Homosolvolysis. Part 2.[1] Di-t-butyl Nitroxide as the Solvent and 2-Methyl-2-nitrosopropane as Internally Generated Spin Trap

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When reactive radicals are formed in a solvolysis using di-t-butyl nitroxide (DTBNO) as solvent, the radical abstracts hydrogen from unchanged nitroxide forming 2-methyl-2-nitrosopropane which acts as an internally generated spin trap.

IN Part 1 [1] we reported that compounds with weak bonds, when dissolved in free radical solvents such as nitroxides, undergo homolysis. In particular we have described the ' homosolvolysis ' of a variety of compounds using di-t-butyl nitroxide (DTBNO) as ' solvent '. In the absence

$$\text{R-X} + \text{Bu}^t_2\text{NO}\cdot \rightleftharpoons \text{R}\cdot + \text{Bu}^t_2\text{NOX} \qquad (1)(-1)$$

of other reagents the radical R· may (a) react with the hydroxylamine derivative to regenerate RX and the nitroxide [*i.e.* reaction (−1)], (b) be persistent, *e.g.* $\text{R}\cdot = (\text{C}_6\text{H}_5)_3\text{C}\cdot$ or cyclo$(\text{C}_6\text{H}_5)_5\text{C}_5\cdot$, (c) couple with more nitroxide to form a hydroxylamine derivative [reaction

$$\text{R}\cdot + \text{Bu}^t_2\text{NO}\cdot \longrightarrow \text{Bu}^t_2\text{NOR} \qquad (2)$$

(2)], or (d) abstract a hydrogen atom from unchanged nitroxide [reaction (3)].

$$\text{R}\cdot + \text{Bu}^t_2\text{NO}\cdot \longrightarrow \text{RH} + \text{Bu}^t\text{NO} + \text{CH}_2\text{=C(CH}_3)_2 \qquad (3)$$

In our original work we detected the persistent radicals formed in reaction (1), by observing the disappearance of the e.s.r. spectrum of the DTBNO and its replacement by the spectrum of the new persistent radical. The evidence for reactions (2) and (3) came from the separation and identification of the products of these reactions, hydroxylamines (Bu^t_2NOR) from reaction (2) and the hydrocarbon RH together with 2-methyl-2-nitrosopropane and 2-methylpropene from reaction (3). There was therefore no direct evidence for the participation of radicals, although any other mechanism seemed unlikely. The present paper concerns the direct observation of non-persistent radicals formed in homosolvolysis. The radicals are trapped by the 2-methyl-2-nitrosopropane formed in reaction (3).

The use of stable nitroso-compounds to trap radicals has been widely developed.[2] Coupling of a radical with a nitroso-compound yields a nitroxide which is often sufficiently stable that its e.s.r. spectrum can be studied in detail and the structure of the trapped radical deduced from the hyperfine splitting. The technique is usually referred to as ' spin trapping '.

The effective trapping of reactive radicals formed in a homosolvolysis reaction by internally generated 2-methyl-2-nitrosopropane was first observed when bromodiphenylmethane was treated with DTBNO. At the start of the reaction it was hoped that the diphenylmethyl radicals formed in the homosolvolysis would have sufficient life for them to be directly observed by e.s.r. Instead the e.s.r. spectrum of the unchanged DTBNO (a broad triplet, a_N 15.3 G) was replaced after two weeks at 50 °C by a triplet of sharp doublets (a_N 14.5 a_H 2.2 G). The new spectrum can only be attributable to the nitroxide formed by the addition of the diphenyl-methyl radical to 2-methyl-2-nitrosopropane.[3]

$$(\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H} + \text{Bu}^t\text{NO} \longrightarrow \text{Bu}^t(\text{N}\dot{\text{O}})\text{CH}(\text{C}_6\text{H}_5)_2 \qquad (4)$$

The unexpected spin trapping of the diphenylmethyl radical encouraged us to re-examine the experiments reported in the previous paper, particularly those reactions where there was a visible yield of the blue 2-methyl-2-nitrosopropane. The overall scheme is given by reactions (1′), (3′), and (4′).

$$\text{R-X} + \text{Bu}^t_2\text{NO}\cdot \rightleftharpoons \text{R}\cdot + \text{Bu}^t_2\text{NOX} \qquad (1')$$

$$\text{R}\cdot + \text{Bu}^t_2\text{NO}\cdot \longrightarrow \text{RH} + \text{Bu}^t\text{NO} + \text{CH}_2\text{=C(CH}_3)_2 \qquad (3')$$

$$\text{R}\cdot + \text{Bu}^t\text{NO} \longrightarrow \text{Bu}^t(\text{N}\dot{\text{O}})\text{R} \qquad (4')$$

The experiments described in our previous paper have been repeated and the e.s.r. spectrum of the solutions has been observed as the reaction progresses. In many cases spin-trapped radicals have been observed. The reactions have to be carried out in an excess of R–X, otherwise the spectrum of the starting nitroxide will completely obscure the spectrum of the ' spin-trap ' nitroxide formed in reaction (4′). There is in some of the reactions, the limited possibility that the radical R· can abstract a hydrogen from the ' secondary nitroxide ' [reaction (5)]. Such a reaction would be most likely

$$\text{R}\cdot + \text{Bu}^t(\text{N}\dot{\text{O}})\text{R} \longrightarrow \text{RH} + \text{CH}_2\text{=C(CH}_3)_2 + \text{RNO} \qquad (5)$$

when R· is an aryl radical. The nitroso-compound RNO could in its turn act as a spin trap to give a ' tertiary nitroxide ' $\text{R(N}\dot{\text{O}})\text{R}$. However, if such reactions have occurred, the concentration of the ' tertiary nitroxide ' has been too small to detect with certainty. There is also the possibility that $\text{Bu}^t(\text{N}\dot{\text{O}})\text{R}$ is formed by a displacement reaction (6). However secondary nitroxides

$$\text{R}\cdot\text{Bu}^t_2\text{NO}\cdot \not\longrightarrow \text{Bu}^t(\text{N}\dot{\text{O}})\text{R} + \text{Bu}^t\cdot \qquad (6)$$

$\text{Bu}^t(\text{N}\dot{\text{O}})\text{R}$ were only observed when both 2-nitroso-2-methylpropane and RH were formed [*i.e.* reaction (3′)]. We do not believe therefore that reaction (6) occurred to a significant extent, and indeed we have many examples of homosolvolysis in which the incipient radicals (R·) do not abstract hydrogen and in these reactions no secondary nitroxide $\text{Bu}^t(\text{N}\dot{\text{O}})\text{R}$ is formed.

In Part 1 we reported the homosolvolysis of benzoyl chloride.[1] Acetyl chloride and acetyl bromide react similarly but very much more rapidly. When DTBNO (0.1 mol. equiv.) was added to acetyl bromide (with benzene as a diluent) there was a rapid reaction, the solution turned green, and by the time mixing was complete and the sample inserted into the probe of the spectrometer the DTBNO spectrum had almost disappeared and was replaced by a much narrower triplet (a_N 8.0 G) characteristic of an acyl nitroxide [*cf.* a_N 8.0 G in C_6H_6 for $CH_3CO(N\dot{O})Bu^t$].[4]

In Part 1 we described the homosolvolysis of *N*-bromosuccinimide as an extremely rapid reaction yielding succinimide, 2-methyl-2-nitrosopropane, and isobutene.[1] When a dilute C_6H_6 reaction mixture was examined in the e.s.r. spectrometer a triplet of sharp triplets was observed, a_N 16.0, $a_{N'}$ 1.7 G [*cf.* a_N 15.9, $a_{N'}$ 1.75 G for $(CH_2CO)_2N(NO)Bu^t$].[5,6] There was in addition a second weaker spectrum superimposed on the spectrum of the trapped succinimidyl radical. This second spectrum had the splitting characteristic of an acyl nitroxide, a_N 7.8 G. A similar radical was reported in the original paper describing the trapping of the succinimidyl radical.[5]

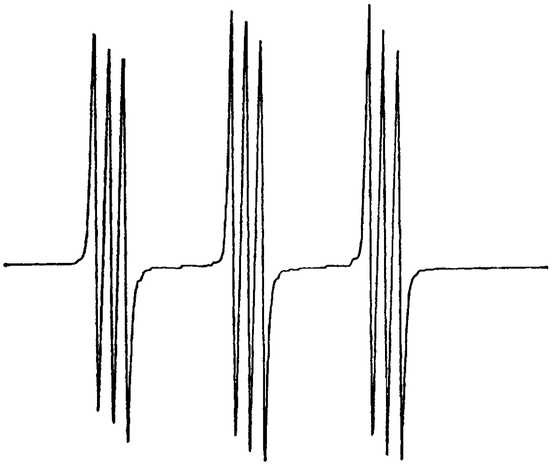

FIGURE 1 Homosolvolysis of *N*-bromophthalimide (5 parts) by DTBNO (1 part) in CCl_4. Spectrum after 5 h, a_N 16.2, $a_N{}'$ 1.8 G

Professor Perkins informs us that he has also encountered this second radical when spin trapping succinimidyl.[7] However, when the reaction was repeated with *N*-bromophthalimide only the expected triplet of sharp triplets, a_N 16.2 G, $a_{N'}$ 1.8 G, of $C_6H_4(CO)_2N(N\dot{O})Bu^t$ (*cf.* Figure 1) was observed suggesting that the acyl nitroxide in reactions with *N*-bromosuccinimide is associated with some ring-opening process.

In our original work we reported that diazonium salts were readily decomposed when added to nitroxide solutions. Benzene- and *p*-nitrobenzene-diazonium salts gave the hydroxylamine derivatives $Bu^t{}_2NOAr$ formed by the coupling of the aryl radicals with unchanged nitroxide, *i.e.* reaction (2). The more electrophilic radicals failed to couple but abstracted hydrogen instead [*i.e.* reaction (3)]. The yields of arylhydroxylamines were poor and some 2-methyl-2-nitrosopropane and isobutene were formed (more with *p*-nitrobenzenediazonium salt than with the unsubstituted benzenediazonium salt). In the present work the diazonium salt (chloride) was in large excess over the nitroxide and benzene was used as a diluent. Benzenediazonium chloride reacted much faster than *p*-nitrobenzenediazonium chloride, as judged by the evolution of nitrogen (this is probably a solubility effect). However, although both diazonium salts clearly yielded the expected aryl radicals which were trapped by the 2-methyl-2-nitrosopropane (*cf.* Figures 2 and 3) the nitroxide $Bu^t(N\dot{O})Ar$ derived from *p*-nitrobenzenediazonium salt was formed more rapidly.[8,9] This can be attributed to the greater electrophilicity of the *p*-nitrophenyl radical which attacks the starting nitroxide to yield 2-methyl-2-nitrosopropane more rapidly. The more electrophilic the radical the more important reaction (3) and correspondingly the less electrophilic the radical the more important reaction (2) which yields no observable radical.

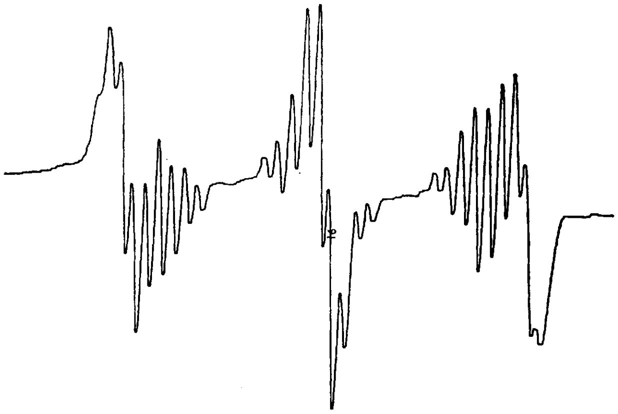

FIGURE 2 Homosolvolysis of benzenediazonium chloride (large excess) by DTBNO in C_6H_6. Spectrum of $Ph(N\dot{O})Bu^t$ after 24 h. Unchanged DTBNO still present

Benzoyl peroxide decomposed rapidly when dissolved in neat nitroxide and the principal products were benzoic acid, 2-methyl-2-nitrosopropane, and isobutene.[1] In the present work, for reasons discussed above, an inert solvent (benzene) was required and the nitroxide was used in a deficiency. The homosolvolysis of a peroxide differs from the reactions we have considered hitherto

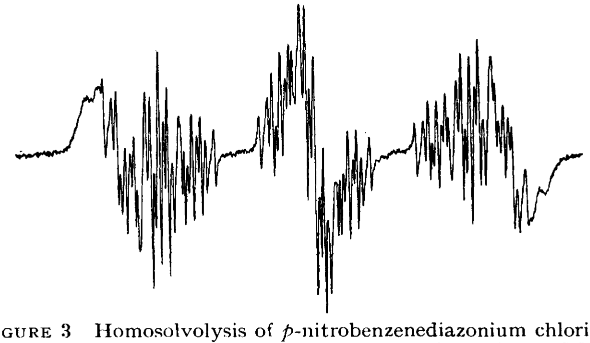

FIGURE 3 Homosolvolysis of *p*-nitrobenzenediazonium chloride (large excess) by DTBNO. Spectrum of $2,4\text{-}(NO_2)_2C_6H_3(N\dot{O})Bu^t$ after 10 h. Unchanged DTBNO still present

because two similar radicals are found [reaction (7)]. The benzoyloxyl radical ($PhCO_2\cdot$) is very reactive and rapidly attacks the starting nitroxide [reaction (8)]. By

$$(PhCO_2)_2 \xrightarrow{Bu_2{}^tNO\cdot} 2PhCO_2. \qquad (7)$$

$$PhCO_2\cdot + Bu^t{}_2NO\cdot \longrightarrow PhCO_2H + Bu^tNO + CH_2{=}C(CH_3)_3 \qquad (8)$$

analogy with the reactions we have described above, we might expect further benzoyloxyl radicals to add to the 2-methyl-2-nitrosopropane. However, such a nitroxide is unlikely to be very stable and as the e.s.r. signal of the starting DTBNO decreases it is replaced by a strong

$$PhCO_2\cdot \longrightarrow Ph\cdot + CO_2 \qquad (9)$$

$$Ph\cdot + Bu^tNO \longrightarrow Ph(NO)Bu^t \qquad (10)$$

spectrum of phenyl t-butyl nitroxide formed by the decomposition of the benzoyloxyl radical, followed by coupling the resulting phenyl radical with the nitrosopropane derivative (*cf.* Figure 4). There is evidence of the presence of other radicals in very low concentration indeed; these could be the unstable ' secondary radical ' [PhCO–O–(N$\dot{O}$)Bu^t] and the ' tertiary radical ' [Ph-(N$\dot{O}$)Ph].

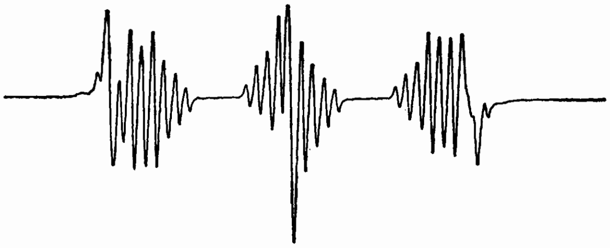

FIGURE 4 Homosolvolysis of benzoyl peroxide (5 parts) by DTBNO (1 part) in benzene. Spectrum of Ph(N$\dot{O}$)Bu^t after 4 days. DTBNO spectrum still visible

In our original work, we provided direct evidence for homolysis of the carbon–halogen bonds in bromotriphenylmethane and in bromopentaphenylcyclopentadiene when these compounds were dissolved in nitroxides (and in solutions of nitroxides). We also provided evidence that a wide variety of other bonds could be broken homolytically when added to nitroxides (or solutions of nitroxides in inert solvents). However the evidence was based on the nature of the products. The present work shows that free radicals are indeed formed in all the types of compound we described before. Every spin-trapped radical requires 2 mol. equiv. of the substrate and 3 mol. equiv. of DTBNO and the spin-trapping reaction (4) is in competition with radical–radical reactions such as reaction (2) and dimerisation of R•. Nonetheless in all the experiments described the yields of spin-trapped radicals were appreciable showing that the radicals were not the result of some minor side reaction.

EXPERIMENTAL

The reactions were performed in the vessel shown in Figure 5. A weighed amount of the reactant was placed in the detachable side arm A, and the nitroxide (with the appropriate inert solvent) was put in arm B. The whole vessel was then attached to a vacuum line and the reactants very thoroughly degassed. The tap was then closed and the vessel removed from the vacuum line and tilted until the reactant in A and the solvent in B had mixed. A portion of the solution was then run into the narrow side arm C which was inserted in the e.s.r. spectrometer. After the spectrum had been run the majority of the reaction mixture was returned to the main arm B. If the spectra was being observed over a time the entire vessel was shaken before a fresh portion of solution was run into the narrow side arm C.

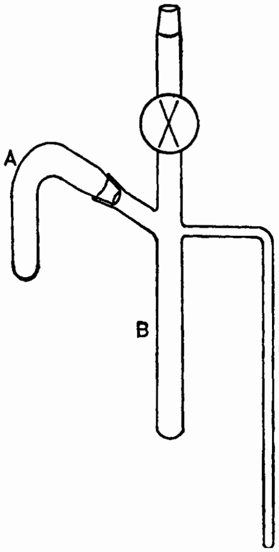

FIGURE 5 Reaction vessel for homosolvolyses

Spectra for Figures 1—3 were run at ambient temperature on a Decca X 3 spectrometer and Figure 4 was obtained with a Bruker ER 200 D spectrometer also at ambient temperature.

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REFERENCES

[1] Part 1, A. C. Scott, S. Mhatre, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1980, 260.
[2] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31.
[3] A. L. Bluhm and J. Weinstein, *J. Org. Chem.*, 1972, **37**, 1748.
[4] H. G. Aurich, K. Hahn, K. Stork, and W. Weiss, *Tetrahedron*, 1977, **33**, 969.
[5] C. Lagercrantz and S. Foschult, *Acta Chem. Scand.*, 1969, **23**, 708.
[6] G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 401.
[7] M. J. Perkins, personal communication.
[8] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 396.
[9] G. A. Razuvaev, G. A. Abakumov, E. P. Sanaev, and L. G. Abakumova, *Bull. Acad. Sci. U.S.S.R.*, 1973, **22**, 61.