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The Formation of the Azoxy-group in the Oxidation of Compounds with Nitrogen-Nitrogen Bonds

V.N.Yandovskii, B.V.Gidaspov, and I.V.Tselinskii

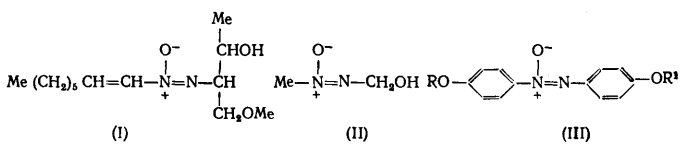
Methods for the formation of the azoxy-group by the oxidation of compounds with nitrogen-nitrogen bonds, namely azo- and hydrazo-compounds, indazoles, and hydrazones, are considered.
The bibliography includes 352 references.

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I. INTRODUCTION

The first example of azoxy-compounds, namely azoxybenzene, was obtained by Zinin in 1845.[1] During the succeeding century only episodic interest was shown in these compounds. The vigorous development of studies on such compounds was stimulated by the presence of the azoxy-group in certain natural products [macrozamin[2-4], elaiomycin (I),[5,6] cycasin[7-17], and LL-BH872α [18-20]] exhibiting a powerful pharmacological activity. It was found that the incorporation in food of the fruit of certain species of the coconut palm can give rise to cancer[7-17], the active principle being methylazoxymethanol (II) substituted in the hydroxy-group by a glycosidic residue[7-17]:



(I) (II) (III)

Methylazoxymethanol proved to be a powerful carcinogen, teratogen, and mutagen[7-17,21-24], the mechanism of the action of which is attributed to the alkylation of the amino-groups in DNA.[12-17,21-24]. Many azoxy-compounds are now known to possess a powerful pharmacological activity[2-48] and the ability of the azoxy-group to induce mutations at a cellular level is used in preparations with tuberculostatic [compound (I)] and fungicidal activities[5,6,18-20]. It is remarkable that chemists were for a long time unable to establish the position of the *N*-oxide oxygen atom in compound (II); it was isolated for the first time as late as 1965 by the enzymatic hydrolysis of cycasin[21].

Another important stimulus of the development of the chemistry of azoxy-compounds was the discovery among azoxyarenes (II) of substances with liquid-crystal properties, exhibiting a positive dielectric anisotropy. In terms of thermal stability and a wide range of the existence of the mesophase, they are superior to many other substances of this type[49,50] and are therefore used in optical instruments, as phases in gas–liquid chromatography (GLC), and also in structural assignments with the aid of NMR and EPR.[49-59]

Finally, the chemistry of azoxy-compounds is of interest in view of the practical applications of pesticides, medicinal preparations, and dyes, whose structures include nitrogen-containing functional groups. The study of ways of converting these groups and the elucidation of the role of azoxy-compounds in the nitrogen turnover constitute an important fundamental task. As a result of the high thermal and chemical stabilities of the azoxy-group, azoxy-compounds serve, together with molecular nitrogen, as "trapping agents" in various changes of the valence state of nitrogen. Azoxy-compounds can be readily obtained from virtually any nitrogen-containing group by oxidation or reduction (including biochemical processes), but the reverse transformations are few and the synthetic value of the azoxy-group is not great.

Familiar monographs[60-67] contain chapters devoted to the azoxy-group. The early studies of the Italian and German schools on azoxyarenes were summarised by Angeli[68] and Bigelow[69]. The individual properties of the azoxy-group—photochemical reactions[70,71] and the Wallach rearrangement[71-73]—have also been considered. The properties of this group are described most fully in Patai's monograph[74] (see also the relevant reviews[75,76]).

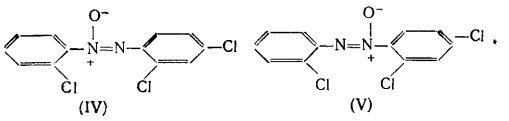
In the present review we shall consider methods for the synthesis of the azoxy-group by the oxidation of compounds with a nitrogen–nitrogen bond. Studies published up to the end of 1979 are discussed.

II. THE NOMENCLATURE OF AZOXY-COMPOUNDS

Publications on the nomenclature of azoxy-compounds[63,67,69] show that there is no unanimous point of view on this problem. The general name "azoxy-" for the group $-N=N^{+}-$ (with O^{-} on the N^{+}) is used most frequently. If the group is linked to two identical substituents, the old nomenclature, in which the prefix "azoxy-" is placed before the name of the corresponding hydrocarbon [for example, azoxybenzene for $C_6H_5N=N(O)C_6H_5$] is entirely suitable. In the case of an asymmetric substitution at the $-N=N(O)-$ group the IUPAC nomenclature recommends the prefixes *–ONN–* or *–NNO–* to define the position of the oxygen atom[63,67,77]. When the atoms are arranged in the sequence *–ONN–*, the position of the substituent at the group linked directly to the

$\overset{+}{N}-O^-$ fragment is designated by a prime or, in the case of the reverse formulation of the azoxy-group (*–NNO–*), the prime denotes the position of the substituent at the group not linked to the NO fragment.

For example, in this nomenclature compound (IV) is called 2,2′,4-trichloro-*ONN*-azoxybenzene and compound (V) is 2,2′,4-trichloro-*NNO*-azoxybenzene:



(IV) (V)

Owing to their inconvenience and ambiguity, the IUPAC rules have not found extensive applications in complex cases.

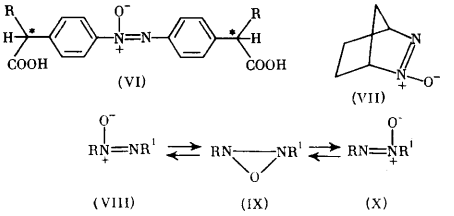
After the publication of the review of Spence et al.[70], the terminology employed by them began to be actively employed. Thus substituents in an aromatic ring linked to the $\overset{+}{N}-O^-$ fragment are given primed numbers and substance (IV), for example, is called 2,2′,4-trichloroazoxybenzene. At the same time a system of alphabetical designations is introduced. α-Compounds is the name given to isomers in which the $\overset{+}{N}-O^-$ fragment is linked to the smaller (phenyl relative to naphthyl) or less substituted aryl. These rules constitute a slight modification of the system of alphabetical designations introduced by Angeli (for examples, see Refs. 61, 62, and 69). At the same time, a nomenclature in which azoxy-compounds are designated as substituted diazene *N*-oxides[78] or di-imide *N*-oxides[79], has been used. The Chemical Abstracts Nomenclature (introduced from Volume 76) is the most promising, unambiguous, and consistent with the nomenclature of other functional groups (–N = N–, –N(O) = N(O)–, $>\overset{+}{N} = N^-$, etc.]. It is based on the name diazene oxide in which numerals 1 and 2 denote the positions of the substituents and the oxygen atom. However, this system is very cumbersome.

The terminology introduced by Moss and Love[80], in which the group linked to the $\overset{+}{N}-O^-$ fragment is designated as proximal and the group remote from the fragment is designated as distal, is suitable for asymmetrically substituted azoxy-compounds. Similarly, the position of oxygen at the nitrogen atom, adjoining the group Z in XN = N(O)–Z, is designated as proximal in relation to Z and the opposite position is designated as distal.

III. ISOMERISM OF THE AZOXY-GROUP AND STRUCTURAL ASSIGNMENTS

Several types of isomerism are possible for azoxy-compounds: the azoxy-compounds–oxadiaziridine valence isomerism, the *cis-trans* isomerism, and the isomerism based on the position of the oxygen atom at the nitrogen atom.

The azoxy-compound–oxadiaziridine isomerism is a special case of the ring–chain valence isomerism in a triad system; the total number of combinations of the CNO atoms has been examined by Greene and Hecht[81]. The asymmetry of the azoxy-group was first demonstrated by Angeli by chemical methods and was later confirmed by physicochemical studies[61–67,72]. Final evidence was provided by the resolution into optical isomers of the *trans*-azoxy-compound (VI, R = Et),[82] formed when the *meso*-azo-compound is oxidised, by the formation of the racemate and the optically active compound (VI, R = Me),[83] and by the asymmetric synthesis of the *cis*-azoxy-compound (VII)[84]:



(VI) (VII)

(VIII) (IX) (X)

After the asymmetry of the azoxy-group as well as the erroneous nature of certain reports of the isolation of oxadiaziridines had been firmly demonstrated, much effort was devoted to the synthesis of this cyclic form.

Numerous attempts to detect 2,3-diaryloxadiaziridines (IX, R,R^1 = aryl) proved fruitless. Neither treatment of azoxy-compounds with strong acids[71,72,85], nor their irradiation[71,86–94,97,98], nor the oxidation of *trans*- or *cis*-azoarenes[95–97], nor other reactions[87] yielded the three-membered ring. However, these negative results did not resolve finally the problem of whether or not the migration of oxygen from $N_{(1)}$ to $N_{(2)}$, i.e. the transformation (VIII) → (IX) → (X), is possible. Together with the categorical view that azoxy-arenes are incapable of such transformation[85–87], reports claiming to demonstrate the possibility of the migration of oxygen in individual instances are being constantly published[92–94,99,100]; for a discussion of this question, see Refs.71, 72, 87, and 99.

The attempt to isolate aliphatic-aromatic oxadiaziridines (IX, R = Ph, R^1 = Me, or Et) in the photoisomerisation of the azoxy-compounds (VIII) and (X) was also unsuccessful. However, the fact that the photolysis of compound (VIII) yields compound (X) and that the addition of O_2 does not affect the results of photolysis apparently indicates the intermediate formation of compound (IX).[101] The difficulty of isolating oxadiaziridines with aryl substituents can be understood if account is taken of the lability of the analogous *N*-aryloxaziridines in relation to the *N*-alkyl derivatives[102,103]. However, it is remarkable that the azoxy-compounds (X, R = Ph, R^1 = Me or Et) are not converted into compounds (VIII),[101] while the latter are the main products of the oxidation of the corresponding diazenes[104].

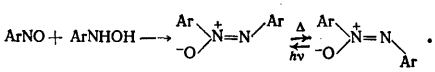
The attempts to synthesise oxadiaziridines with alkyl substituents were more successful. Compounds (IX, R = R^1 = t-Bu,[81,105] n-Bu,[81] or iso-Pr[106]) were obtained by the photolysis of the corresponding azoxy-compounds, into which they are reconverted at the usual temperatures with a half-life of several hours. The oxadiaziridine (IX, R = Me, R^1 = t-Bu) proved to be unstable[81] and *cis*-oxadiaziridine is not formed on photolysis of compound (VII).[81] In a recent study[107] the methods of synthesis and the properties of oxadiaziridines were carefully investigated.

The possibility of the migration of oxygen in the azoxy-sulphones (VIII, R = Ar, R^1 = SO_2Ar^1) via the intermediate formation of an oxadiaziridine has been examined[108,109] (cf.Neiman et al.[86]).

The second type of isomerism of azoxy-compounds, namely *cis*(*E*)–*trans*(*Z*) isomerism, is a consequence of the double bond between the nitrogen atoms. In the acyclic series *cis*-azoxy-compounds are obtained by the photochemical isomerisation of the corresponding *trans*-isomers[70,87–91,93,97–99,106,107,110] or by the oxidation of the *cis*-azo-compounds at reduced temperatures[95,97,106,111,112].

Having analysed the initially seemingly puzzling results of Reisserts's study[113], Muller and coworkers[114,115] showed that the condensation of hydroxylamines with nitroso-compounds in an alkaline medium yields a mixture of *cis*- and *trans*-azoxyarenes, while under neutral conditions only the

trans-isomer is formed:

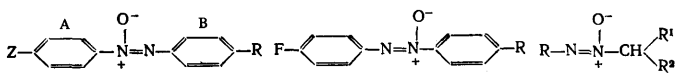


The validity of the structural assignments for pairs of isomers has been confirmed[116-118], but the influence of the pH of the medium has not so far been satisfactorily explained[119].

Aliphatic *cis*-azoxy-compounds can be obtained in a mixture with the *trans*-isomers by the thermolysis of acid-catalysed opening of the oxadiaziridine ring[106,107]. The observation that the azoxidation of *trans*(*Z*)-azoisopropane yields a certain amount of the *cis*(*E*)-azoxy-derivative together with the *trans*-isomer is also remarkable[107].

Acyclic *cis*-azoxy-compounds are unstable substances which are converted into the *trans*-isomers at the usual or slightly elevated temperatures. The mechanism of this transformation is obscure, but is apparently analogous to the *cis*–*trans* isomerisation of azo-compounds[87,98]. The instability of the *cis*-azoxy-compounds is associated solely with their easy conversion into the *trans*-isomers and not with the loss of functionality. Skeletal azoxy-compounds, in which the *cis*–*trans* transition is impossible, are highly stable[120] and can be obtained by various methods—by oxidising the N = N compound, by the interaction of vicinal nitrogen-containing groups, etc. A reliable method now exists for the identification of *cis*-azoxy-compounds, which made it possible to correct individual erroneous assignments to the *cis*-series[20,101,121]; nevertheless, acyclic *cis*-azoxy-compounds are still being inadequately investigated.

The third type of isomerism—the isomerism based on the position of the nitrogen atom at $N_{(1)}$ or $N_{(2)}$—is a consequence of the asymmetry of azoxy-group. Thus ring A in azoxybenzene (XI, Z = R = H) is deactivated in relation to electrophilic reactions; on the other hand, ring B is readily brominated, nitrated, etc.[61-64,68,69] and the azoxy-group in the distal position acts as an *ortho-para*-directing substituent, while in the proximal position it is *meta*-directing. The transmission of electronic effects via the conjugation chain in compounds (XI, Z = F) and (XII), determined from the chemical shifts of the ^{19}F signal in NMR spectra, takes place with different transmission factors and confirms the anisotropy of the polarisability of the π-system of the azoxy-group[112,122]. In aliphatic compounds (XIII) the group R in the distal position exhibits a tendency towards homolytic elimination[123], while the group RR^1CH in the proximal position can be converted into a functional group, for example, via the corresponding carbanion, and then subjected to classical addition, dehydration, etc. reactions[80]:



(XI) (XII) (XIII)

The need to synthesise substances with specific properties is dictated by the necessity to solve the problem of the location of the oxygen atom in azoxy-compounds. Infrared and ultraviolet spectroscopic methods are hardly useful for this purpose. In the aliphatic series the structural assignments of the *trans*-isomers are based on Freeman's classical study[104] using ^1H NMR; the systematic data of Snyder et al.[124] and also those of Taylor and coworkers[107,119] may prove useful for the *cis*-isomers. In the case of azoxyarenes the chemical shifts of the protons in the *o*- and *p*-positions as well as the signals of the methyl groups in the *p*-positions (for example, in azoxytoluene) are different as a result of the distal and proximal orientations of the aryl substituents[53,95,125]. ^1H NMR using shift reagents is more fruitful[53,54,126-128]. Few mass-spectrometric data are available as yet[125,129-134].

It is now possible to distinguish certain approaches to the solution of the problem: firstly, the search for new specific methods of synthesis which do not require structural proof for each individual compound; secondly, the determination of the general characteristics of the synthetic reactions in order to unify the methods for the separation and identification of the isomers. By combining all these tasks, investigators are developing methods for the simplest and fastest determination of the structure, which is demonstrated by the spectroscopic studies quoted above.

IV. OXIDATION OF AZO- AND HYDRAZO-COMPOUNDS

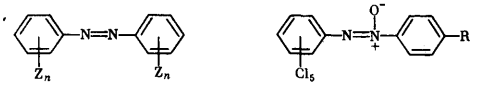
The oxidation of azo-compounds by peracids is preparatively the most convenient method for the introduction of the azoxy-group. Starting with the studies of Angeli[135-139], this procedure has been frequently used by a number of workers (see the relevant reviews of the early studies[68,69,140]). The reaction is equally applicable to aromatic and aliphatic compounds and the oxidation of *cis*- and *trans*-azo-compounds proceeds with retention of the geometry of the N = N bond[63,95,106]. The oxidation of azoarenes has been most fully studied; the investigations by Badger and coworkers[111,141,142] played a major role in explaining the mechanism of this process. It was shown that the oxidation of azobenzenes[111,141] and other azoarenes[142] by perbenzoic acid is a bimolecular reaction, the rate of which increases with electron density at the nitrogen atoms. The introduction of electron-donating substituents increases and that of electron-accepting substituents decreases the rate of oxidation, the rate constant being satisfactorily correlated with the Hammett σ constants[141] (apart from some deviation of the points for *p*-NO_2 and *p*-MeO, the best correlation was achieved with the σ* constants[143]). The oxidation of *cis*-azobenzene is 50–60 times faster than that of the *trans*-isomer and the ratio $\lg(k_{cis}/k_{trans})$ is fairly constant in the range 20–30 °C. Badger and coworkers explained this by the fact that the *trans*-azobenzene molecule is planar and there is a possibility of the delocalisation of electrons over the entire conjugation chain. Owing to the steric interaction of the phenyl groups, in the *cis*-isomer they are displaced from the plane of the azo-group by 56° and the coplanarity of the system is infringed[111] (see also, Webb and Jaffe[95] and Mitchell and Phillips[112]). This decreases the degree of conjugation and the localisation of electron density at the neighbouring nitrogen atoms, which leads as a consequence to an increase of the rate of interaction with the electrophile (the peracid)†. [111]

The influence of two substituents in the *m*- and *p*-positions in azobenzene on the rate of oxidation corresponds to the expectation based on the sum of their σ constants. The oxidation of 2-(2-naphthyl)-1-phenyldiazene yields a mixture of

† The difference between the heats of formation of the *cis*- and *trans*-isomers of azobenzene is approximately 10 kcal,[144] makes an additional contribution to the free energy of activation, and explains the increase of the rate of oxidation of the *cis*-isomer. The corresponding quantity for stilbene is small (3.0 kcal),[145] which is reflected in an insignificant difference between the rates of epoxidation of its *cis*- and *trans*-isomers[146,147].

isomeric azoxyarenes in proportions corresponding to the ratio of the rate constants for the oxidation of the individual azobenzene and 2,2′-azonaphthalene[142].

The conclusion that the oxidation of the N=N bond by peracids has an electrophilic mechanism was supported by experimental findings in a number of subsequent studies. Thus azobenzenes# (XIV) were not oxidised by the peracids usually employed (performic, peracetic, and perbenzoic) and only trifluoroperacetic acid converted them into azoxybenzenes. Similarly, compound (XV) [125] is obtained on treatment with this oxidant, while other oxidants give rise to its formation at a low rate and only at elevated temperatures.

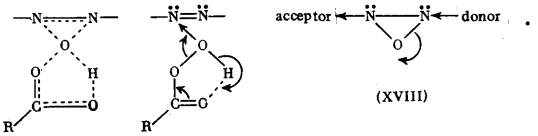


(XIV) (XV)

$Z_n = F_5$ [148] (cf.[149]); $Z_n = F_4$ [148,149]; $Z_n = Cl_5$ [125] (cf.[150]).

Since the oxidising capacity of the peracid varies in parallel with the pK_a of the corresponding acid (the acyloxy-anion of a strong acid is more stable and is therefore satisfactorily eliminated), it follows that, among all the peracids, CF_3COOOH is the strongest oxidant[151]. The need for its employment arises as a consequence of the depletion of the N=N bond in electrons.

All these findings lead logically to the question whether or not the oxidation of azo-compounds involves a spirocyclic transition state (XVI) analogous to that proposed by Bartlett for the oxidation of the C=C bond[151-154] or whether the reaction proceeds via direct transfer of electrophilic oxygen to the nitrogen atom in (XVII) [96,154,155]:



(XVI) (XVII) (XVIII)

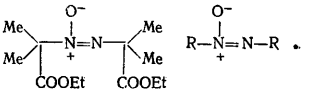
The conclusion that the addition to the N=N bond is asymmetric apparently also follows from a study[142] in which it was shown that the oxidation of azo-compounds with different substituents leads to a mixture of two isomers in proportions corresponding to their electron-donating influences. If the transition state has the symmetrical structure (XVI), then its conversion into the final product via (XVIII) leads to a ratio of isomers inversely proportional to their electron-donating influences. This idea was developed in another investigation[96].

The hypothesis of a symmetrical structure of the transition state (XVI) and the consequent possibility of the formation of oxadiaziridines was also disproved by an investigation of the oxidation of *cis*-azoarenes[95]. Among aliphatic compounds, where the stability of oxadiaziridines is sufficiently high for their identification[81,101,107], the low-temperature oxidation of azo-t-butane, for example, yields the azoxy-compound immediately, which was demonstrated by infrared spectroscopy[81] (see also Taylor et al.[107]).

At the present moment the question of the structure of the transition state in the oxidation of the N=N bond by peracids must be regarded as resolved in favour of the asymmetric structure. Comparison of the rate constants for the oxidation of stilbenes[146,147,151] and azobenzenes[111,141] showed that the latter are oxidised at a rate higher by an order of magnitude. This may also constitute a piece of evidence showing that the interaction of the electrophilic oxygen with a free electron pair is preferred to the interaction with the π-electron system. The electrophilic oxidation of different heteroatoms (N, P, and S) has been considered in a number of studies[154,155] and analysis of the available data shows that it is usually faster than epoxidation. In full conformity with this observation, it was found[156,157] that the oxidation of compounds with the C=C–N=N or C=C–C–N=N structural unit leads to azoxidation and not to the formation of epoxides.

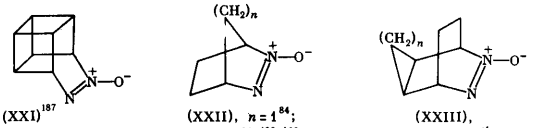
The oxidation of the N=N bond by peracids is widely used in practice, particularly for the synthesis of azoxyarenes (see the relevant reviews[61-64,68,69,74-76,140], the examples already quoted, as well as a number of other communications[158-178]).

Azoxidation has been used much less among aliphatic compounds. Thus Aston and Parker[179] were the first to obtain a ditertiary azoxy-compound (XIX) by treating an azo-compound with the H_2O_2 + MeCOOH mixture:



(XIX) (XX)

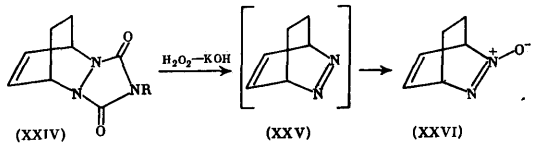
Subsequently, it was shown that this oxidising mixture is sometimes unsuitable for the preparation of diprimary and disecondary azoxy-compounds, since the transformation of the initial azoalkanes into hydrazones, catalysed by acetic acid, is faster than azoxidation. The difficulty was overcome by employing aromatic peracids, for example, perbenzoic acid; a satisfactory yield of the corresponding azoxy-compounds (XX, R=Me, n-Pr, iso-Pr, or $PhCH_2$) was then obtained[3,4]. The fact that the MeCOOH + H_2O_2 mixture is not equivalent to MeCOOOH has been frequently mentioned[151]. The employment of the former creates an excess acidity of the medium owing to the high concentration of MeCOOH at the beginning of the reaction and the slow stage involving equilibration with the peracid. It is therefore not surprising that azoisobutane (XX, R=iso-Bu) (disecondary azoalkane) was oxidised smoothly under the influence of MeCOOOH.[104] Evidently, both peracetic and perbenzoice acids are very suitable for the oxidation of ditertiary and disecondary azoalkanes. The oxidation of diprimary azoalkanes, for example, azobutane and particularly compounds of the type of ω-azotoluene, where the possibility of a prototropic transformation into hydrazones is facilitated, requires the use of aromatic peracids[104,180]. The use of trifluoroperacetic acid may be complicated by secondary reactions of the latter with azoxyalkanes[81,181,182]. Compounds are known in which the structural unit N=N(O) is a partly aromatic system (see, for example, a number of reviews[183-185]). In 1962 Freeman also obtained several Δ^2-pyrazoline *N*-oxides[186], which are isomeric with azoxy-compounds. Nevertheless, the ease with which cyclic azo-compounds are oxidised to skeletal azoxyalkanes (XXI–XXIII) and the high thermal stability of the latter were found to be somewhat surprising.



(XXI)[187] (XXII), $n = 1$[84]; $n = 1$-4[124,188,189] (XXIII), $n = 1, 2$[124,188,189]

Here and throughout the review the *trans*-configuration of the azo- and azoxy-compound is understood unless stipulated otherwise.

In order to obtain the azoxyalkanes (XXI)–(XXIII) as well as certain others, for example (XXVI), bicyclic and polycyclic triazolinediones were oxidised with hydrogen peroxide in an alkaline medium[120,188–190]:

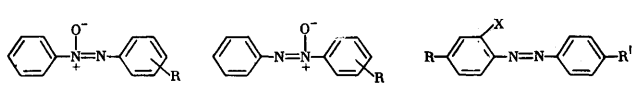


A similar synthetic procedure, involving the removal of the protective group with simultaneous oxidation, had been used earlier to synthesise 3-alkyldiazirines[191,192], since the latter are not oxidised further to the corresponding azoxy-compounds[193] (see also, Snyder et al.[120]). However, the azo-compound (XXV), which could have been a precursor of compound (XXVI), is extremely unstable (the decomposition period at −78 °C is ≤30 s), while the transformation (XXIV) → (XXVI) proceeds at much higher temperatures (80–100 °C). Evidently, azoxidation in an alkaline medium involves a sequence other than (XXIV) → (XXV) → (XXVI).[120,124]

Apart from triazolinediones, other precursors of azo-compounds, for example dialkyl- or diaryl-hydrazines, can be oxidised. *sym*-Disubstituted hydrazines are oxidised even on storage in air; various oxidants, including H_2O_2, are used to convert them into azo-compounds[194–196]. It is therefore natural that azoxyarenes are obtained by the single-stage oxidation of hydrazobenzenes with an excess of a peracid[197,198]. It is of interest that, for a 1:1 reactant ratio, an azoxy-derivative may be formed together with the azo-compound[198], apparently because the rates of oxidation of the NH–NH and N=N groups are comparable.

A serious obstacle to a more vigorous synthetic employment of the oxidation of azo-compounds or their precursors is the formation of isomers with different positions of the *N*-oxide oxygen. As early as 1911, Angeli concluded that the oxidation of 3- and 4-nitro-azobenzenes does not yield individual substances[136,137]; this conclusion was later confirmed[99,171–173,197].

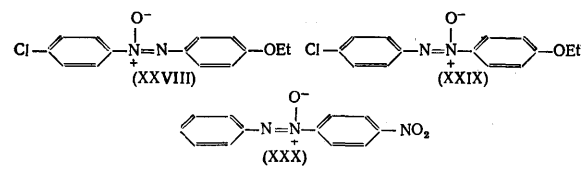
Two reviews[68,69], giving a systematic account of early data, and numerous reports by Italian chemists[136–139,158–173] quote tens of examples of the formation of a mixture of azoxyarenes in the oxidation of azobenzenes by peracids, but the lack of a quantitative estimation of the isomeric composition greatly reduces the value of these studies. Kinetic measurements of the rates of oxidation of azo-compounds seemingly suggested the possibility of estimating the ratios of the isomers from the σ constants of the substituents in azobenzenes[141,142] (see also, Mitsuhashi[96]). However, Risaliti[172,173] found that, although electron-accepting groups do direct the oxidation preferentially to the distal position, there is *no linear* relation between the ratios of the isomers and the σ constants:



R = *m*- and *p*-NO_2, SO_2Ar, NHAc, F, Cl, or Br.

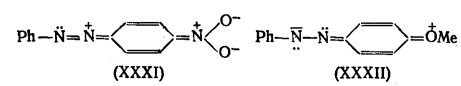
The picture is more complex for disubstituted azobenzenes. Thus it has been shown[54,199,200] that, when compounds (XXVII, X = H) with substituents R and R^1 = H, Me, MeO, COOR, or Cl in different combinations, are oxidised, the standard ratio of the isomeric azoxy-benzenes (1:1) is hardly altered. The explanation of these data requires the use of more detailed features of the azo-group and leads to a fairly complex picture. Firstly, the authors of the above reports[54,199,200] worked with the H_2O_2–MeCOOH–(H_2SO_4) § mixture, while the kinetic experiments were performed with perbenzoic acid[96,141,142] and Badger[111] emphasised specially that perbenzoic acid did not contain even an admixture of benzoic acid. Evidently, in the presence of acids stronger than acyl hydroperoxides, the nitrogen atom of the asymmetrically substituted azoarenes, which should have been preferentially azoxidised, is protonated (and hence blocked). The sum of these effects leads to an average ratio of the isomers. This hypothesis is supported by the finding that, in the presence of the chelate dipivaloylmethanemolybdenum(VI), t-butyl hydroperoxide oxidises 4-methoxyazobenzene exclusively to a single isomer[133]; the mechanism of the action of this oxidant is analogous to the mechanism of electrophilic oxidation by peracids, but the reaction is not complicated by protonation. At the same time peracetic and perbenzoic acids lead to a mixture of azoxy-compounds.

Other observations which can be interpreted from these standpoints have also been made. Thus the oxidation of 4-chloro-4′-methoxyazobenzene with hydrogen peroxide in 100% acetic acid yields compound (XXVIII), while the isomer (XXIX) is formed in 80% acetic acid[201]:

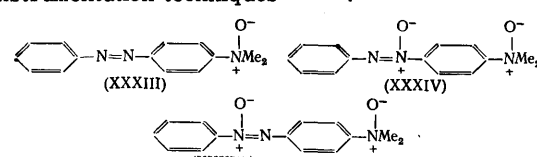


The oxidation of 4-nitroazobenzene with 30% H_2O_2 in acetic acid similarly gives a mixture in which the α-isomer (in Angeli's terminology) of compound (XXX) predominates, while anhydrous hydrogen peroxide in acetic acid gives preferentially the β-isomer[99].

Secondly, the presence of groups similar to NO_2 and MeO in the *p*-position leads to an appreciable contribution of the boundary structures (XXXI) and (XXXII) to the ground state of substituted azobenzene. Evidently, the nitro-group deactivates both nitrogen atoms, but the distal atom is deactivated much less; the methoxy-group activates both positions, but the distal position is activated to a much greater extent. Accordingly, in the azoxidation of *p*-nitro- and *p*-methoxy-derivatives (XXXI) and (XXXII) the distal isomer predominates in both cases[133]:



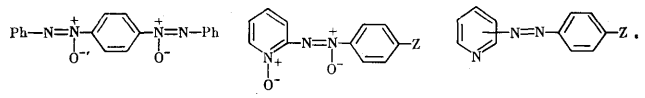
The difficulty of taking into account all these factors is effectively illustrated by the oxidation of *p*-dimethylamino-azobenzene. Starting with the work of Angeli in 1915, who attributed structures (XXXIII) and (XXXIV) to the monoxidation and dioxidation products[68,202], there have been periodic attempts to explain the course of these reactions in terms of the new advances in the electronic theory of structure and instrumentation techniques[203–207]:



§ The mixture H_2O_2–MeCOOH to which small amounts of sulphuric acid have been added is sometimes used in the synthesis of azoxyarenes without isolating peracetic acid by distillation.

Whereas the structure of the primary oxidation products (XXXIII) gives rise to no doubts so far, the views of investigators diverged as regards the dioxidation product, which can have structure (XXXIV) [68,202,205,207] or (XXXV) [204,206].

The divergence of views concerning the directing effect of the dimethylamine oxide group extends also to other instances. The azoxy-group is an electronic analogue of the $Me_2\overset{+}{N}\overline{O}$ group and, since Angeli attributed structure (XXXIV) to the product of the dioxidation of dimethylaminoazobenzene, he defended formula (XXXVI) also for the product of the dioxidation of bisazobenzene[208,209]:

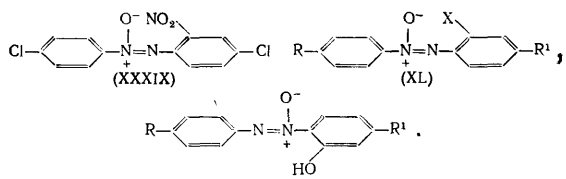


(XXXVI) (XXXVII) (XXXVIII)

According to other investigators, the dimethylamine oxide group directs oxidation to the distal position. Therefore its analogues, for example, the pyridine oxide group, act similarly and azoarenes (XXXVIII, Z = H [210-214] or NO_2 [215]), in which the nitrogen atom in the pyridine ring is oxidised first, give rise to the azoxy-derivatives (XXXVII).

The competitive involvement of nitrogen atoms in the oxidation of the compound (XXXVIII, Z = NMe_2) by peracids is of interest. The nitrogen of the NMe_2 is oxidised first, being followed by the nitrogen of the pyridine ring, while the N = N bond is unaffected[216]. Certain examples of competitive oxidation processes have been examined in a review[69].

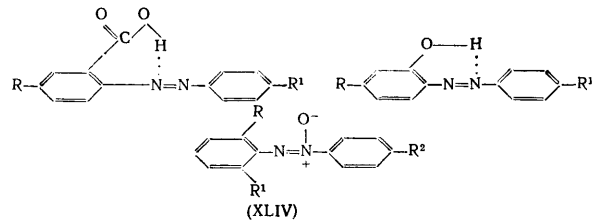
An important feature of the oxidation reactions of azoarenes is the marked influence of *ortho*-substitution on the position of the *N*-oxide oxygen atom. The influence of *ortho*-substitution (OH, COOMe, OCOPh) on the course of the oxidation of azoarenes was first investigated by Bigiavi and coworkers[159-163], but they did not obtain an unambiguous result. Other investigations were more decisive in this respect[54,197,217,218]. It was shown, for example, that the azoxybenzenes (XXXIX), (XL), and (XLI) are formed as the sole products in the oxidation of the corresponding azobenzenes:



(XXXIX) (XL)

(XLI)

These seemingly relatively incompatible results were explained and developed by Berwick and Rondeau[54]. They found that, in the presence of the *ortho*-substituents X = Me, MeO, Cl, COOMe, or COOH in one of the aryl groups, azobenzenes give rise preferentially to isomer (XL) with the distal location of the oxygen atom relative to this group regardless of the nature of R and R^1. The selectivity (the quantity defined as the ratio of the isomers formed with the distal and proximal location of the oxygen atom) varies for different X and, although the effective volume of the COOMe group is greater than that of COOH, the process selectivity is greater in the presence of COOH than in the case of COOMe. The influence of the *o*-hydroxy-group, which caused a complete rearrangement of the position of the oxygen atom in favour of the proximal isomer (XLI) is still more surprising. All these findings were explained by Berwick and Rondeau[54] (see also Dziomko and Dunaevskaya[217]) by the fact that the influence of the *ortho*-substituent is in general related to the shielding of the neighbouring nitrogen atom. On the other hand, the introduction of specific substituents (COOH, HO), capable of forming a hydrogen bond with the N = N group, increases the selectivity of the β-oxidation (for COOH) or, on the contrary, leads to a complete rearrangement (for the OH group) ¶:

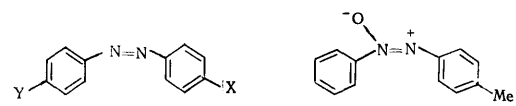


(XLIV)

Protonation of the distal nitrogen atom (and hence its deactivation in relation to oxidation) creates an unprecedented situation where the group in the *ortho*-position directs oxidation to the proximal position[54,217]. It is therefore natural that the oxidation of 2-alkyl-2'-hydroxyazoarenes yields exclusively a single isomer[217].

In the presence of two substituents in the 2- and 6-positions in the phenyl group, their directing effect is greatly enhanced and the oxidation of such azo-compounds by peracids[167,222] or the CrO_3–HNO_3 mixture[223,224] leads to only the distal isomer (XLIV).

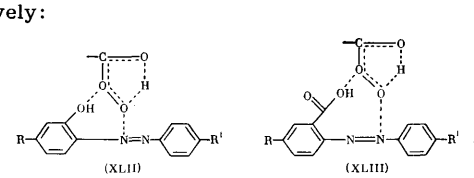
In the oxidation of the *cis*-azoarene (XLV, Y = H, X = Me) it was possible to isolate only one isomer (XLVI). However, it was shown that both isomers are formed in reality, but the azoxy-compound with the proximal location of oxygen in relation to the tolyl groups is converted much more readily into the corresponding *trans*-isomer and compound (XLVI) and it was therefore not possible to identify it[95]:



(XLV) (XLVI)

In the oxidation of compounds (XLV, Y = F, X = Me, MeO, or CF_3) one isomer was also obtained; it was postulated that the oxygen atom is located in the proximal position relative to the fluorine-containing aryl group[112]. In the case of *cis*-azoarenes (XLV, Y = H, X = Cl or Br) only one *cis*-azoxy-compound was also isolated, but its structure was not determined[95].

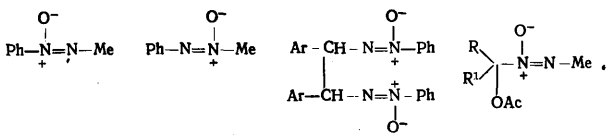
¶ Another explanation of the directing effect of hydroxyl-containing substituents can be the acceleration of the azoxidation of the N = N bond in the proximal (for the OH group) or distal (for COOH) position as a result of the additional stabilisation of the transition complex (XLII) or (XLIII) respectively:



(XLII) (XLIII)

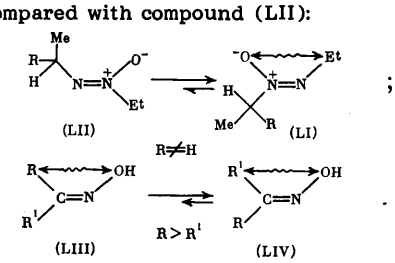
The formation of a hydrogen bond facilitates the elimination of the anion. Examples of the acceleration of the reactions by neighbouring groups as well as the consequence of hydrogen bonding in the epoxidation of allyl alcohol, *o*-allyl-phenols, etc. are well known[219-221].

The problem of the location of oxygen in the oxidation of aliphatic-aromatic azo-compounds and asymmetric azoalkanes by peracids has not been studied systematically and only a few observations have been made. The oxidation of methylphenyldiazene yields predominantly the azoxy-compound (XLVII) with a small admixture of the isomer (XLVIII)†.[104] Similarly the azoxy-compound (XLIX) was obtained in the oxidation of the bisazo-compound[121] and the location of oxygen agrees with Freeman's data[104], already quoted, concerning the preferential formation of compound (XLVII) compared with compound (XLVIII):



(XLVII) (XLVIII) (XLIX) (L)

The oxidation of α-acetoxyazoalkanes gives rise to azoxy-compounds [L, $R = R^1 = Me$, $R, R^1 = (CH_2)_5$],[226] although the oxygen atom in the natural products macrozamin[2-5] and cycasin[9,12,13,21], containing methylazoxymethanol as the aglycone, is located in the proximal position relative to the methyl group and not in the distal position as in compounds (XLVII) and (L). In this connection one should recall that irradiation at 254 nm of the azoxyalkanes (LI) or (LII) in hexane leads to a steady-state mixture of two isomers in the proportions (LI) : (LII) = 1.28,[227] which reflects the weak steric interactions of the alkyl group with the oxygen atom in compound (LI) compared with compound (LII):

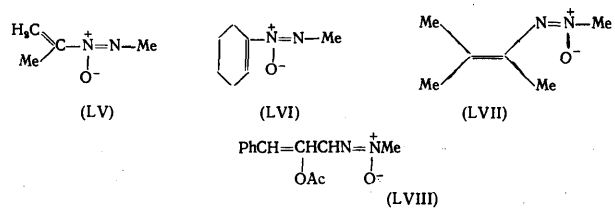


(LII) (LI) (LIII) (LIV)

Similarly the Z-configuration (LIV) is preferred in the case of the ketoximes (LIII) and (LIV).[228]

The question of the stability of the isomeric azoxyalkanes for asymmetric substitution at the $N_{(1)}$ and $N_{(2)}$ atoms, arising in the photochemical reactions and on opening of the oxadiaziridine ring, has been discussed[107].

The natural antibiotics and carcinogens elaiomycin[5,6] and LL-BH872α [18-20] are α,β-unsaturated azoxy-compounds and this is why several studies have been devoted to the oxidation of model compounds with the structural elements N=N–C=C and N=N–C–C=C. The corresponding azoxy-compounds (LV)–(LVII) [156] and (LVIII) [157] were obtained, but the regioselectivity of the oxidation process was not discussed by the authors:

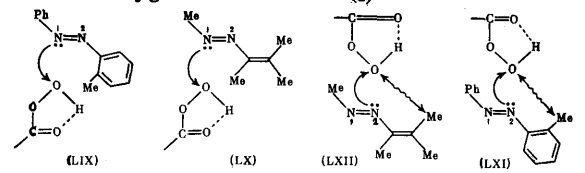


(LV) (LVI) (LVII)

(LVIII)

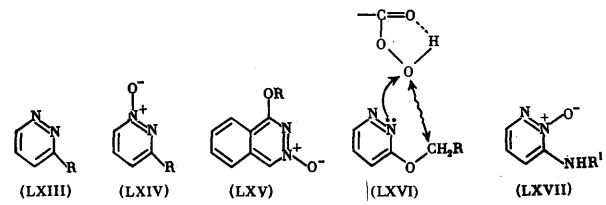
† We may note incidentially that the oxidation of phenylazoformamide yields $PhN(O)=NCONH_2$,[48,225], i.e. oxygen is also located at the nitrogen atom of the aryl group.

All these data on the oxidation of aliphatic and aliphatic-aromatic azo-compounds do not throw light on the question which factors determine the attack by oxygen of a particular nitrogen atom in the N=N bond, namely the inductive, resonance, or steric effects of the substituents. Nevertheless, many experimental data concerning the isomeric composition of azoxy-compounds can apparently be explained on the hypothesis that the location of oxygen in azoxidation is determined by the kinetic parameters of the irreversible reaction and is strongly subject to the steric effect of the groups located at the N=N bond. Distal groups have a weak influence in the approach of electrophilic oxygen [see compounds (LIX) and (LX)], while the influence of the proximal group is more significant [see compounds (LXI) and (LXII)] and in the oxidation reactions of the azo-compounds listed below oxygen is located at $N_{(1)}$:



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

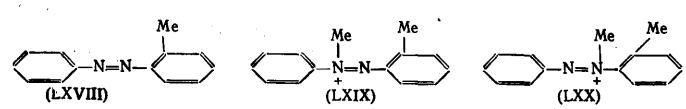
Data for the oxidation of 3-substituted pyridazines (LXIII) [185,229] confirm the marked influence of the substituent on the course of oxidation. For example, when R = Me, a mixture of *N*-1- and *N*-2-oxides is obtained[185,229,230], while for R = MeO, EtO, PrO, or $C_6H_5CH_2O$,[185,229-233], the products are only the *N*-1-oxide (LXIV). The oxidation of 1-alkoxyphthalazines yields the *N*-3-oxides (LXV) [229,234,235].



(LXIII) (LXIV) (LXV) (LXVI) (LXVII)

The structure (LXVI) is not formed [cf. (LXI) and (LXII) [54,197,217]]. The 2-oxide (LXVII) is formed exclusively from the compounds (LXIII, $R = NH_2$ [185,229,236-239] or NHR [1,185,229,240]), and the analogy with the proximal directing effect of the *o*-hydroxy-group in the oxidation of azoarenes[54,217] is evident.

It is of interest to compare the azoxidation reaction with other processes involving electrophilic addition to the N=N bond. Thus Fergusson[241] investigated the quaternisation of azoarenes by methyl fluorosulphonate and found that the azoarene (LXVIII) gives rise to a mixture of isomers (LXIX) and (LXX). The distal isomer is known to predominate appreciably in azoxidation[54].



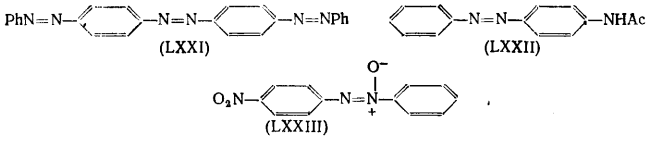
(LXVIII) (LXIX) (LXX)

This can be explained by the fact that the quaternisation is a reversible reaction and leads to a product ratio determined by process thermodynamics, while azoxidation is irreversible and the final isomer ratio reflects the results of a kinetically controlled reaction. A comparative study of the steric factors in the oxidation and quaternisation of pyridines has been described by Foucart et al.[242].

The irreversible nature of the azoxidation reaction has been confirmed experimentally. For example, the oxidation of methylphenyldiazene yields the isomer (XLVII),[104] which is converted by photolysis into the isomer (XLVIII).[101] Since

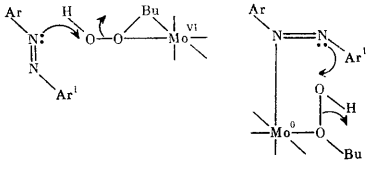
equilibrium conditions are apparently obtained on irradiation of azoxy-compounds and substance (XLVIII) cannot be converted into (XLVII),[101] the isomer (XLVIII) is evidently thermodynamically more stable than the isomer (XLVII).

Apart from the difficulty of identifying the structural isomers, the peracid method suffers from yet another disadvantage, associated with the effect of the peracid on other functional groups. Thus the oxidation of 4-aminoazobenzene involves primarily the amino-group and the product is trisazobenzene (LXXI).[243] The latter can be oxidised further, giving rise to monoazoxybisazobenzene and trisazoxybenzene[243,244]:



Protection of the amino-group by the acyl group in compound (LXXII) favours the "normal" oxidation of the N = N bond with formation of the proximal and distal isomers[243], but in this case nitroazoxyarene (LXXIII) is formed as a side product owing to the hydrolysis of the amide linkage[169,170,245]. Several examples of secondary reactions in azoxidation were examined above and are dealt with more fully in Bigelow's review[69].

Apart from peracids, other reagents have also been used occasionally for the azoxidation of the N = N bond. A remarkable variant of the peracid method is oxidation of azo-compounds by alkyl hydroperoxides in the presence of transition metal complexes[133]. Coordination to transition metal complexes causes the polarisation of the O—O bond and the peroxides, which are usually homolysed at this bond, become sources of electrophilic oxygen[153,246-249]. The complexes $Mo^{VI}[MoO_2(dipivaloylmethane)_2]$ or $Mo^0[Mo(CO)_6]$ with t-butyl hydroperoxide oxidise substituted azobenzene to azoxy-compounds, while vanadium(IV), manganese(III), and cobalt(II) complexes, which promote the homolytic decomposition of t-BuOOH, proved to be inert[133] (for the principles of the selection of the transition metal, see Gould et al.[249]). Two different types of transition states, taking into account the selectivity in the location of oxygen at the N = N bond for the molybdenum(VI) complex and the statistical distribution of the isomers for zero-valent molybdenum, have been proposed:

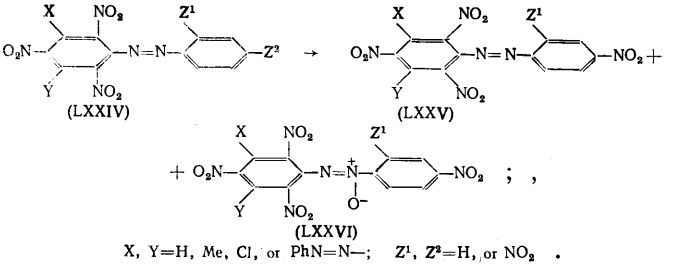


The involvement of transition metals and mild reaction conditions constitute a similarity between these processes and those in living organisms, and, together with the oxidation of diacylhydrazines to azoxyalkanes, by-passing the azo-compound stage[120,124], and the fixation of oxygen by hydrazyl radicals[250], demonstrates the multiplicity of pathways leading to the formation of the N = N(O) group under conditions close to those in biological systems. A number of azoxy-compounds[2-21] and those formed in the microbiological or photochemical oxidation of amines[251-253] can be obtained not only by the classical reaction between RNO and RNHOH, but also by the direct microsomatic oxidation of azo- and hydrazo-groups by *N*-oxidase. The detection of the familiar carcinogens and mutagens azoxymethane and methylazoxymethanol in the product of the metabolism of 1,2-dimethylhydrazine evidently demonstrates the validity of this point of view[254,255]. The general problems of the biogenetic relations in the series of nitrogen-containing functional groups have been examined in a number of studies[17,22].

The azoxidation of the N = N bond in the nitration of azobenzenes was first reported by Petriew[256] and this observation was confirmed by subsequent studies[223,224,257-261]. The nitration process is normally accompanied by the formation of the *p*-isomer, but if both *p*-positions are blocked, as in 4,4'-dichloro-[257,260] or 4,4'-dinitro-azobenzene[259], then, together with nitration products, the *o*-azoxy-derivative is formed.

The formation of 2,4,3'-trinitroazoxybenzene in the nitration of azobenzene[258] has also been reported (cf. Sharnin and Buzykin[223]; for the review of early studies on the nitration of azo- and azoxy-arenes, see, Werner and Stiasny[259]). Among aliphatic compounds, oxidation by nitric acid has been used to synthesise azoxycyclohexane from azocyclohexane[3], but a negative result was obtained for 1-azoheptane and 2-azopropane[4]. When the menthylhydrazone of menthone was treated with nitric acid, the product was azoxymethane[262].

A detailed study showed[223,224] that the nitration of azoarenes (LXXIV) by various reagents (98% HNO_3, HNO_3–H_2SO_4, and HNO_3–CrO_3) leads to mono- and dinitration products (LXXV) and also to azoxy-derivatives (LXXVI):



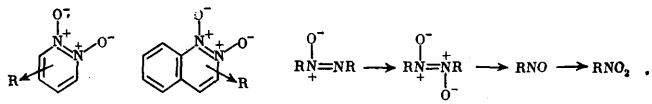
X, Y=H, Me, Cl, or PhN=N–; Z^1, Z^2=H, or NO_2 .

Sharnin and Buzykin[223,224] observed several interesting features: (1) the azoxy-compounds (LXXVI), with a distal location of oxygen relative to the picryl group, are formed in oxidation processes; (2) the azo-compounds (LXXIV, $Z^1 = NO_2$, Z^2 = H or NO_2) do not give rise to azoxy-compounds at all or produce them with much difficulty under the influence of the most powerful oxidant ($CrO_3 + HNO_3$); (3) the accumulation of electronegative substituents in the picryl ring of compounds (LXXIV, X, Y = Cl) hinders the formation of azoxy-compounds.

Evidently, these features are the same as those in the electrophilic oxidation of azoarenes by peracids, in particular the pronounced directing effect of the *ortho*-substituent, the retardation of oxidation in the presence of 2,2'-substituents, the distal directing effect of electron-accepting groups at the N = N bond, and the need for a more "electrophilic" oxidant on accumulation of electronegative substituents at the N = N bond. All this apparently constitutes evidence supporting an electrophilic mechanism of oxygen transfer to the azo-group.

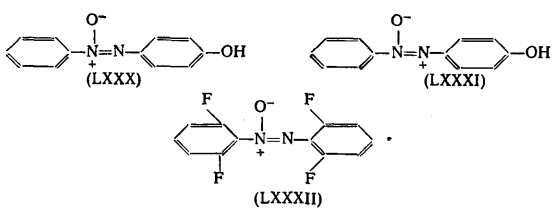
The formation of azoxy-compounds is observed in the oxidation of azo- and hydrazo-arenes by chromium trioxide in MeCOOH,[256] dimethyl sulphoxide at 110 °C,[198] ozone,[263] hydrogen peroxide[188-190,264,265] (cf. Singh[182]), and a mixture of hydrogen peroxide and sodium tungstate[266]. Studies have been published on the use of polymers containing peracid groups for the oxidation of azobenzene[267,268]. Such polymers are obtained, for example, by modifying cross-linked structures with polyacrylic acid.

The oxidation of azo-compounds results in the incorporation of one oxygen atom. It is of interest to attempt to introduce also a second atom and thus form azo-dioxy-derivatives. Among heteroaromatic compounds, such cases have been described. For example, when pyridazines[269], cinnolines[270-274], and benzocinnolines[274] are acted upon by peracids under conditions more severe than those in the usual azoxidation, the dioxides (LXXVII) and (LXXVIII) are obtained together with azoxy-derivatives. The stepwise course of the process was demonstrated by the conversion of the monoxides into the dioxides under the reaction conditions[269-274]:



(LXXVII) (LXXVIII) (LXXIX)

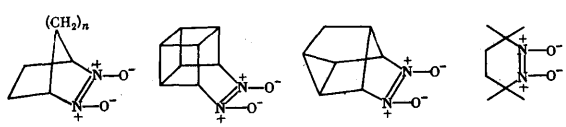
In the case of linear azoxy-compounds it is difficult to detect the individual stages, since on monomerisation and subsequent oxidation of the diazene dioxides (LXXIX) formed, nitro-compounds are produced[202]. Thus compound (LXXX) is oxidised by hydrogen peroxide to nitrophenol[158], which does not, however, demonstrate the validity of the mechanism described and can be explained by the primary effect of the oxidant on the hydroxy-group and subsequent decomposition of the quinonoid intermediate at the nitrogen–nitrogen bond:



(LXXX) (LXXXI) (LXXXII)

In conformity with this hypothesis, it has been found that, in contrast to compound (LXXX), azoxyphenol (LXXXI) is not oxidised by H_2O_2, $KMnO_4$, or HNO_2, since the azoxy-group deactivates the neighbouring aryl group[158,275,276]. On the other hand, indirect data show that the sequence azoxy-compound → azodioxy-compound → nitroso-compound → nitro-compound is possible. Thus the azoxyarenes (LXXXII)[277] and (LXXVI) (see above) are exceptionally resistant to the action of the most vigorous oxidants (CF_3COOOH, HNO_3–CrO_3), since the non-quaternised nitrogen atom is blocked by the *ortho*-substituents and its basicity is reduced due to the electron-accepting effect.

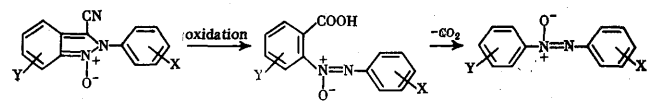
It has been shown in a recent series of studies that diazene dioxides can be obtained by the direct oxidation of the corresponding azoxy- or azo-compounds by hydrogen peroxide, *m*-chloroperbenzoic acid[189,266], and trifluoroperacetic acid[182].



An attempt has been made to explain why the usual monomerisation of nitroso-dimers does not occur in the case of highly strained rings[189,266].

V. OXIDATION OF INDAZOLES

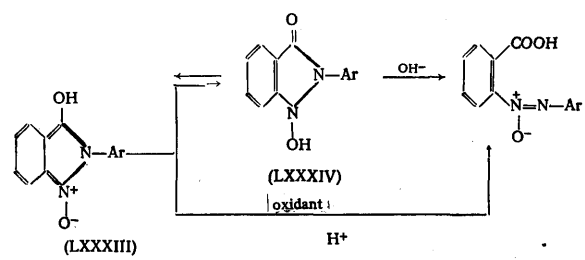
An elegant method of synthesis of azoxyarenes was developed by Behr[278,279]:



Y = H, X = 4-Br, 4-EtO, or 3-NO_2 X = H, Y = 4-Br, 4-EtO, or 3-NO_2.

The comparatively readily available 2-aryl-3-cyanoindazole 1-*N*-oxides, obtained from the corresponding *ortho*-substituted nitrobenzaldehydes (or nitriles of *o*-nitro-mandeleic acids) and arylamines (see the reviews of methods of their synthesis[280,281]) are subjected to oxidative cleavage. Starting with well known compounds, in which the positions of substituents have been determined and none of the subsequent stages of the synthesis entail the loss of asymmetry by the N=N(O) fragment, it is possible to obtain specific isomers of substituted azoxybenzenes. Behr's method played an important role in its time in the solution of this confused problem. We may note that the structural assignments of pairs of isomers of *p*-bromo- and *p*-ethoxy-substituted azoxybenzenes made by this method agree with those of Angeli.

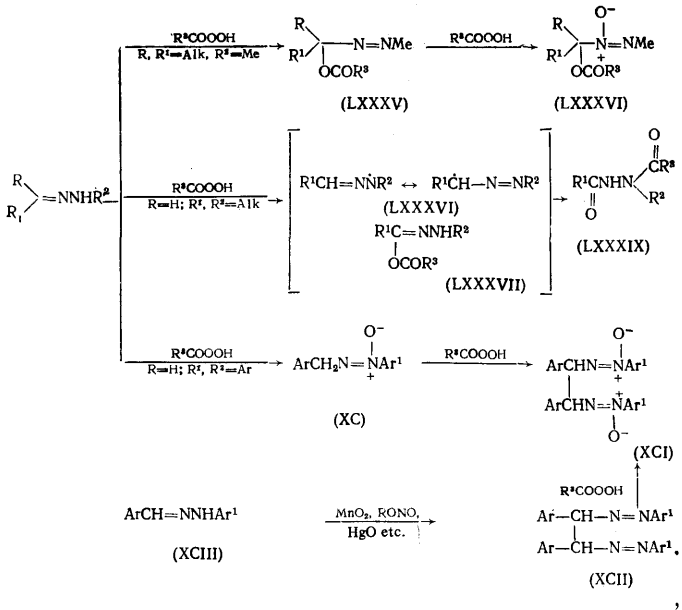
In analysing Behr's procedure for the synthesis of azoxybenzenes, one may conclude that the protection of the 3-position in indazole by the cyano-group is unnecessary since this group undergoes oxidative decarboxylation with formation of 1-hydroxyindazol-3-one (LXXXIV), which is tautomeric with 3-hydroxyindazole 1-*N*-oxide (LXXXIII). Subsequent cleavage of the tautomeric pair in an acid medium [via compound (LXXXIII)] involves the decomposition of the hemiaminal linkage and the nitrone–azoxy-migration of the double bond[186]. The oxidative hydrolysis of the N–CO bond in the intermediate (LXXXIV) proceeds also in an alkaline medium, like the oxidation of compound (XXIV):



(LXXXIII) (LXXXIV) H+

VI. OXIDATION OF HYDRAZONES

Hydrazones are isomeric with azo-compounds, but their oxidation with peracids proceeds quite differently. Typical instances are presented schematically below:



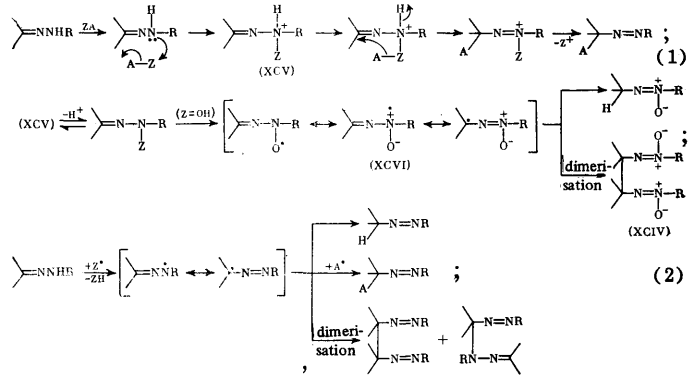
The simplest case is that of the oxidation of alkylhydrazones of ketones (acetone, cyclohexanone).[157,226]. For the ratio peracid : hydrazone = 1 : 1, a mixture of the azo-compound (LXXXV) and azoxy-compound (LXXXVI) is formed; for the reactant ratio 2 : 1, the only product is the azoxy-compound, but in a low yield (17%). The oxidation of alkylhydrazones of α,β-unsaturated ketones (cyclohexenone, cyclopentenone) with one equivalent of a peracid confirms that the primary products are acyloxyazoalkanes[157].

The oxidation of alkylhydrazones of aliphatic aldehydes does not lead to azoxy-compounds, the products being diacylhydrazines (LXXXIX).[226] Different mechanisms, involving intermediate acyloxyhydrazones (LXXXVII) or radicals (LXXXVIII), can be put forward. The oxidation of the methylhydrazone of cinnamaldehyde yields the azoxy-compound (LVIII).[157]

The oxidation of alkyl(aryl)hydrazones of aromatic aldehydes by peracids has been frequently studied[282-289]. Different structures have been attributed to the high-melting products formed as a result of the reaction and, whereas the general view inclined towards the *cis*-azoxy-compounds (XC),[154,288,289] Woodward and Wintner[121] showed that they are in reality bisazoxy-compounds (XCI). In the oxidation of the *p*-bromophenylhydrazone of *p*-chlorobenzaldehyde, they succeeded in isolating the intermediate (XC), which gave rise to a dimeric azoxy-compound (XCI) on further oxidation; thus the primary oxidation product is an azoxy- and not an azo-compound, in contrast to the aliphatic analogue[121]. Compound (XC) had been isolated earlier, but its reactions were incorrectly interpreted (see, for example, Brough et al.[288]). It is also known that the oxidation of the phenylhydrazones of aromatic aldehydes by HgO, MnO_2, $C_5H_{11}ONO$, etc. yields the bisazo-compound (XCII) (together with other products) as a result of the dimerisation of a centred radical[290-293]. The oxidation of this dimer by perbenzoic acid leads to the formation of the bisazoxy-compound (XCI), identical with the product of the oxidation of a hydrazone or the monoazoxy-compound (XC).[121]

The interaction of peracids with an NH group can be interpreted in two ways—from the standpoint of the electrophilic addition of oxygen to the nitrogen or the radical abstraction of hydrogen from the NH group. In the oxidation of the aryl hydrazones of aromatic aldehydes (XCIII) Lynch and Pausacker[286] found a direct relation between the electron-donating properties of the substituent in the aromatic ring Ar^1, linked to the extreme nitrogen atom, and a second-order reaction rate constant, which is consistent with an electrophilic oxidation mechanism (see also Pausacker[283]). However Gillis and LaMontagne[157] defended the radical mechanism involving the primary capture of the NH proton (see also Woodward and Wintner[121,292]).

Accordingly, it is possible to put forward two mechanisms# involving as the primary step the electrophilic addition of a peracid (1) or the radical capture of a hydrogen atom (2) (Z = OH, A = OCOR):



Z = OH, $Pb(OAc)_3$, OH, Hal, RC(=O)O, or NO_2;
A = OCR, OAc, OH, Hal, RCOO, or NO_2.

Mechanism (1), involving the primary (electrophilic) addition of the oxidant to the nitrogen atom, was put forward by Busch and Dietz[294] and still remains attractive. In the specific instance of oxidation by peracids this possibility is supported by the following findings: (1) in the oxidation of a secondary nitrogen atom, for example, in diarylamines, the product is a nitroxy-radical[295-298]; (2) the direct dependence of the rate of reaction of peracids on the electron density at the NH group in compound (XCIII), discovered by Lynch and Pausacker[286], is consistent with the slow stage of the bimolecular reaction (1); (3) the dimerisation of the C-centred radical, containing the complete N = N(O) functional group, leads to the bisazoxy-compound (XCIV), since the isolation of an azoxyazo-product of the monoxidation of the N = N bond in the bisazo-compound (XCII) has not been reported[121,282-289]; (4) the oxidation of the *p*-bromophenylhydrazone of *p*-chlorobenzaldehyde leads to 4,4′-dibromoazoxybenzene as a side product[121], which is apparently a dimer of the fragment obtained in the homolysis of the N = N bond in the intermediate (XCV) or (XCVI).

We may note that the oxidation of the phenyl hydrazones of 2- and 4-formylpyridines with perbenzoic acid involves the pyridine nitrogen atom[299]. The fundamental mechanisms of

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Mechanisms (1) and (2) represent in a general form the mechanisms of the oxidation of hydrazones by peracids, lead tetra-acetate, hydrogen peroxide, halogens, diacyl peroxides, and nitrogen tetroxide.

the oxidation of hydrazones by various reagents have been examined in detail in a monograph[300].

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Thus the methods of synthesis of azoxy-compounds are simple and varied, which is one of the reasons for the great interest in these substances. Nevertheless, both in the series of methods considered here and among other possibilities, the oxidation of azo-compounds is used most frequently as the method of synthesis of azoxy-derivatives. The availability of the initial azo-compounds and the simplicity of the isolation of the final product make the method of practical importance. This is indicated, for example, by numerous patent data on the synthesis of azoxyarenes used as liquid crystals or forming part of such compositions.

Since this review was written, fairly numerous studies on alkoxy-compounds, mainly devoted to the practical applications of liquid crystals and to the study of their physicochemical properties, have been published. The carcinogenic properties of azoxymethane [301-308] and the influence of various substances on the inhibition of carcinogenesis[309-314] are being vigorously investigated. There is much similarity in the action of 1,2-dimethylhydrazine and azoxymethane, but the mechanism of the oxidative transformation of this pair of compounds *in vivo* is obscure; methylazoxymethanol has been detected in the products of their metabolism.

The physicochemical properties of azoxy-compounds are being vigorously investigated. The ^1H and ^{19}F NMR spectra of polyfluoroazoxybenzenes[315], the ^1H NMR spectra of partly deuterated azoxyanisoles[316], the ^{14}N and ^{15}N spectra of various compounds containing the N(O)=N fragment[317,318], and the ^{14}N NQR spectra of *p*-azoxyanisole and related compounds[319] have been studied. Calculations by the CNDO method of the spin–spin coupling constants for compounds containing single and double nitrogen–nitrogen bonds agree satisfactorily with experiment[320]. The ultraviolet spectra of azoxybenzenes[317,321] as well as the mass spectra of azoxybenzenes[321], azoxycyanides ArN(O)=NCN,[322] tetranitroazoxytoluenes[323], and compounds of the type PhN(O)=NOR, where R = alkyl or $CH_2C(OH)R^1R^2$, [324-326] have been examined.

The crystal and molecular structures of deuterated azoxyphenetole[327], *cis*-2-cyclohexyl-1-methyl- and *cis*-1-cyclohexyl-2-methyl-diazene 1-oxides[328], as well as the structure of complexes of azoxybenzenes with chloranil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, etc.[329-331] have been studied. Calculations have been made by the CNDO method of the electron densities, dipole moments, and overall energies of various conformations of *p*-azoxyanisole[332]. The thermo- and photochemical transformations of azoxyalkanes and related oxadiaziridines have been examined[333-335]. New data have been obtained on the photochemical transformation of azoxybenzenes into 2-hydroxyazobenzenes, demonstrating the involvement of the diazonium ion in this reaction[321,336,337]. The radical decomposition of *p*-alkoxyazoxybenzenes in the solid phase under the influence of X-rays has been studied[338].

Oxidation with H_2O_2 + AcOH mixtures has been used for the synthesis of azoxyarenes having the general formula $4\text{-}RC_6H_4N(O)=NC_6H_4R^1\text{-}4$ (R and R^1 are alkyl or alkoxy-groups containing between 1 and 10 carbon atoms), which are widely used as liquid crystals, phases in GLC, dye sensitisers, etc.[321,339-344]. The addition of acid anhydrides, particularly boron trioxide, improves the process[345]. The direct oxidation of mixtures of ArNO and $ArNH_2$ to azoxyarenes, by-passing the stage involving the isolation of the corresponding azo-compounds, has been described in a patent[346]. In all these cases a mixture of isomers was usually obtained. Permaleic acid or the $H_2O_2 + CF_3COOH$ mixture is used for the synthesis of asymmetric azoxy-compounds of the type $4\text{-}RC_6H_4N(O)=NR^1$ (XCVIII), where R^1 = COOMe, CN, or C(O)Ph, which contain electron-accepting groups[347-349]. The azoxy-cyanides (XCVIII, R^1 = CN, R = alkyl, halogen, or NO_2) are of interest because of their microbiological activity[347-350].

It has been shown[351] that the one-electron reduction of $PhN(O)=NC_6H_4NO_2\text{-}4$ by potassium cyclo-octatetraenide in tetrahydrofuran does not involve the migration of the oxygen atom to the neighbouring nitrogen atom. It has also been shown that there is no exchange of ^{18}O between labelled dimethyl sulphoxide and azoxybenzene when their mixture is heated for a long time in toluene[352].

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Zhdanov Leningrad State University

Lensovet Leningrad Technological Institute