Homosolvolysis

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Nitroxides, when used as solvents, promote the homolysis of a variety of weak bonds. Strong chemical evidence for the formation of free radicals is confirmed by e.s.r. studies in which the formation of free radicals has been monitored. This fission of single bonds of solute molecules dissolved in solvents with unpaired electrons is called *homosolvolysis,* in contrast to the common bond fission observed in polar solvents which is called *heterosolvolysis.*

In polar solvents the fission of bonds in a solute molecule, *i.e.* solvolysis,[1] is associated with the transfer of an electron pair from the solvent to the incipient cation and the acceptance of an electron pair from the incipient anion. The present paper shows that if the solvent has an unpaired electron, a similar fission of bonds in a solute molecule can occur, and this is associated with the transfer of single electrons to and from the fragments.

$$\underset{(X-Y)}{R-Cl} + \underset{(A:B)}{H-OH} \rightleftharpoons \underset{(X^{+}\ :Y^{-})}{R^{+}\ :Cl^{-}} + \underset{(A^{+}\ :B^{-})}{H^{+}\ :OH^{-}} \rightleftharpoons \underset{(X-B)}{R-OH} + \underset{(A:Y)}{H-Cl} \qquad (1)$$

$$\underset{(X-Y)}{R-Cl} + \underset{(2\ A\cdot)}{2\ R'_{2}NO\cdot} \rightleftharpoons \underset{(X\cdot\ \cdot Y)}{R\cdot\ \cdot Cl} + \underset{(2\ A\cdot)}{2R'_{2}NO\cdot} \rightleftharpoons \underset{(X-A)}{R-ONR'_{2}} + \underset{(A-Y)}{R'_{2}NO-Cl} \qquad (2)$$

We have proposed that the two different types of solvolytic reactions are distinguished by introducing the terms *heterosolvolysis* and *homosolvolysis*.[2] The purpose of the present paper is to indicate the very wide variety of homosolvolytic reactions. Many of the examples merit far more detailed investigation.

$$X-Y + A:B \rightleftharpoons [X^{+}\ :Y^{-}] \rightleftharpoons X-A + Y-B \qquad (3)$$

Heterosolvolysis

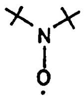
$$X-Y + 2A\cdot \rightleftharpoons [X^{\cdot}\ \ {}^{\cdot}Y] \rightleftharpoons X-A + Y-A \qquad (4)$$

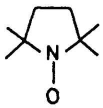
Homosolvolysis

The exceptional stability of nitroxides (I)—(III) used in the present study is attributed partly to delocalisation of the unpaired electron and partly to the steric crowding round the free radical centre. This means that bimolecular S_H2 type displacements involving these nitroxides are unlikely. The fission of a carbon–halogen bond in a reactive alkyl halide when the alkyl halide is dissolved in a nitroxide must be initiated by attack on the halogen similar to an S_N1 process where the reaction involves attack by the solvent molecules on the halogen. Nitroxides are usually regarded as efficient traps for radicals but it is important to appreciate that the 'trapping' by nitroxides like (I)—(III) may involve hydrogen abstraction (5) instead of coupling (6).

Exactly similar hydrogen abstraction reactions occur with the two cyclic nitroxides. Very often the first clear evidence that a homosolvolysis reaction, using di-t-butyl nitroxide, is in progress, is the formation of a volatile green-blue liquid [$(CH_3)_3CNO$]. With the cyclic nitroxides the green nitroso-compounds are not particularly volatile but their presence is disclosed by the darkening of the solution from the orange-red of the nitroxide to a deep red-brown (due to the combined colour of the nitroxide and the nitroso-compound). When the radical formed in the homosolvolysis is not too reactive it may couple with the nitroso-compound to give an unsymmetrical nitroxide. This formation of secondary nitroxides, which depends critically on concentration and relative reactivity, will be the subject of a future publication.

Many of the homosolvolytic reactions are accompanied by the formation of crystalline precipitates. This is particularly noticeable when the nitroxide is the only solvent or if the co-solvent is a non-polar organic liquid. These precipitates are the nitroxide halides which appear to have considerable ionic character. They can be recrystallised from ethanol or acetonitrile. However, it has been established that the nitroxide halides can be in equilibrium with persistent radicals and free nitroxide (see below) and is thus not surprising that it has been impossible to obtain good analytical data for them.


(I)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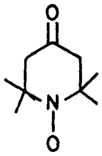
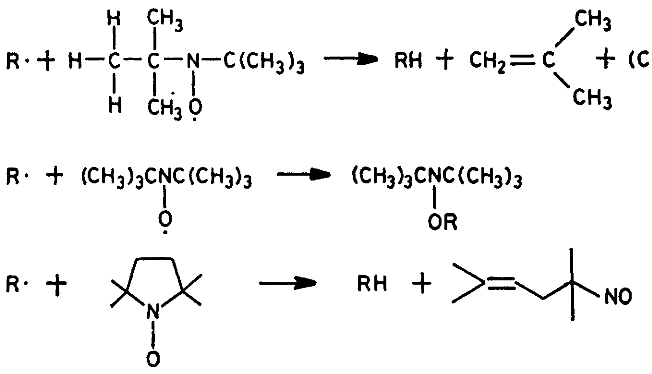
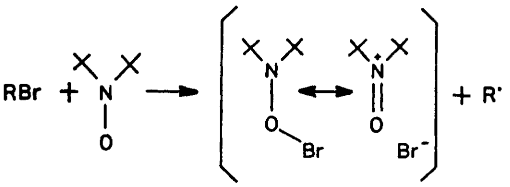

(III)

Examples of Homosolvolyses.—(a) *Carbon–halogen bonds.* When bromotriphenylmethane is dissolved in a nitroxide a fairly rapid reaction ensues. The homosolvolysis is represented by reaction (9) but two further equilibria (10) and (11) are involved. The study of these equilibria by e.s.r. spectroscopy is discussed below. Triphenylmethyl radicals do not attack the nitroxide but in the presence of atmospheric oxygen the more reactive triphenylmethylperoxyl radicals are formed and rapidly attack the excess nitroxide [reaction (14)]. The proportions of bistriphenylmethyl peroxide and triphenylmethyl hydroperoxide, both of which were fully characterised, depends on the oxygen concentration, *i.e.* the rapidity with which air is admitted.


(5)
(6)
(7)


(IV)
(8)

The reaction between bromotriphenylmethane and nitroxides is rapid; reaction with other alkyl halides is slower. Both benzyl bromide and allyl bromide react slowly with nitroxides when heated together in the absence of additional solvents.

$$(C_6H_5)_3C\cdot + O_2 \rightleftharpoons (C_6H_5)_3CO_2 \quad (12)$$

$$(C_6H_5)_3CO_2\cdot + (C_6H_5)_3C\cdot \rightleftharpoons (C_6H_5)_3CO_2C(C_6H_5)_3 \quad (13)$$

$$(C_6H_5)_3CO_2 + [(CH_3)_3C]_2NO\cdot \rightleftharpoons (C_6H_5)_3CO_2H + (CH_3)_2C{=}CH_2 + (CH_3)_3CNO \quad (14)$$

The nitroxide bromides crystallise out, and when the reaction is carried out in an inert solvent the associated disappearance of the nitroxide signal in the e.s.r. spectrum can be monitored (see below). Unfortunately, it has not been possible to isolate the *O*-benzyl- or *O*-allyl-hydroxylamines from the unchanged nitroxide. Since the *O*-triphenylmethylhydroxylamine is substantially dissociated into radical and nitroxide at room temperature, it is likely the *O*-benzyl- and *O*-allyl-hydroxylamines are very thermolabile and are decomposed when normal separations are attempted.

Treatment of *meso*-1,2-dibromo-1,2-diphenylethane with excess of 2,2,5,5-tetramethylpyrrolidine nitroxide in an evacuated tube for six days at 60° resulted in the formation of *trans*-stilbene [reaction (15)] in almost quantitative yield. The 2-bromo-1,2-diphenylethyl radical formed in the first homosolvolysis step, readily loses the second bromine atom.

The halogen atom in an acyl halide is more reactive in heterosolvolysis than those in alkyl halides so it is perhaps not surprising that it is also more reactive in homosolvolysis reactions. The reaction between benzoyl chloride and either (I) or (III) is rapid and yields the corresponding *O*-benzoylhydroxylamines (V) and the nitroxide chloride.

$$[(CH_3)_3C]_2NO\cdot + (C_6H_5)_3CBr \rightleftharpoons [(CH_3)_3C]_2NOBr + (C_6H_5)_3C\cdot \quad (9)$$

$$2(C_6H_5)_3C\cdot \rightleftharpoons \text{Dimer} \quad (10)$$

$$(C_6H_5)_3C\cdot + [(CH_3)_3C]_2NO\cdot \rightleftharpoons (C_6H_5)_3CON[C(CH_3)_3]_2 \quad (11)$$

(b) *Carbon–nitrogen bonds in diazonium salts.* Diazonium salts react readily with reducing agents which are capable of supplying a single electron. Since the homosolvolysis experiments already described involve the donation of a single electron by nitroxide molecules we would anticipate the rapid reaction (18) between diazonium salts and nitroxides. The aryl radical so produced can undergo three possible reactions (19)—(21). The addition of crystalline diazonium fluoroborates or chlorides to liquid nitroxides resulted in the expected evolution of nitrogen. In no case was biphenyl or a substituted biphenyl isolated [reaction (19)]; instead the aryl radical either coupled with the nitroxide [reaction (20)] or abstracted hydrogen from the nitroxide [reaction (21)]. Interestingly, phenyl radicals (from the diazonium chloride) and *p*-nitrophenyl radicals (from the diazonium fluoroborate) coupled to give *O*-phenyl-*N*-di-t-butylhydroxlamine and *O*-(4-nitrophenyl)-*NN*-di-t-butylhydroxylamine (75%), respectively [reaction (20)] while the more electrophilic 2,4-dinitrophenyl and 2,4,6-tribromophenyl radicals abstracted hydrogen [reaction (21)] to yield *m*-dinitrobenzene (22%) and 1,3,5-tribromobenzene (13%), respectively. In these experiments the yield of nitrogen was poor and both unchanged nitroxide and diazonium salt were recovered. The poor yields reflect the insolubility of the diazonium fluoroborate in the nitroxide. The prior addition of carbon tetrabromide to the diazonium salt suspension before the addition of the nitroxide trapped *p*-nitrophenyl radicals yielding 4-nitrobromobenzene in a pseudo-Sandmeyer reaction. Attempts were made to ring-close diazotized 2-aminobenzophenone to form fluorene but hydrogen abstraction from the nitroxide was always the predominent reaction. It is established that the Pschorr reaction often goes *via* a heterolytic and not a radical pathway[3] so that the predominance of abstraction was perhaps to be expected.

$$\begin{tikzcd}
C_6H_5CHBrCHBrC_6H_5 \arrow[r, "R_2NO\cdot"] & C_6H_5CHCBrC_6H_5 \arrow[d, "-Br\cdot"] \\
 & C_6H_5CH{=}CHC_6H_5 + 2R_2\overset{+}{N}O\bar{B}r \quad (15)
\end{tikzcd}$$

$$C_6H_5COCl + 2R_2NO\cdot \longrightarrow C_6H_5CO{\cdot}ONR_2 + R_2\overset{+}{N}{=}O\ Cl^- \quad (16)$$

$$C_6H_5\overset{+}{N}{\equiv}N + e^- \longrightarrow C_6H_5^{\cdot} + N_2 \quad (17)$$

$$ArN_2^+X^- + R_2NO\cdot \rightleftharpoons Ar\cdot + R_2\overset{+}{N}{=}O + X^- + N_2 \quad (18)$$

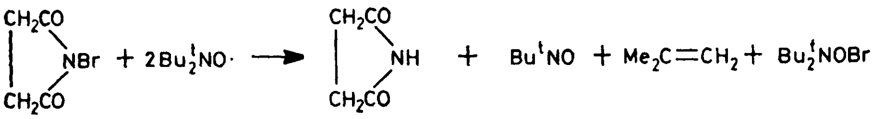
$$Ar\cdot + Ar\cdot \longrightarrow Ar_2 \quad (19)$$

$$Ar\cdot + R_2NO\cdot \longrightarrow ArONR_2 \quad (20)$$

$$Ar\cdot + R_2NO \longrightarrow ArH + R(-H) + RNO \quad (21)$$

$$\begin{tikzcd}
4\text{-}(O_2N)C_6H_4N_2^+X^- \arrow[r, "R_2NO\cdot"] & 4\text{-}(O_2N)C_6H_4\cdot \arrow[d, "CBr_4"] \\
 & 4\text{-}(O_2N)C_6H_4Br\ (20\%) \quad (22)
\end{tikzcd}$$

(c) *Halogen–nitrogen bonds in* N-*halogenoamides*. Although it has been established that allylic bromination by *N*-bromosuccinimide involves low concentrations of bromine atoms[4] and not, as was originally thought, succinimidyl radicals; recent work by Skell has shown that under appropriate conditions succinimidyl radicals can be formed and they will abstract hydrogen.[5] The reaction between *N*-bromosuccinimide and the nitroxides is extremely rapid. The principal products with di-t-butyl nitroxide (I) and *N*-bromosuccinimide are succinimide, isobutene, 2-methyl-2-nitrosopropane, and, unexpectedly, 2-bromo-2-methylpropane. The first three products would be expected to be accompanied by the nitroxide bromide [*cf.* reaction (23)]. Instead a little nitroxide bromide was formed and the yield of 2-methyl-2-nitrosopropane exceeded the yield of isobutene. In a separate experiment it was found that the nitroxide bromide (isolated from the products of another homosolvolysis reaction) when treated with *N*-bromosuccinimide decomposed into 2-methyl-2-nitrosopropane and 2-bromo-2-methylpropane (24). The mechanism of this disproportionation, which has only been observed in the presence of *N*-bromosuccinimide, remains uncertain. Attempts were made to ring close 2-acetoaminobenzophenone by converting it into the *N*-chloroacetamide derivative and then treating the halogenoamide with a nitroxide. In practice the acetamide radical abstracted hydrogen from the nitroxide.


(23)

$$Bu^t_2\overset{+}{N}O\bar{B}r \xrightarrow{NBS} Bu^tNO + Bu^tBr \quad (24)$$

(d) *Oxygen–oxygen bonds*. When benzoyl peroxide was added to di-t-butyl nitroxide a rapid reaction ensues. The green colour of 2-methyl-2-nitrosopropane was apparent and benzoic acid was formed in almost quantitative yield. The induced decomposition of benzoyl peroxide by diphenylhydroxylamine has been reported.[6] It is possible that this latter reaction goes by a completely different mechanism, but there are two other possibilities. First, the decomposition we have observed with di-t-butyl nitroxide may be due to traces of hydroxylamine. This is unlikely since the nitroxide had been carefully purified by preparative g.l.c. and certainly no hydroxylamine was detected. The remaining possibility is that in the studies with diphenylhydroxylamine a trace amount of the hydroxylamine was oxidised (by atmospheric oxygen?). A simple chain would then be possible. Reaction (29) is only an initiation step, thereafter reactions (30) and (32) form a chain sequence which is likely to be very long since there are no simple chain-termination processes. This mechanism is in perfect accord with the kinetic results reported[6] and is supported by the observation that the diphenyl nitroxide and benzoyl peroxide undergo no detectable reactions when mixed.[6] Although the equilibrium represented by (30) and (31) may be established, no overall reaction will be observed unless there is a reactive hydrogen.

The Nitroxide-induced Homolysis of Triphenylmethyl Halides observed by E.s.r. Spectroscopy.—The rapid

$$(C_6H_5CO_2)_2 + Bu^t_2NO\cdot \longrightarrow C_6H_5CO_2ONBu^t_2 + C_6H_5CO_2\cdot \qquad (26)$$

$$C_6H_5CO_2ONBu^t_2 \rightleftharpoons C_6H_5CO_2\cdot + Bu^t_2NO\cdot \qquad (27)$$

$$C_6H_5CO_2\cdot + Bu^t_2NO\cdot \longrightarrow C_6H_5CO_2H + Me_2C{=}CH_2 + Bu^tNO \qquad (28)$$

$$(C_6H_5)_2NOH \xrightarrow{[O]} (C_6H_5)_2NO\cdot \text{ [Initiation only]} \qquad (29)$$

$$(C_6H_5)_2NO\cdot + (C_6H_5CO_2)_2 \longrightarrow (C_6H_5)_2NOOCOC_6H_5 + C_6H_5CO_2\cdot \qquad (30)$$

$$(C_6H_5)_2NO\cdot OCOC_6H_5 \rightleftharpoons (C_6H_5)_2NO\cdot + C_6H_5CO_2\cdot \qquad (31)$$

$$(C_6H_5)_2NOH + C_6H_5CO_2\cdot \longrightarrow (C_6H_5)_2NO\cdot + C_6H_5CO_2H \qquad (32)$$

reaction between bromotriphenylmethane and nitroxides has been described above. In these reactions the nitroxide was present as a solvent, *i.e.* in great excess. Clearly such a system is unsuitable for study by e.s.r. methods since the large excess of nitroxide would simply saturate the detector and there would be no opportunity to observe the triphenylmethyl radical. Chlorotriphenylmethane can be converted into triphenylmethanol in a polar solvent in which water is only present in low concentration and although such a reaction would not be called a solvolysis according to the current definition there is no doubt this reaction involves the ***heterolysis*** of the carbon–chlorine bond. In an exactly similar way the ***homolysis*** of the same carbon–chlorine bond has been induced by dissolving chlorotriphenylmethane in an inert solvent such as benzene to which low concentrations of nitroxide have been added. Writing K_9 for the equilibrium constant of the forward reaction, but the constants K_{11} and K_{10} as the dissociation constants

$$Ph_3CBr + Bu^t_2NO\cdot \rightleftharpoons Ph_3C\cdot + Bu^t_2NOBr \qquad (9')$$

$$Ph_3C\cdot + Bu^t_2NO\cdot \rightleftharpoons Ph_3CONBu^t_2 \qquad (11')$$

$$Ph_3C\cdot + Ph_3C\cdot \rightleftharpoons \text{Dimer} \qquad (10')$$

$$Bu^t_2NOBr_{(solution)} \rightleftharpoons Bu^t_2\overset{+}{N}{=}O\ Br^-_{(solid)} \qquad (33)$$

of the *O*-triphenylmethyl-*N*-butylhydroxylamine and the ' dimer ' respectively, we find the concentration of triphenylmethyl radicals is proportional to the half power of the bromotriphenylmethane concentration [equation (34)]. This in effect means that a considerable

$$[Ph_3C\cdot] = \left(\frac{K_9K_{11}[Ph_3CBr][Ph_3CONBu^t_2]}{[Bu^t_2NOBr]}\right)^{\frac{1}{2}} \qquad (34)$$

excess of bromotriphenylmethane is necessary if the radical is to be observed [equation (35)]. However, the

$$[Ph_3C\cdot] = (K_{10}[\text{Dimer}])^{\frac{1}{2}} \qquad (35)$$

triphenylmethyl radical concentration also depends on the independent equilibrium (10). It is well established that K_{10} depends on the medium with a value of 0.02 mol dm^{-3} when benzene is the medium and *ca.* 0.25 mol dm^{-3} when *m*-xylene is the medium.[7] There is no data on the dissociation constant of the *O*-triphenylmethylhydroxylamine (K_{11}). In a preliminary experiment a solution of the triphenylmethyl radical (prepared from $Ph_3CCl + Zn$) was added to a solution of di-t-butyl nitroxide; the e.s.r. signals of both radicals dropped reaching a constant lower value after 3 h. This experiment suggests the hydroxylamine derivative is weakly associated. However like K_{10}, K_{11} is certain to depend on the medium. A further important factor governing the final overall equilibrium position is the fact that the nitroxide bromide (or chloride) crystallises out of solution in the more concentrated reactions. This means that in these reactions the concentration of the nitroxide bromide in solution remains constant once the solution is saturated. This removal of the nitroxide bromide from the solution undoubtedly was an important factor in the spectroscopic observation of the triphenylmethyl radicals.

Di-t-butyl nitroxide is completely stable in benzene solution and the e.s.r. spectrum of such a solution remains unchanged after months. The first experiment involved very low concentrations. The nitroxide spectrum disappeared rapidly after the addition of a large excess of bromotriphenylmethane; but the initial concentration of nitroxide was $<10^{-3}$ mol dm^{-3} and since K_{10} is of the order of 2×10^{-2}, the triphenylmethyl radical concentration was too small to be detected. Nonetheless there was sufficient excess of bromotriphenylmethane for the disappearance of the nitroxide to follow a first-order rate (see Figure 1). Experiment 2 employed very much more concentrated solutions but there was now insufficient excess of bromotriphenylmethane for the equilibrium concentration of the radical to be observable. Further trityl bromide was added (experiment 2a) and the triphenylmethyl radical spectrum appeared (Figure 2). The triphenylmethyl radical

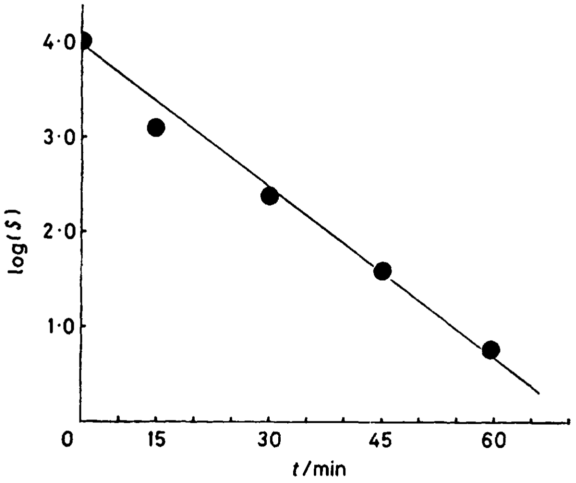


FIGURE 1 First-order kinetics observed when excess of bromotriphenylmethane and di-t-butyl nitroxide. S = nitroxide signal in arbitrary units

spectrum intensified and the nitroxide spectrum weakened as the reaction proceeded. Unfortunately in order to add the extra bromotriphenylmethane the mixture had to be briefly open to the atmosphere and there was therefore some unavoidable introduction of oxygen which has the effect of reducing the total available nitroxide from the equilibrium system [*cf.* reactions (12)—(14)]. This is indicated in the Table by writing the nitroxide concentration in experiment 2a as less than that in experiment 2. By making use of the greater dissociation constant of the triphenylmethyl dimer in xylene it was hoped it would be possible to observe the homosolvolysis process in a single reaction.[7] Bromotriphenylmethane proved rather insoluble in xylene, but eventually satisfactory conditions were developed and in experiment 3 the successive change from the nitroxide spectrum, to the spectra of both and finally to triphenylmethyl spectrum alone was observed. The reaction was repeated using trityl chloride in place of the bromide (experiment 4). As the Table shows the reaction was much slower than the corresponding reaction with the bromide and it took longer for the spectrum of the radical to appear. There could be two reasons for this, either a purely kinetic matter or a change in one or more of the equilibrium constants especially the solubility product for the nitroxide chloride.

Reaction of triphenylmethyl halides in nitroxides in inert aromatic solvents

Experiment no.	Halide	Nitroxide	Inert solvent	$[Ph_3CX]$/ mol dm^{-3}	$[R_2NO\cdot]$/ mol dm^{-3}	Spectroscopic observation
1	Br	DTBNO	C_6H_6	0.01	0.000 7	Nitroxide signal * dropped to 20% in 60 min
2	Br	DTBNO	C_6H_6	0.15	0.025	Nitroxide signal dropped to 50% in a few hours
2a	Br	DTBNO	C_6H_6	0.20	<0.025 †	More Ph_3CBr added to experiment 2, $Ph_3C\cdot$ signal appeared, and nitroxide signal weakened †
3	Br	DTBNO	*m*-Xylene	0.44	0.025	Nitroxide signal disappeared and $Ph_3C\cdot$ appeared after 12 h (solubility difficulties)
4	Cl	DTBNO	*m*-Xylene	0.5	0.025	Nitroxide signal disappeared in 45 h, and $Ph_3C\cdot$ signal appeared
5	Br	TMPNO	*m*-Xylene	0.5	0.025	Nitroxide signal dropped to 50% in 12 h
5a	Br	TMPNO	*m*-Xylene	0.75	0.025	More Ph_3CBr added to experiment 5. Nitroxide signal decreased and $Ph_3C\cdot$ appeared after 72 h
5b	Br	TMPNO	*m*-Xylene			The combined solution of 5a was decanted off the precipitate of nitroxide bromide and a fresh solution of $Ph_3C\cdot$ (*ca.* 0.02 mol dm^{-3}) was added. The $Ph_3C\cdot$ spectrum disappeared and the TMPNO spectrum reappeared

* See Figure 1 for the first-order plot for reaction (1). † See e.s.r. spectrum in Figure 2. DTBNO = Di-t-butyl nitroxide, TMPNO = 2,2,5,5-tetramethylpyrrolidine nitroxide.

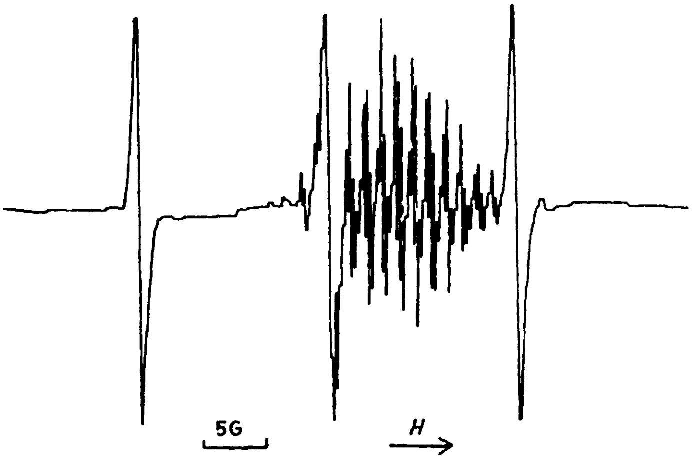


FIGURE 2 E.s.r. spectrum of the reaction mixture $(C_6H_5)_3CBr + Bu^t{}_2NO\cdot$

Experiments 5 and 5a correspond to 2 and 2a (with DTBNO) and confirm that tetramethylpyrrolidine behaves similarly, although the equilibrium constants are different. Experiment 5b is extremely important. At the end of experiment 5a all the supernatant solution was decanted off the crystalline nitroxide bromide. A solution containing a relative deficiency of the triphenyl methyl radical–dimer mixture (prepared from bromotriphenylmethane and zinc) was added to the nitroxide bromide crystals and the system degassed. The nitroxide bromide dissolved, the triphenylmethyl spectrum disappeared, and the nitroxide spectrum took its place. This result confirms that the whole system [reactions (9)—(11) and (33)] are in equilibrium and shows that the analogy with ionic equilibria is justified.

The Nitroxide-induced Homolysis of Bromopentaphenylcyclopentadiene.—The formation of the pentaphenylcyclopentadienyl radical when bromopentaphenylcyclopentadiene is dissolved in solution containing a nitroxide presents some new features of the homosolvolysis process. The pentaphenylcyclopentadiene radical does not dimerise so that very much more dilute solutions could be studied. The spectrum shown in Figure 3 is from an experiment in which the concentrations of both the nitroxide and the bromopentaphenylcyclopentadiene were an order of magnitude lower than in the similar experiments with the triphenylmethyl radical. No nitroxide bromide separated out in this very dilute experiment, which shows that although separation of the nitroxide halide must affect the equilibrium in the triphenylmethyl radical experiments, it is not a prerequisite for this type of homosolvolytic reaction.

Relative Rates of Homosolvolysis.—In dilute solutions the reaction of triphenylmethyl bromide with di-t-butyl nitroxide the nitroxide e.s.r. signal virtually disappeared in 1 h (see Table). In a similar experiment with bromodiphenylmethane the nitroxide signal experiment took five days to disappear completely. When benzyl bromide was the organic halide the e.s.r. signal of the nitroxide took more than a week to disappear even though the temperature was raised to 45°. However in each case a control experiment using the same concentration of nitroxide in the same solvent was kept under exactly the same conditions and in each case the nitroxide signal in the control remained unchanged. A study of the relative rates of homolysis of substituted benzyl bromides is in progress and will be reported later; the important observation is that those substituents which when in the *para*-position of the benzene rings stabilise the triphenylmethyl radical also enhance the rate of homosolvolysis of *para*-substituted benzyl bromides.

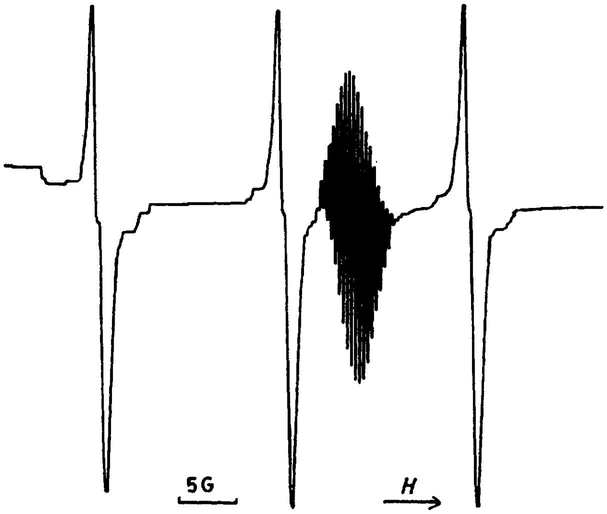


FIGURE 3 E.s.r. spectrum of the reaction mixture of bromopentaphenylcyclopentadiene and di-t-butyl nitroxide

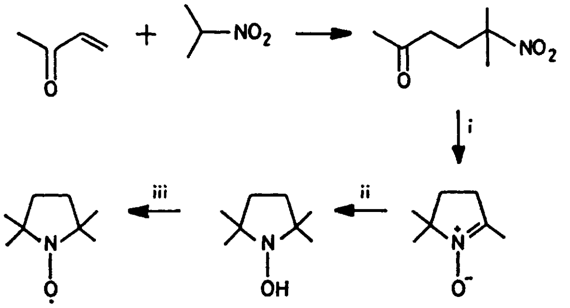
EXPERIMENTAL

Materials.—Di-t-butyl nitroxide (I) [8] was prepared from 1,1-dimethyl-1-nitrobutane.[9] 2,2,6,6-Tetramethyl-4-piperidone nitroxide (II) was prepared from 2,2,6,6-tetramethyl-4-piperidone.[10] 2,2,5,5-Tetramethylpyrrolidine nitroxide was prepared as in the Scheme.*

Bromotriphenylmethane and bromopentaphenylcyclopentadiene were prepared according to well established procedures. The remaining reagents were standard laboratory chemicals purified when necessary. The diazonium chloride salts were prepared by normal diazotisation procedures, and were converted to fluoroborates by well established methods.

Homosolvolysis Reactions.—The experiments were performed *in vacuo*, using carefully degassed reagents. The solvent nitroxide was placed in the reaction vessel and the solute in a side-arm which could be tilted allowing the solute to fall into the nitroxide. A magnetic stirrer was employed to ensure good mixing. After carefully degassing, the reaction vessel with its rotatable side arm was isolated from the remainder of the vacuum line and the reactants were mixed. At the end of the reaction period the vessel was reconnected to the vacuum line and volatile products (*e.g.* 2-methylpropene and 2-methyl-2-nitrosopropane from di-t-butyl nitroxide) were collected in a trap surrounded by liquid nitrogen. These volatile components were analysed by n.m.r. and coupled g.l.c.–m.s. In the experiments with diazonium salts the nitrogen evolved was estimated by a manometer. The residue left in the reaction vessel was then taken up in a solvent such as hexane or chloroform in which the nitroxide halides were almost insoluble, filtered, and then worked up by standard procedures. The nitroxide halides were crystalline, but recrystallisation tended to make poor analytical values worse, *e.g.* di-t-butyl nitroxide bromide, crude [Found (crude): C, 45.3; H, 9.9; N, 6.7; (recrystallised from CH_3CN): C, 41.8; H, 9.4; N, 5.9. $C_8H_{18}NOBr$ requires C, 42.9; H, 8.1; N, 6.3%]. This is to be expected since in solution they are in equilibrium with the free nitroxide and halogen atoms. When treated with aqueous silver nitrate there was an immediate precipitate and the released hydroxylamine rapidly oxidised to yield regenerated nitroxide.

The products were characterised by the spectral properties, u.v., n.m.r., i.r., m.s., m.p., and mixed m.p. (where appropriate). If no authentic material was available the identification was confirmed by analysis. The new products isolated had the following properties and analysis.



SCHEME Reagents: i, Zn dust; ii, CH_3MgI; iii, $[Ox^-]$

O-*Phenyl*-NN-*di-t-butylhydroxylamine* was an oil, $\delta(CDCl_3)$ 1.25(18 H, s) and 7.73 (5 H, m) (Found: *m/e*, 221.179. $C_{14}H_{23}NO$ requires *M*, 221.178). O-(p-*Nitrophenyl*)-NN-*di-t-butylhydroxylamine* had m.p. 114°, $\delta(CDCl_3)$ 8.1 and 8.2 (2 H, d), 7.65 and 7.55 (1 H, d), 6.95 and 6.85 (1 H, d), and 1.23 (18 H, s) (Found: C, 63.35; H, 8.55; N, 10.7. $C_{14}H_{22}N_2O_3$ requires C, 63.15; H, 8.35; N, 10.5%).

O-*Benzoyl*-NN-(1,1,4,4-*tetramethyltetramethylene*)*hydroxylamine* had $\nu_{max.}$ 1 700 cm^{-1}, $\delta(CDCl_3)$ 1.23 (12 H, s), 1.76 (4 H, s), 7.45 (m), and 8.0 (m), (Found: *m/e*, 247.157 8. $C_{15}H_{21}NO_2$ requires *M*, 247.157 2). O-*Benzoyl*-NN-*di-t-butylhydroxylamine* had m.p. 90°, $\nu_{max.}$ 1 775 cm^{-1}, *m/e* 249 (M^+), 234 ($M - CH_3$), and 192 ($M - Bu^t$) (Found: *m/e*, 249.172 5. $C_{15}H_{23}NO_2$ requires *M*, 249.172 9), $\delta(CDCl_3)$ 1.33 (18 H, s), and 7.45 (5 H, m).

The e.s.r. measurements were made using a Decca X3 e.s.r. spectrometer. Relative concentrations were obtained from peak-to-peak signal heights, and absolute values

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were based on carefully degassed solutions of the nitroxides in which the concentrations were accurately known.

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