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Progress in the Chemistry of Nitroxyl Radicals

E.G.Rozantsev and V.D.Sholle

Methods of obtaining nitroxyl radicals by the dehydrogenation of hydroxylamines, oxidation of amines, reduction of nitro- and nitroso-compounds and radical addition to nitrones are considered. Problems of the stability of nitroxyl radicals and their reactivity are discussed—redox reactions, radical reactions, complex formation, and reaction without use of the unpaired electron. There is a bibliography of 283 references.

CONTENTS

I. Introduction 233
II. Methods of obtaining nitroxyl radicals 233
III. Chemical properties of nitroxyl radicals 236

I. INTRODUCTION

Nitroxyl radicals are compounds which contain the >N–O group with one unpaired electron. The structure of this fragment can be represented as the superposition of two valence structures:

$$>\dot{N}^{+}\!-\!O^{-} \longleftrightarrow >\ddot{N}\!-\!\dot{O}\,.$$

Depending on the effects of conjugation and the polarity of the medium the contribution of the first or second boundary structure to the principal state of the radical can be different.

There have been many studies, theoretical and experimental, to find the electronic structure of the nitroxyl radical. Unfortunately, the various results do not agree satisfactorily. Thus, some investigators[1-3] give values of ~ 0.8–0.9 for the spin density on the nitrogen atom ρ_{π}^{N} for non-aromatic radicals (0.6 for aromatic), whereas others[4-6] give $\rho_{\pi}^{N} = 0.3–0.4$.

Wieland referred to aromatic nitroxyl radicals as nitroxide or azoxyl radicals. In several studies this terminology was later extended to hetero-chain and heterocylic radicals which were non-aromatic in behaviour. Generally speaking, the term "nitroxide", and also "aminoxide" is unfortunate since it does not reflect the radical nature of these species and contradicts the rules of official nomenclature of organic compounds. In the Soviet literature the term "iminoksily" (iminoxyls) is used for non-aromatic nitroxyl radicals.

II. METHODS OF OBTAINING NITROXYL RADICALS

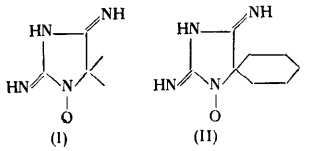
1. Dehydrogenation of Hydroxylamines

The O–H bond of hydroxylamines undergoes homolysis under the action of various reagents and nitroxyl radicals are formed.

In 1901 Piloty and Schwerin[7] obtained the first organic nitroxyl†, porphyrexide (I), by the action of potassium hexacyanoferrate(III) on 1-hydroxy-2,4-di-imino-5,5-dimethylhydantoin; the structure and free radical nature of (I) was established later[9].

† Fremy had obtained the first inorganic nitroxyl ion in 1845 by the oxidation of potassium hydroxylammonium disulphonate with lead(IV) oxide[8].

A spirocyclohexyl analogue of porphyrexide (II) was obtained by the same method in 1944[10]:



(I) (II)

In 1914–1922 Wieland developed a general method for making aromatic nitroxyls which is still widely used. The first stage was the preparation of diarylhydroxylamines:

$$ArNO + XMgAr' \rightarrow Ar\!-\!\underset{\underset{OMgX}{|}}{N}\!-\!Ar' \rightarrow Ar\!-\!\underset{\underset{OH}{|}}{N}\!-\!Ar'$$

The second stage was the single-electron oxidation of the hydroxylamine to a nitroxyl:

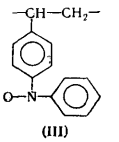
$$Ar\!-\!\underset{\underset{OH}{|}}{N}\!-\!Ar' \xrightarrow{-H^{\cdot}} Ar\!-\!\underset{\underset{O}{|}}{N}\!-\!Ar'$$

Wieland used Ag_2O as the oxidant in the second stage. Diphenyl-, phenyl-*p*-tolyl-, and di-*p*-tolyl-nitroxyls were obtained by this method[11-13]. The first stage of the method can be regarded as a general procedure for obtaining diaryl-, arylalkyl-, and dialkyl-hydroxylamines. In studying the mechanism of this reaction, Murayama showed that the best yields of hydroxylamines are obtained when a large excess of a Grignard reagent is used[14].

Using the Wieland method, Hückel and Liegel[15] obtained phenyl-9-*trans*-decalylnitroxyl in good yield by the action of phenylmagnesium bromide on 9-nitrosodecalin with subsequent oxidation of the hydroxylamine by air.

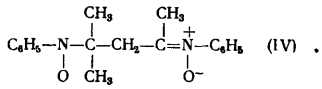
Deguchi and coworkers[16] obtained a series of methyl derivatives of diphenylnitroxyl by the same method.

The macromolecular polyradical (III) was obtained by the reaction of *p*-nitrosopolystyrene with phenylmagnesium bromide followed by oxidation of the hydroxylamine with silver oxide[17]:



(III)

The so-called Kenyon–Benfield radical (IV) is formed in good yield when the condensation product of acetone and phenylhydroxylamine is oxidised[18]‡:

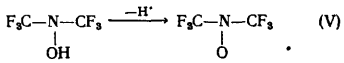


(IV)

Subsequently a series of derivatives of this radical were obtained[19].

Forrester[20] obtained a series of aryl-t-butylnitroxyls by the reaction of ArMgX with t-nitrosobutane and investigated their decomposition products. t-Butylferrocenylnitroxyl was obtained[21] by the action of t-nitrosobutane on ferrocenylmagnesium bromide followed by autoxidation of the hydroxylamine which is formed.

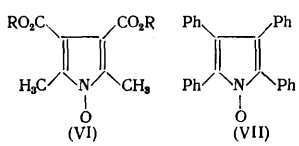
In 1965 Soviet[22,23] and American[24] investigators described the preparation of bis(trifluoromethyl)nitroxyl (V) by the oxidation of the corresponding hydroxylamine:



(V)

The oxidants used were $KMnO_4$, Ag_2O, F_2, and HgO.

In 1963 Rozantsev and coworkers[25] showed that oxidation of certain heterocyclic hydroxylamines of the pyrrol series leads to the formation in the solution of the corresponding nitroxyls (VI):



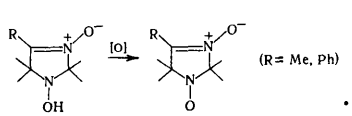
(VI) (VII)

A nitroxyl of similar structure (VII) was isolated by Rio and coworkers[26] in 1968 from the products of the oxidation of 1-hydroxytetraphenylpyrrol by PbO_2.

The same oxidant was used for obtaining acylalkyl-, acylaryl-[27], and arylaminocarbonylarylnitroxyls which are stable in solution[28]. In 1965 Aurich[29] obtained acylphenylnitroxyls by oxidation of the corresponding *N*-hydroxyamides with nickel peroxide[29].

Short-lived aliphatic nitroxyls can be obtained both by the oxidation of hydroxylamines[30,31] and also by photolysis of the latter[31,32].

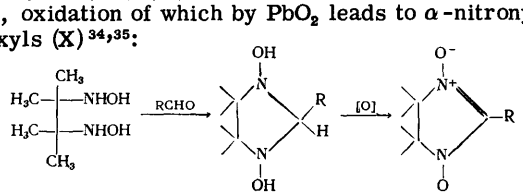
In 1968 Volodarskii and coworkers[33] obtained nitroxyls of structure (VIII) by the oxidation of 1-hydroxy-2,2,5,5-tetramethyl-4-R-3-hydroxyimidazoline by Tollen's reagent or hydrogen peroxide:



(R = Me, Ph)

(VIII)

In the same year Ullman condensed 2,3-bis(hydroxylamino)-2,3-dimethylbutane with aldehydes and obtained 1,3-dihydroxy-4,4,5,5-tetramethyl-2-R-tetrahydroimidazole, oxidation of which by PbO_2 leads to α-nitronylnitroxyls (X)[34,35]:



(IX) (X)

‡ Note added in proof. A cyclic structure has been suggested[283] for (IV).

where R = H, CH_3, C_2H_5, $[CH_2]_{12}CH_3$, CH_2OH, $CH(CH_3)_2$, $CH(OC_2H_5)_2$, C_6H_5, *p*-HOC_6H_4, or *p*-$NO_2C_6H_4$.

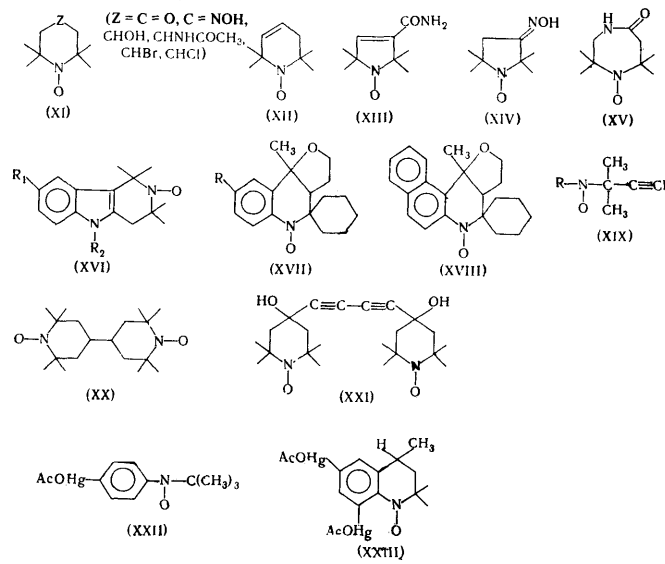
When R = alkyl, the corresponding imidazole can be smoothly oxidised by potassium periodate.

2. Oxidation of Amines

Despite the fact that the preparation of nitroxyls by the oxidation of amines was developed later than the method of dehydrogenation of hydroxyamines, it is now the most important method of making nitroxyls (especially cyclic dialkylnitroxyls).

In 1956 Hoskins[36] recorded the EPR signal of diphenylnitroxyl on passing oxygen into a solution of diphenylamine. Subsequently a large number of nitroxyls was obtained in solution by the oxidation of the corresponding aromatic, aliphatic–aromatic, aliphatic, and acyclic amines. The oxidants used were: hydroperoxides[37–39], hydrogen peroxide with cerium salts[40], RO_2 radicals[41–43], Ag_2O,[44] an alkaline solution of hydrogen peroxide[45], PbO_2,[46] various per-acids[47], the pertungstate ion[48], and benzoyl peroxide[49]. These oxidants can be useful in studying reaction mechanisms and in finding the structure of the nitroxyls.

Oxidation of secondary amines with hydrogen peroxide in the presence of salts of tungstic acid is a convenient method for the preparation of nitroxyls. By this method, developed in our laboratories, stable nitroxyls of the piperidine series (XI) and (XII)[50–53], of hydrogenated pyrrole (XIII) and (XIV)[54,55], of homopiperidine (XV)[56], of carboline (XVI)[57,58], of hydrogenated quinoline (XVII)[59,60], of hydrogenated benzoquinoline (XVIII)[61], aliphatic nitroxyls (XIX)[62], the first non-conjugated biradical (XX)[63], the biradical (XXI)[64], and radicals stable in solution of the benzoxazine, indoline, and carbazole series[65], and organomercury nitroxyls (XXII) and (XXIII)[66] were obtained.



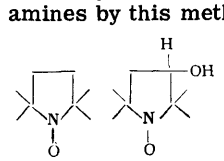
(XI) (XII) (XIII) (XIV) (XV)

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

(XX) (XXI)

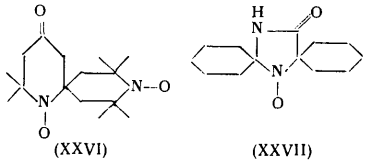
(XXII) (XXIII)

Rassat and coworkers obtained t-butylphenylnitroxyl[67] and certain nitroxyls of the pyrrolidine series (XXIV) and (XXV)[68] on oxidising amines by this method:



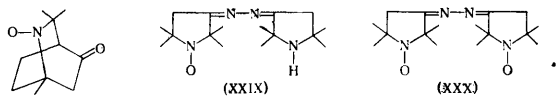
(XXIV) (XXV)

Murayama[69] used the same method to obtain the biradical (XXVI). Then by oxidising 3-oxo-2,5-bicyclohexylimidazoline with hydrogen peroxide in the presence of sodium tungstate in acetic acid medium he obtained the nitroxyl (XXVII)[70].



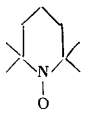
(XXVI) (XXVII)

Oxidation of amines with hydrogen peroxide is readily effected when tungstophosphoric acid and ammonium molybdate are used as catalyst[71]. The monoradicals (XXVIII)[72] and (XXIX)[73] and the biradical (XXX)[73] were obtained by this means. Despite the fact that the use of tungstophosphoric acid accelerates the oxidation the yields of nitroxyls are reduced:



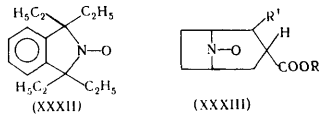
(XXVIII) (XXIX) (XXX)

The mechanism of oxidation of the secondary amines was studied by Lebedev and Kazarnovskii[74], who showed that the oxidant in this instance is the pertungstate ion. They obtained the stable heterocyclic nitroxyl (XXXI):



(XXXI)

Subsequently the method of oxidising amines with hydrogen peroxide in the presence of Na_2WO_4 was extended to tertiary amines. In this way nitroxyls of the isoindoline series (XXXII)[75] were isolated and radicals of the alkaloids of the tropane series (XXXIII) were studied in solution[76]:



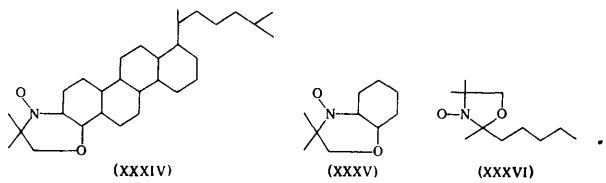
(XXXII) (XXXIII)

In 1964 Tokumaru and coworkers[77] obtained diphenyl, di(methoxyphenyl)-, and di(chlorophenyl)nitroxyls by the action of perbenzoic acid on diarylamines. Di(nitrophenyl)- and dimethoxycarbonyl diphenylnitroxyls are obtained in this instance in very low yields.

Maender and Janzen[78] obtained a large number of triphenylmethyl(alkyl)nitroxyls by oxidation of the corresponding secondary amines with *p*-nitroperbenzoic acid.

Ozone[79], benzoyl peroxide[80], and t-butyl hydroperoxide[81] were used as oxidants in the preparation of nitroxyls from secondary amines.

A specific method for the conversion of ketones into stable nitroxyls has been suggested[82]. On reaction with 2-methyl-2-aminopropanol in the presence of *p*-toluenesulphonic acid, ketones give oxazolidines, which are oxidised by *p*-chloroperbenzoic acid to form the corresponding nitroxyls. The nitroxyls (XXXIV)–(XXXVI) were obtained by this method:

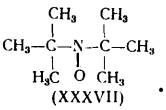


(XXXIV) (XXXV) (XXXVI)

This method was convenient for obtaining certain "spin-labelled" analogues of lipids[83] and steroids[84].

3. Reduction of Nitro-compounds

On reducing $(CH_3)_3CNO_2$ with metallic sodium or polarographically, Hoffmann[85,86] obtained in 1961 di-t-butylnitroxyl (XXXVII):

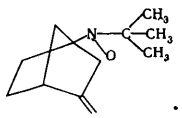


(XXXVII)

In several later studies[87] he made a detailed investigation of the mechanism of this reaction and showed that the primary act of the reduction is the formation of the anion-radical $(CH_3)_3CNO_2^{\cdot-}$ which is then decomposed into NO_2^- and $t\text{-}C_4H_9^{\cdot}$. Recombination of the anion-radical with $t\text{-}C_4H_9^{\cdot}$ leads to the formation of the anion of *NN*-di-t-butylhydroxylamine oxide. The hydrolysis of this salt gives (XXXVII). An analogous mechanism was also proposed for the reactions of tertiary nitroso-compounds with organosodium and organolithium compounds. Several asymmetric nitroxyls were obtained in this way. However, it is noteworthy that the yields of nitroxyls, with the exception of (XXXVII), are extremely low.

The mechanism of reduction of nitro-compounds was also considered by Rassat[88], who used a Grignard reagent[89,90] and $LiAlH_4$ [91,92] as reductants. In studying the reactions of various *para*-substituted nitrobenzenes with t-butylmagnesium chloride[93] the EPR spectra of 22 nitroxyls were recorded, but their structure was judged solely on the basis of the EPR results, which are inadequate.

Rassat and coworkers obtained a stable, optically active nitroxyl (XXXVIII) by the action of t-butylmagnesium chloride on 1-nitrocamphene[94]:

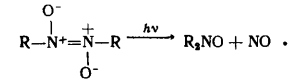


(XXXVIII)

Results have now been obtained[95] which show that not only tertiary but also secondary nitro-compounds can be reduced by this method.

4. Reduction of Nitroso-compounds

In 1964 a group of Japanese investigators described the preparation of nitroxyls in the photolysis of substituted derivatives of nitrosobenzene[96]. Strom and coworkers[97] greatly increased the number of aromatic nitroxyls obtained by this method and found a correlation between the hyperfine splitting constants of the nitrogen atom a_N and the Hammett constant (reviewed by Janzen[98]). Strom and Bluhm[99] assume that the dimer of the nitroso-compound is responsible for the formation of nitroxyls, and that it disproportionates when irradiated:



Despite this assertion a group of Dutch scientists give a strong proof of the formation of nitroxyls directly from the monomeric form[100,101] by the scheme:

$$RNO \xrightarrow{h\nu} R^{\cdot} + NO$$
$$R^{\cdot} + RNO \rightarrow R_2NO^{\cdot}$$

Aliphatic nitroso-compounds form nitroxyls even when irradiated with red light. The formation of nitroxyls also takes place during the thermal decomposition of nitroso-compounds. Tertiary nitroso-compounds thereby yield nitroxyls very readily, but secondary and primary nitroso-compounds require an elevated temperature, which is evidently necessary for the conversion of the dimer into the monomeric form. Ultraviolet irradiation of nitrosoadamantane produced diadamantylnitroxyl[102]. Evidently bistrichloromethylnitroxyl is formed similarly from CCl_3NO.[103]

Photochemical and thermal decomposition of alkyl nitrites evidently also leads to the production of nitroxyls, via the intermediate formation of nitroso-compounds[104-106].

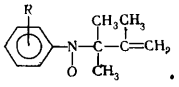
Wajer and coworkers[107] showed that nitroxyls are formed in both the thermal reduction of nitroso-compounds by hydroxylamines[107]:

$$RNO + R'NHOH \rightarrow \underset{\underset{O}{|}}{R-NH} + \underset{\underset{O}{|}}{R'NH}$$

and also in the photochemical reduction of thiophenol[108]:

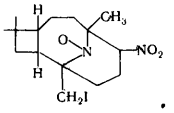
$$2RNO + 2PhSH \rightarrow 2\underset{\underset{O}{|}}{R-NH} + PhSSPh$$

In 1966 Sullivan[109] described the production of alkenylarylnitroxyls (XXXIX) by the reaction of nitrosoaryls with 2,3-dimethylbut-2-ene. Here a hydroxylamine is formed as an intermediate, which is oxidised by the nitrosoaryl or by oxygen into the corresponding nitroxyl:



(XXXIX)

Possibly the formation of caryophyllene "iodo-nitrosite" (XL) takes place similarly[110]:



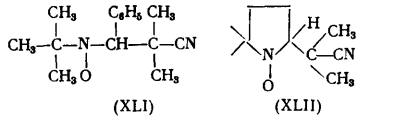
(XL)

As already noted, nitroso-compounds are capable of reacting with active radicals, to form relatively stable nitroxyls. Their ability to do this is now widely used for the collection and establishment of the structure of various radicals formed in polymerisation[111,112], radiolysis[113], photolysis[114,115], and other chemical reactions[101,116-119]. t-Nitrosobutane and nitrosobenzene are most frequently employed as "traps" for radicals.

Nitroxyls are also formed in the reaction of nitrobenzene with stable radicals—triphenylmethyl and 2,4,6-tri-t-butylphenoxyl[120]. A series of aryl-(2-cyanoisopropyl)nitroxyls was obtained by the reaction of nitrosoaryls with the 2-cyanoisopropyl radical[6].

5. Free-radical Addition to Nitrones

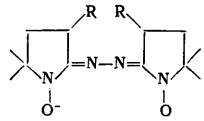
As Brown noted[121], nitrones can give nitroxyl radicals on adding radicals at the double bond. This was confirmed by the experiments of Iwamura and Inamato[122], who obtained the stable nitroxyl (XLI) in 3.2% yield by the reaction of azobutyronitrile with *N*-t-butyl-α-phenylnitrone. The cyclic nitroxyl (XLII) obtained by this method was unstable and rapidly disproportionated in solution:



(XLI) (XLII)

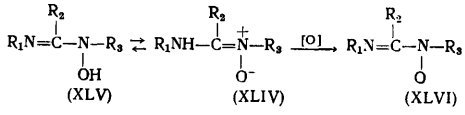
It has been shown[123] that certain nitrones are capable of removing a hydrogen atom from a solvent with the formation of nitroxyl radicals. The ability of nitrones to react with radicals allows them to be used together with nitroso-compounds as "traps" for active radicals[124-126].

Forrester and coworkers[127] described the addition of short-lived radicals to nitrones. They reduced the corresponding azo-1-pyrroline-1-oxide with sodium to give the anion-radical (XLIII)[127]:



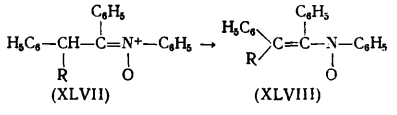
(XLIII)

The oxidation of *C*-aminonitrones (XLIV), which are in tautomeric equilibrium with the corresponding hydroxylamines (XLV), leads to nitroxyls which are stable in solution (XLVI)[128-130].



(XLV) (XLIV) (XLVI)

At the moment the nitrone (XLVII) is produced it is dehydrated with the formation of a derivative of the phenyl(vinyl)nitroxyl (XLVIII)[131]:



(XLVII) (XLVIII)

A survey of the methods of obtaining nitroxyl radicals cannot be concluded without mentioning the old but preparatively convenient method of Meyer[132,133]. In this method oxidation of phenol esters with nitric acid followed by treatment with perchloric acid leads to oxides of diarylammonium salts, reduction of which gives the nitroxides.

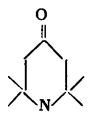
Selective specific reactions of radicals which do not involve the free valency are widely used for obtaining various functional derivatives of nitroxyls[134]. This method of preparation will be discussed in Section III.

III. CHEMICAL PROPERTIES OF NITROXYL RADICALS

1. Decomposition and Stability of Nitroxyls

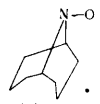
Thermochemical data[135,136] show that the gain in energy of the delocalisation of an electron for the N–O fragment is ~ 30.4 kcal mole^{-1} for heterocyclic nitroxyls.

It is remarkable that 2,2,6,6-tetramethyl-4-oxo-1-piperidyl radical (XLIX)[137] is unstable owing to the impossibility of delocalisation of the unpaired electron.



(XLIX)

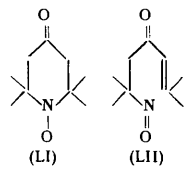
Many heterocyclic amines form nitrones on oxidation[138-141]. Oxidation of heterochain amines leads, through the intermediate formation of nitroxyls, to nitrones[30]. In 1956 Rogers and coworkers[142] proposed that nitroxyl radicals would be stable if their nitrogen atom was framed by tertiary α-carbon atoms, since then the formation of a nitrone would be excluded. Subsequent work showed that actually the absence of α-hydrogen atoms ensures the stability of the nitroxyls. The bicyclic nitroxyls (L)[143], (XXVIII)[72], and (XXXIII)[76], which have α-hydrogen atoms, cannot form nitrones without destruction of a ring owing to Bredt exclusion[144] and therefore should be stable:



(L)

The stability of the nitroxyl (XLI) is explained by the impossibility of its disproportionating to form a nitrone owing to steric hindrance in the region of the reaction centre[122]; the analogous cyclic radical (XLII) is unstable.

According to Murayama[145], the relative instability of (LI) is the result of the carbonyl group activating the hydrogen atoms in position 3 and 5 of the piperidine ring and the radical disproportionating with formation of nitrogen(II) oxide, phorone—of which the nitroso-compound (LII) is a precursor—and 2,2,6,6-tetramethyl-1-hydroxy-4-oxopiperidine:



(LI) (LII)

When irradiated for 15 h the nitroxyl (XIII) decomposes according to the first-order law with formation of the diene (LIII) and probably nitrogen(II) oxide[146]. Photolysis of other nitroxyls proceeds only when the radiation is more prolonged:

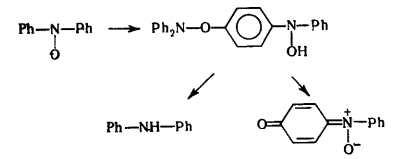


(LIII)

Photolysis of biradicals also leads to their destruction[147], the EPR spectrum of the biradical being transformed initially into the spectrum of a monoradical and only then does the EPR signal of the monoradical start to disappear.

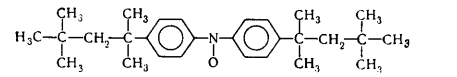
Thermogravimetric investigation of silicon-containing bi- and mono-radicals shows[147] that all these compounds, irrespective of molecular weight and structure, decompose at 195°C with evolution of heat and a decrease in the weight of the specimen.

The decomposition of aromatic radicals was first studied by Wieland and Roth[12], who showed that diphenylnitroxyl disproportionates into diphenylamine and quinone imine oxide:



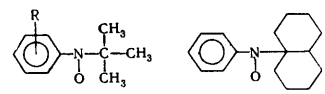
Subsequently an analogous disproportionation was observed with 4,4'-dichlorodiphenylnitroxyl[77]. Aryl alkyl nitroxyls[20,148] and the nitroxyls of the tetrahydroquinoline series[65] decompose similarly, and in the decomposition of certain 4-alkylphenyl-t-butylnitroxyls dimers and trimers were isolated[20].

The most stable series of diarylnitroxyls are 4,4'-dianisylnitroxyl[12,132], 4,4'-dinitrodiphenylnitroxyl[12], 2,2'-dimethyl-4,4',6,6'-tetramethoxydiphenylnitroxyl[132], and the nitroxyl (LIV)[149]; the most unstable are 4,4'-ditolylnitroxyl[11,12]; 2,2',4,4'-tetramethoxydiphenylnitroxyl[132,133], and diphenylnitroxyl[12]. The stability of (LIV) can probably be explained by steric hindrances to dimerisation according to Wieland's scheme:



(LIV)

In studying aryl-t-butylnitroxyls (LV) Calder and Forrester[150] concluded that their somewhat greater stability in comparison with phenyl-t-butylnitroxyl is due to steric factors.



(LV) (LVI)

A noteworthy fact is that unlike phenyl-t-butylnitroxyl (LV; R = H) the structurally similar phenyl-*trans*-decalylnitroxyl (LVI)[15] and the Kenyon–Benfield radical (IV)[18] are stable.

It has been shown[151] that an increase in the stability of the nitroxyls of the hydrogenated quinoline series can be achieved by the introduction into position 2 of the heterocycle of two methyl groups of the geminal type. The introduction of a spiran cyclohexyl screen in this position of the heterocycle sharply increases the stability of the nitroxyls of the hydrogenated quinoline and benzoxazine series[59-61].

The decomposition products and stability of the α-nitronylnitroxyls (XVIII) was not investigated, but it is noteworthy that radicals with alkyl substituents are less stable than those with aromatic[34,35].

2. Redox Reactions of Nitroxyls

Usually the presence not only of an electron donor but also a proton donor is necessary for the reduction of nitroxyls. This evidently explains the stability of nitroxyls in relation to the alkali metals[87].

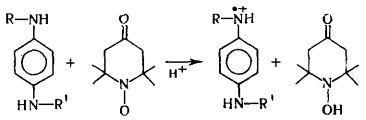
The nature of the products of the reduction of nitroxyl radicals depends on the reductant used or, in hydrogenation with hydrogen, on the catalyst. In the presence of platinum catalyst Adams hydrogenation leads exclusively to the formation of the corresponding hydroxylamines both

for monoradicals[57,84,152,153] and for polyradicals[63]. The use of Raney nickel catalyst leads to the formation of amines[62,154]. Here the reaction proceeds through the stage of formation of hydroxylamine. Reduction with tin(II) chloride in hydrochloric acid[12], zinc in acetic acid[13], and hydrogen iodide also lead to amines[11]. The last reaction enables nitroxyls to be titrated iodometrically[155]. Bistrifluoromethylnitroxyl reacts with gaseous HCl and HBr with the formation of hydroxylamine[23,156]. Phenylhydrazine[12], hydrazine[157], lithium tetrahydroaluminate[158], and formic acid[159] reduce nitroxyls to hydroxylamines. (Lithium tetrahydroaluminate does not reduce the nitroxyl group of the radicals of the hydrogenated pyrrol series[160].) Hydrazobenzene is also a strong reductant of nitroxyl radicals[161]. Kinetic investigation allows the following scheme of reduction to be proposed:

$$>N\dot{-}O + Ph{-}NH{-}NH{-}Ph \rightarrow Ph{-}\dot{N}{-}NH{-}Ph + >N{-}OH$$
$$>N\dot{-}O + Ph{-}\dot{N}{-}NH{-}Ph \rightarrow Ph{-}N{=}N{-}Ph + >N{-}OH\,.$$

In the polarographic reduction of nitroxyls at the dropping mercury electrode[162] hydroxylamines are formed, transfer of an electron preceding the protonisation of the radical.

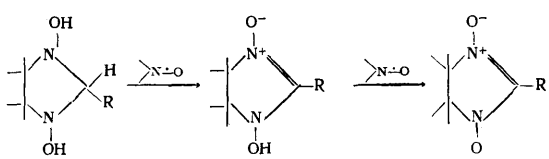
Nitroxyl radicals are widely used in chemistry as mild one-electron oxidants. Thus in acid medium the reaction of nitroxyls with substituted *p*-phenylenediamines leads to the formation of stable cation-radicals[163,164]:



Phenols are oxidised by nitroxyls to quinones[165]; sterically hindered phenols form stable phenoxyl radicals[166].

Nitroxyls of the piperidine series oxidise Fe^{2+} to Fe^{3+}, thereby being converted into hydroxylamines[167]. Interestingly, nitroxyls of the isoindoline and pyrrolidine series do not react with Fe^{2+}. Nitroxyls are also reduced to hydroxylamines by dihydropyridines[168,169] and plastoquinones[170].

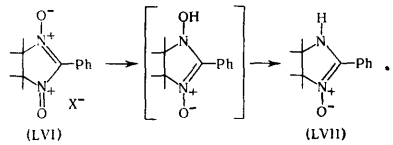
α-Nitronylhydroxylamines are oxidised by nitroxyl radicals to the corresponding α-nitronylnitroxyls[34]:



Nitroxyls are capable not only of accepting electrons but also of donating them, forming highly reactive salts of an immonium oxide $>\overset{+}{N}{=}O,\ X^-$.[34,132,158] To avoid further conversions of the salts of the immonium oxide the oxidation is carried out in an inert medium, using chlorine or bromine as oxidant. Unlike chlorine[171], the use of bromine usually leads to perbromides[172]. Biradicals form salts of an immonium oxide just like monoradicals[158,171,172]. The salts of immonium oxides oxidise primary alcohols to aldehydes and secondary alcohols to ketones, thereby being converted into hydroxylamines. This process can proceed both by a radical and by an intramolecular cyclic mechanism[158]. Nitroxyl halides react violently with tertiary amines with the formation of the amine hydrohalide and a nitroxyl radical. A cation-radical of the amine is formed as an intermediate[158]. Iodometric titration of immonium oxide salts leads to hydroxylamines[158]:

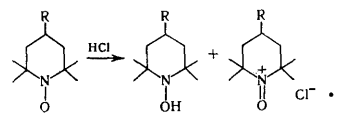
$$>\overset{+}{N}{=}O \xrightarrow{\bar{e}} >N\dot{-}O \xrightarrow[H^+]{\bar{e}} >N{-}OH\,.$$

Immonium oxide salts oxidise aqueous alkali to hydrogen peroxide[35] and are reduced by water to the initial nitroxyl[158]. Boiling (LVI) in alcoholic solution leads to the amine (LVII) through the intermediate formation of a hydroxylamine[35]:



(LVI) (LVII)

Under the action of dry hydrogen chloride, nitroxyls disproportionate according to the scheme[158]:



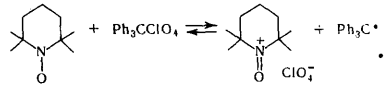
The Kenyon–Benfield radical also reacts[18]. Under the action of dry hydrogen chloride di-t-butylnitroxyl (XXXVII) forms hydroxylammonium chloride[86].

Under the action of acids, nitroxyls rapidly disproportionate[35,158]; the first stage of this process is the reversible protonisation of the nitroxyl group[173,174]:

$$>N\dot{-}O \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} >\overset{+}{N}{-}OH\,.$$

Aprotic acids act specifically on the ketone-radical (LI). The radical disproportionates into hydroxylamine and immonium oxide salt, which decomposes with the formation of the nitroso-compound (LII)[175]. [As already noted[145], the thermal decomposition of the ketone radical also leads to (LII)]. To explain this process it is not necessary to assume the existence of an ion–radical equilibrium in the solution of the nitroxyl.

Reaction of nitroxyls with Ph_3CClO_4 in the presence of oxygen leads to a salt of the immonium oxide[176]:



This process is complicated by the decomposition of Ph_3CClO_4 with the formation of $HClO_4$ under the action of which the nitroxyl disproportionates as usual.

Nitroxyls of the piperidine series are oxidised by Cu^{2+} ions in methanol solution[159]. This reaction does not take place in water. Interestingly, a reduction product of the radical is formed finally—hydroxylamine, probably as a result of the transfer of a hydride ion from methanol to the oxidised form of the radical:

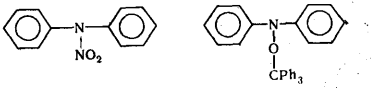
$$>N\dot{-}O + Cu^{2+} \rightarrow >\overset{+}{N}{=}O + Cu^+$$
$$>\overset{+}{N}{=}O + CH_3OH \rightarrow >N{-}OH + \overset{+}{C}H_2OH$$
$$\overset{+}{C}H_2OH \rightarrow CH_2O + H^+\,.$$

A similar process is observed in the reaction of 2,2,6,6-tetramethyl-1-hydroxypiperidine with $Cu(ClO_4)_2$ in triethyl orthoformate solution[177]. In this instance a reduction product of the nitroxyl is also formed—2,2,6,6-tetramethylpiperidine.

Di-t-butylnitroxyl (XXXVII) is capable of promoting the catalytic oxidation of methanol into formaldehyde[178] and is involved in the redox cycle.

3. Radical Reactions of Nitroxyls

Nitroxyls, like all radicals, undergo recombination. (Nitroxyls do not recombine amongst themselves, except for bistrifluoromethylnitroxyl[22]). Diphenylnitroxyl recombines with nitrogen(II) oxide and with triphenylmethyl to form the corresponding derivatives (LVIII) and (LIX)[18].



(LVIII) (LIX)

4,4'-Dinitrophenylnitroxyl is formed with nitrogen(IV) oxide. As Wieland and Roth showed[12], this reaction takes place with saturation of the free valence and with subsequent oxidation of the hydroxylamine formed.

The recombination of diphenylnitroxyl with 2,4,6-tri-t-butylphenoxyl has also been described[179].

Owing to the presence of bulky substituents near the reaction centre, non-aromatic nitroxyls do not react with triphenylmethyl[176] or 1,1-diphenyl-2-picrylhydrazyl[159].

The reaction of nitroxyls with 2-cyanoisopropyl radical, obtained in the decomposition of azoisobutyronitrile, leads to the *O*-2-cyanoisopropylesters of hydroxylamines[159,180].

The presence of phenyl radicals in the system also leads to the corresponding esters, as is observed as side reactions in the reduction of nitroxyls with phenylhydrazine[153].

Nitroxyls are capable of reacting with thiyl radicals formed from benzenethiols[181], thiamine disulphide[182], and tetramethylthiuram disulphide[183].

Aromatic nitroxyls react with both alkyl and peroxide radicals, whereas non-aromatic ones react only with alkyl radicals[184,185], which allows them to be used as acceptors of alkyl radicals[186].

The ability of nitroxyls, in reacting with active radicals, to break radical chains allows them to be used as inhibitors of the radical polymerisation of tetrafluoroethylene[187], chloroprene[188], styrene[189], and 2-vinylpyridine[190]. Nitroxyls can be used as inhibitors for the thermal oxidative destruction of polyamines[191,192], polypropylene[193,194], and polyformaldehyde[194,195], as inhibitors of the photo- and thermodegradation of polyethylene[196] and of poly(vinyl chloride)[197]. Nitroxyls inhibit the autoxidation and polymerisation of styrene[198]. In studying the inhibition of the polymerisation of α-methylstyrene it was shown[199] that the reactivity of the biradicals differs significantly from that of monoradicals.

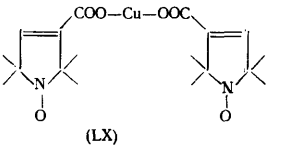
At elevated temperature nitroxyls are capable of removing hydrogen from hydrocarbons[200]. The reactivity of biradicals and polyradicals in reactions involving the removal of hydrogen depends significantly on the spin–spin exchange between the paramagnetic fragments[201].

Kreilick and Weissman[202] observed by the NMR method that in a solution containing a nitroxyl radical and the corresponding hydroxylamines, hydrogen rapidly migrates from the hydroxylamine to the radical. This process resembles the Wieland exchange reaction[13], where the reaction of diphenyl nitroxyl and tetra(methoxyphenyl)-hydrazine leads to di(methoxyphenyl)nitroxyl and tetraphenylhydrazine.

Specific addition reactions of bis(trifluoromethyl)nitroxyl[23,24,156,203–206] will not be discussed in the present review.

4. Complex Formation

The copper salt of 3-carboxy-2,2,5,5-tetramethyl pyrroline-1-oxyl[207] (LX):



(LX)

is diamagnetic, unlike the true biradicals and copper(II) salts, which shows the formation of a complex with participation [in spin pairing (Ed. of Translation)] of the unpaired electrons of both nitroxyl groups and copper ion. Similar complexes with metals of variable valence are formed by paramagnetic Schiff bases[208,209] and xanthogenates[210].

On reacting with palladium salts, di-t-butylnitroxyl (XXXVII) forms the diamagnetic complexes $XPd[ONC(CH_3)_3]_2$.[211] With cobalt halides, (XXXVII) forms paramagnetic complexes which dissociate on dissolution[212].

2,2,6,6-Tetramethylpiperidine-1-oxide forms complexes[177] on reacting with the perchlorates of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}. Nitroxyls form stable complexes with Lewis acids[213,214] and the EPR spectrum shows splitting from the magnetic nuclei of aluminium (for AlX_3) and gallium (for GaX_3).

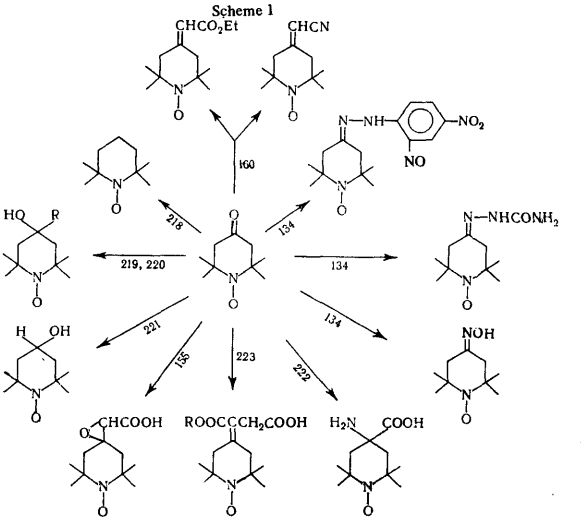
5. Reactions without Use of the Free Valence

The presence in many nitroxyls of the hydrogenated pyridine and hydrogenated pyrrole series of a second functional group separated from the radical centre by a chain of σ-bonds, and the reliable steric screening of the nitroxyl group allowed a class of reactions new in principle to be effected—reactions of radicals without use of the free valence[53,134,215].

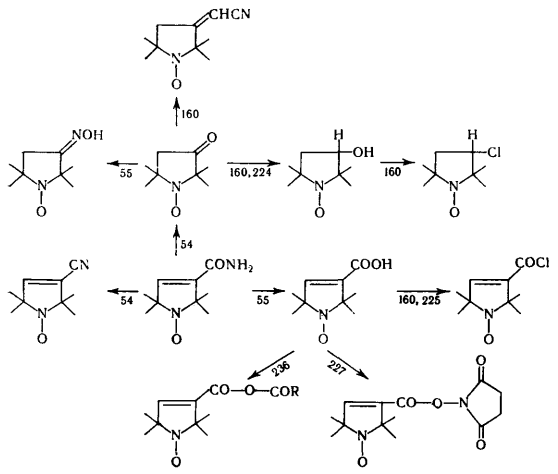
As already noted[216], it is possible that certain reactions of porphyrexide (I) proceed without participation of the unpaired electron, but experimental proof of this has not yet been obtained.

The scheme advanced by Forrester[217] for the reaction of chlorine with (I) is subject to doubt since it was not confirmed experimentally.

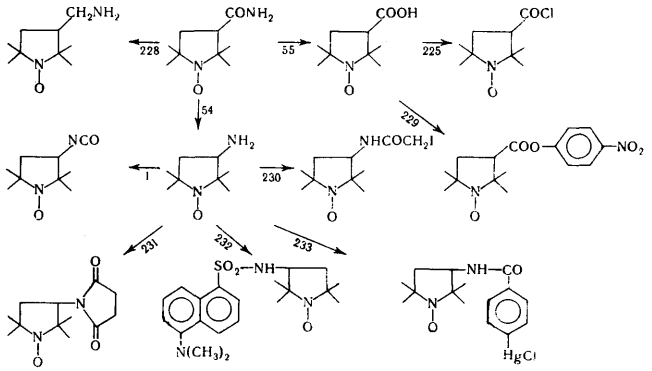
Scheme 1



Scheme 2



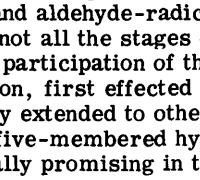
Scheme 3



Schemes 1–3 give an idea of the synthetic possibilities of reactions of radicals not involving the unpaired electron. It is noteworthy that the insignificant yield of paramagnetic products in the reduction of the ketone-radical (LI) with hydrazine and in its reaction with ethylmagnesium bromide undoubtedly show the dominating role in this instance of trivial reactions involving the unpaired electron.

The application to five- and six-membered ketone-radicals of the modified Wittig reaction[234] allowed the corresponding acid- and aldehyde-radicals to be synthesised[160]. However, not all the stages of this preparation are reactions without participation of the unpaired electron.

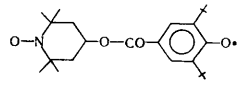
This type of reaction, first effected with ketone-radical (LI), was subsequently extended to other bifunctional nitroxyls. Six- and five-membered hydroxy- and amino-radicals were especially promising in this respect:



(LXI) (LXII)

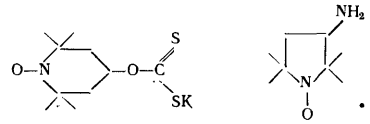
The method of preparation of paramagnetic esters most usually employed is the condensation of an alcohol radical (LXI) with acid chlorides[53,235–237]. In the reaction of alcohols with acid chlorides, hydrogen chloride is released, under the action of which the nitroxyls disproportionate. To avoid this the reaction is carried out in the presence of tertiary amines. As well as acid chlorides, anhydrides[157] and carboxylic acids can be used for the synthesis of paramagnetic esters; in the latter instance dicyclohexylcarbodi-imide was used as condensing agent[228,238]. Reaction of the alcohol-radical (LXI) with the chlorides of dicarboxylic acids leads smoothly to biradicals[239–242]. This method is general for the preparation of polyradicals[242–244]. A series of individual polyradicals was prepared under the action on pyridine solutions of pyrocatechol, hydroquinone, and phloroglucinol of 2,2,5,5-tetramethyl-1-hydroxypyrroline-3-carbonyl chloride[225].

By the action on the alcohol-radical (LXI) of 3,5-di-t-butyl-4-hydroxybenzoyl chloride with subsequent dehydrogenation of the phenol, mixed nitroxyl–phenoxyl biradical (LXIII) was obtained:



(LXIII)

In addition to organic acid chlorides, phosphorus, sulphur and silicon chlorides can be used for obtaining polyradicals[243–247]. Nitroxyl analogues of esters of phosphorus acids were synthesised in this way[248–250]. The alcohol radical (LXI) reacts smoothly with isocyanates. Both monoradicals[53] and polyradicals[239] can be obtained in this way[239]. The reaction of an alcohol-radical with carbon disulphide in alkali leads to the xanthogenate (LXIV), which forms the corresponding biradical under the action of iodine[210]:



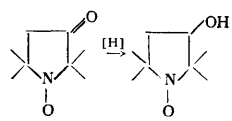
(LXIV) (LXV)

The reaction of the amine-radicals (LXII) and (LXV) with acid chlorides enables a large number of a variety of paramagnetic amides to be obtained[235,236]. The reaction of the amine-radical (LXII) with aromatic aldehydes leads to paramagnetic Schiff bases[208]. The action of di-isocyanates on (LXII) gave the corresponding biradicals[251].

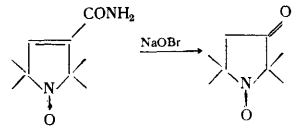
Reactions which do not involve a free valence allowed paramagnetic polymers to be prepared. Thus, the reaction of the alcohol-radical (LXI) with the acid chloride of poly(acrylic acid) leads to the formation of a paramagnetic polymer with a lattice structure[252]. Another approach has also been employed[253]. A paramagnetic polymer is obtained by the polymerisation of the 2,2,6,6-tetramethyl-1-hydroxy-4-piperidine ester of methylacrylic acid.

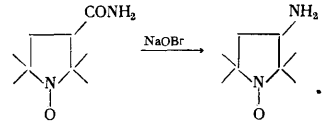
A paramagnetic polymer is also formed in the reaction of sulphur dichloride with diallyl-(2,2,6,6-tetramethyl-1-hydroxy-4-piperydyloxy)silane[254].

Reactions of radicals not involving the use of the free valence can assist in the preparation of nitroxyls which are almost impossible to obtain by other methods. For example, 2,2,5,5-tetramethyl-3-hydroxypyrrolidine 1-oxide cannot be obtained by direct oxidation of an amine, but it is readily obtained by the reduction of 2,2,5,5-tetramethyl-3-oxopyrrolidine 1-oxide with aluminium isopropoxide[255].

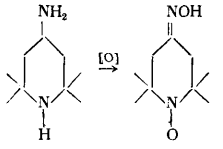


It is also impossible to obtain 2,2,5,5-tetramethyl-3-oxopyrrolidine 1-oxide and 2,2,5,5-tetramethyl-3-aminopyrrolidine 1-oxide by direct catalytic oxidation but they were obtained by the following scheme[54]:



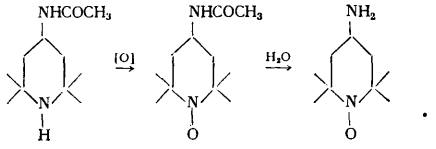


Catalytic oxidation of 2,2,6,6-tetramethyl-4-aminopiperidine with hydrogen peroxide leads to the oxime-radical (LXVI):



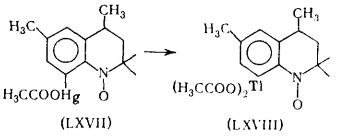
(LXVI)

The amine-radical (LXII) can be obtained by the following scheme[52]:



(LXII)

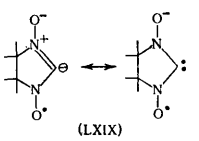
In studying the reaction of the organomercury nitroxyl (LXVII) with thallium(III) isobutyrate replacement of mercury by thallium was observed, with the formation of the organothallium nitroxyl (LXVIII)[256]:



(LXVII) (LXVIII)

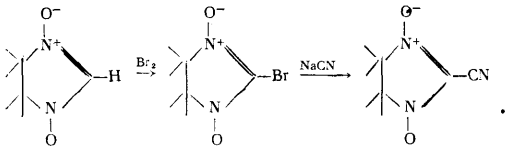
This reaction is evidently an example of a reaction without participation of free valence radicals with a strongly delocalised unpaired electron.

Reactions which do not involve a free valence are also observed in the α-nitronylnitroxyl series (X). Thus (X; R = H) in D_2O rapidly exchanges hydrogen for deuterium[35]. In alkaline media this process takes place with the formation of the anion-radical (LXIX), the existence of which in a solution of potassium dimethylsulphoxide-t-butyoxide was confirmed by the EPR method:

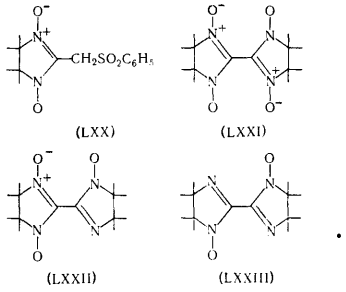


(LXIX)

Replacement of hydrogen by halogen, and then of halogen atoms by hydroxy- and cyano-groups was effected in the α-nitronylnitroxyl series[257]:



Sulphones (LXX)[258] and the conjugated biradicals (LXXI), (LXXII), and (LXXIII)[259] were obtained by such reactions which do not involve the free valence:



(LXX) (LXXI)

(LXXII) (LXXIII)

The change in the form of the EPR spectra of the biradicals on varying the distance between the paramagnetic fragments in conjugation with reactions not involving the free valence can be used for finding the spatial configuration of organic molecules[260].

For example, in the reaction of 2,2,6,6-tetramethyl-4-hydroxypiperidine 1-oxide with the acid chlorides of *cis*- and *trans*-cyclopropanedicarboxylic acids, the corresponding *cis*- and *trans*-esters of these acids were obtained. The *cis*-biradical exhibited a five-component EPR spectrum, which showed the proximity of the two paramagnetic centres. The three-line spectrum of a *trans*-biradical shows the lack of interaction through space of the unpaired electrons, as a result of which electronic exchange is absent.

The discovery and development of the reactions of radicals without involvement of the free valence allowed a new method of investigation to be created, widely used in biochemistry, biophysics, and molecular biology, the so-called "spin-label" method, (see reviews elsewhere[261,262]).

The development of this method, stimulated by the brilliant studies of McConnell, has proceeded in two directions. The first is connected with spin-labelled biomolecules, for example, albumens[263-267], nucleic acids[227,268,269], lipids[270-273], etc. The second direction is the synthesis of paramagnetic analogues and models of physiologically active compounds[78,228,249,250,274,275].

The ability of nitroxyls to migrate in polymers[276] allowed a new method of investigation of molecular motions in polymers[277-279], liquids[280], and biopolymers[281,282] to be investigated—the so-called "spin-probe" method.

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Institute of Chemical Physics,
Academy of Sciences of the
USSR, Moscow