines[146,148,177] proceed exclusively at the nitrogen atom.

Another important feature is the increase of the amount of the *O*-isomer with increase of the bulk of the alkyl group. Comparison of Nos.1 and 12 in Table 1 shows that the methylation of isopropylnitroamine results in the formation of the *N*,*N*-isomer, while isopropylation gives preferentially the *O*,*N*-isomer. The progressive increase in the bulk of the group in both the alkylating agent and in the initial nitroamine (Nos.5–8 and 11–13) has a similar influence. Evidently the steric hindrance to the approach of the alkylating agent in structure (LIX) is manifested to a greater extent than in compounds (LX) or (LXI):

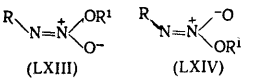


(LIX) (LX) (LXI) (LXII)

In conformity with the hypothesis put forward previously in the interpretation of the alkylation of diazotates (see Section II) (see also the earlier review[10]), the steric interactions with the vicinal group in structure (LXII) are less important than the steric interactions with the geminal group. It is also evident that, when R and R^1 are cumbersome groups, a situation may arise where the approach of the reagent to either the nitrogen atom [structure (LIX)] or to the oxygen atoms [structures (LX) and (LXI)] is impossible. Thus the failure of a reported attempt at the cyclohexylation of the sodium salt of cyclohexylnitroamines[161] was apparently caused by the high steric constant (−0.79)[178] for the cyclohexyl group.

It follows from the inspection of formulae (LX) and (LXI) that they are non-equivalent. The steric hindrance of the approach of the reagent in compound (LXI) is smaller, since in the case of compound (LX) the interactions with group R are superimposed (see the footnote in Section II). This non-equivalence of the oxygen atoms in the limiting structure (LVI) has been confirmed in practice by the preferential formation of the *trans*-isomers in the alkylation of the silver salts of nitroamines.

The possibility of the existence of geometrical isomers of 1-alkoxydiazene 1-oxides (LI) was already suggested by Umbgrove and Franchimont[159] and was demonstrated experimentally in later studies[77,165]. Analysis of kinetic data for the alkaline hydrolysis of the products of the reaction of silver salts of alkylnitroamines led the authors[77,165] to the conclusion that compounds (LI), which had been believed for a long time to be chemical individuals, are in reality mixtures of the *cis*-isomer (LXIII) and the *trans*-isomer (LXIV). The latter are more resistant to the action of acids, alkalies, and light and can be obtained in a pure form.



(LXIII) (LXIV)

The content of the *cis*-isomer was estimated on the basis of the kinetics of the decomposition of "crude" reaction mixtures, (see Table 2).

Evidently the *trans*-isomers predominate quantitatively in the mixtures of products; a general tendency towards a decrease of the content of the *cis*-isomer with increase of the bulk of the groups R and R^1 is also evident. This tendency was confirmed in another investigation. For example, in the methylation of $RNHNO_2$ by diazomethane both the total amount of the O-isomer and its content of the *trans*-isomer increase in the sequence R = Me < Et < iso-Pr < t-Bu.[179]

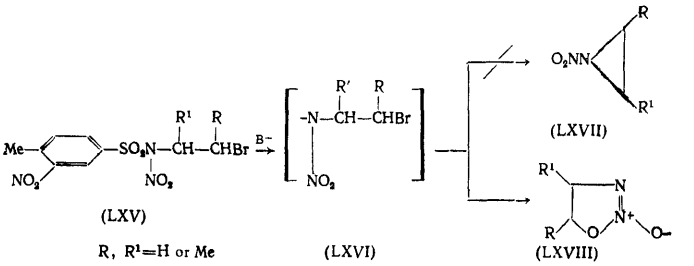
The estimate of the content of the *cis*-isomer in mixtures is not always objective, since its amount depends strongly on the action of light on the silver salt, the reaction time, the excess of the alkylating agent, etc.[77] It has been shown recently that the reaction of dicyclohexylcarbodiimide with ethyl nitroamine leads to the exclusive formation of the *trans*-isomer of the *O*,*N*-diethylnitroamine. This method has been proposed as a promising procedure for the synthesis of the pure product[166].

Table 2. The content of the *cis*-isomer (LXIII) in the reaction of silver salts of alkylnitroamines with alkyl iodides (according to the data of Lamberton and Newton[165]).

$R/RNHNO_2$	R^1/R^1I	Content of *cis*-isomer, %	$R/RNHNO_2$	R^1/R^1I	Content of *cis*-isomer, %
Methyl	Ethyl	15—20	Isopropyl	Methyl	20
Methyl	Isopropyl	15—20	Propyl	Methyl	10
Ethyl	Methyl	30	t-Butyl	Methyl	—

The silver salt of methylnitroamine reacts with methyl iodide, giving rise to a mixture of the *cis*- and *trans*-isomers of *O*,*N*-dimethylnitroamine[169], although it had been postulated earlier that the pure *trans*-isomer was produced in an analogous reaction[165].

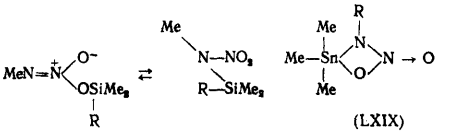
The intramolecular alkylation of nitroamine anions has also been investigated. When alkylnitrosulphonamides (LXV) are acted upon by alkali, the anion (LXVI) is displaced and, as a result of intramolecular alkylation, can give rise to both the *N*-alkyl derivative (LXVII) and the *O*,*N*-alkyl derivative (LXVIII):



(LXV) (LXVI) (LXVII) (LXVIII)

R, R^1=H or Me

In reality the second possibility is realised and it has been shown in relation to the isomeric compounds (LXV, R = H, R^1 = Me) and (LXV, R = Me, R^1 = H) that nitroaziridine (LXVII) is neither the final nor the intermediate product of this reaction[180]. Silylation of methylnitroamine or its silver salt leads to an equilibrium mixture of the *O*- and *N*-derivatives, the content of the *O*-isomer increasing with increasing temperature and in the sequence R = H < Me < iso-Pr ≪ t-Bu.[181,182]



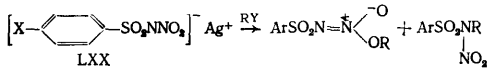
(LXIX)

In contrast to the unstable silyl derivatives, trialkylstannylation of nitroamines or their silver salt leads to stable *N*-derivatives (LXIX).[183] It has been suggested that tin is

coordinated to the oxygen atom of the nitro-group. This conclusion concerning the preferential *N*-stannylation conflicts with the results of the silylation of nitroamine salts[181,182]. Nevertheless, the possibility of *O*-stannylation has been rejected[183] on the basis of the analysis of the infrared spectra of the products.

We have already mentioned the alkylation of nitroamines by diazomethane. Degner and Pechmann[184] showed for the first time that the interaction of methylnitroamine with diazomethane leads to the exclusive formation of the *N*-methylation product, although it was found later that the mixture of products nevertheless contains also the *O*-methylation product[179]. The reaction with isopropylnitroamine gave a mixture of *N*- and *O*-methylation products in proportions of 7 : 3,[162] while other workers[185] ethylated triethylenetetranitroamine with diazoethane and obtained only the *N*-ethyl derivative. Despite certain discrepancies, one may conclude that the *N*-alkylation reaction predominates, but this requires certain comments. If it is assumed that the alkylating species is R^+ or the extremely unstable ion MeN_2^+, then preferential *O*-alkylation is to be expected. A mechanism involving the intermediate formation of a complex of MeN_2^+ with the nitroamine anion has been proposed[146]; this complex subsequently decomposes with evolution of nitrogen. The mechanism is apparently based on the familiar hypothesis by Smith[186] that the combination of diazomethane with a proton and the subsequent attack on methyldiazonium involve the same centre, since, in consequence of its rapid decomposition, the MeN_2^+ cation does not leave the sphere of action of the atom in the substrate. The prospect of testing for prototropic equilibria with the aid of diazomethane is attractive, but unfortunately this possibility is not confirmed in practice[186]. Phenylnitroamine, which has more pronounced acid properties than methylnitroamine, gives rise to the *O*-methylation product on interaction with diazomethane.

The anions of alkylnitroamides (LXX) also exhibit a dual reactivity. Like the anions of primary nitroamines, they can be attacked at the N or the O atom. The reactions of the silver salts of the nitroamides of arenesulphonic acids with alkyl halides give rise to *O*- and *N*-alkylation products[187,188]:



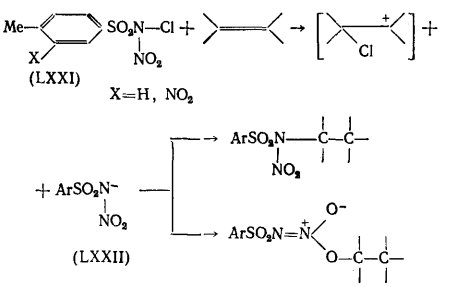
LXX

It has been shown[187] that the ratio of the *O*- and *N*-alkylation products for compound (LXX, X = Me, R = benzyl) is 3.5. Luk'yanov et al.[188] studied in detail the influence of various factors on the ratio of the products of the *O* and *N*-alkylation of compound (LXX). They found that the decrease of solvent polarity in the sequence DMF > acetonitrile > diglyme > ethyl acetate > ether > hexane and the increase of the effective volume of group R in the alkylating agent from the methyl group to the isopropyl group entail an increase of the fraction of the *O*-alkylated product. The latter also increases on passing from alkyl iodides to alkyl bromides.

The salts (LXX, X = Me) form trimethylsilyl and diethylboryl derivatives exclusively via the oxygen atom[189]. The trimethylsilyl group is rigidly bound to the oxygen atom and reversible migration to the nitrogen atom is not observed. Both trimethylsilyl and diethylboryl derivatives are readily hydrolysed and, on raising the temperature slightly, decompose with evolution of N_2O.[189]

Primary *N*-nitroamides have stronger acid properties than nitroamines, but, like the latter, they are alkylated by compounds with small rings (oxirans, aziridines) exclusively at the nitrogen atom[190].

N-Chloro-*N*-nitroamides of arenesulphonic acids (LXXI) add to olefins with formation of *O*- and *N*-alkulation products whose ratio (N/O) increases in the range from 2.0 (cyclohexene, X = H) to 1.4 (styrene, X = H).[191]



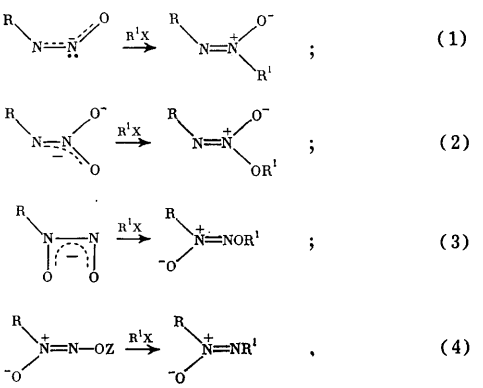
(LXXI)

(LXXII)

Luk'yanov et al.[191] proposed a mechanism involving the primary attack by the positively charged halogen on the double bond with subsequent alkylation of the anion (LXXII). If the intermediate existence of the cation is postulated, the *O*-alkylation product should be formed. In reality mainly the nitrogen atom is attacked. A situation analogous to that in the methylation of the *N*-nitroamines by diazomethane arises[146]. The formation of a cationic intermediate may be postulated, but alkylation proceeds contrary to the Kornblum rule. Additional studies will help to resolve these problems.

VI. CONCLUSION

Generalising the data described, one may note that the alkylation of ambident anions with nitrogen–nitrogen bonds can be divided into reactions of two types. Alkanediazotates of primary *N*-nitroamines give rise to azoxy-compounds with the proximal fixation of the *N*-oxide oxygen atom in relation to the incoming group; *N*-nitrosohydroxylamines and 1-alkoxy-(fluoro, toluenesulphonato)-diazene 2-oxides give rise to isomers with the distal fixation of the oxygen.



(1)

(2)

(3)

(4)

All these reactions represent new methods for the synthesis of azoxy-compounds. For example, reaction (1) was described for the first time in 1969[11] and reaction (4) was

described in 1964[74]§. Reactions involving the alklation of primary nitroamines or *N*-nitrosohydroxylamines were elucidated only after studies by Lamberton (1955–1961), Woodward, Freeman, and Stevens (1963–1969). Whereas the competitive alkylation of the O and C atoms has been investigated in comparative detail in relation to the enolate anions or nitroso-compounds[148,173,193,194] (at least in terms of the volume of factual data obtained), the analogous processes for the O–N or O–O atoms have been studied much less. The number of experimental studies whose main aim was preparative synthesis of the final products in the field indicated has been small; there are also difficulties in structural aspects (see, for example, Section III). Many characteristics of reactions (1)–(4) are therefore still obscure. There are no systematic data concerning the influence of the solvent, the metal cation, the salt concentration in solution, etc. on the alkylation processes. The significant role attributed to the study of the influence of these factors on the activity of ambident anions in recent years makes it probable that studies on these lines will be published in the immediate future.

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§The exchange reaction (4) was investigated for the first time by Wright and coworkers[70] in relation to 1-alkoxy-2-phenyldiazene 2-oxides, but, since they attributed an incorrect formula to the initial reactant, the experimental results were also incorrectly interpreted. Furthermore, they introduced benzylmagnesium halide into the substitution reaction and obtained a compound whose structure, incidentally, served as a touchstone throughout half a century, but was not [properly] elucidated until the study by Woodward[192]. In view of the enormous factual data contained in the publications by Wright and coworkers, Wright can be regarded as the pioneer in this field.

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