A Probe for Homolytic Reactions in Solution. Part VII.[1] Hindered Phenols as Spin Traps

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Information from spin-trapping experiments employing the bifunctional spin trap (1) can be obtained equally well with mixtures of the nitrone (3) and 2,4,6-tri-t-butylphenol. The two scavenger systems are compared, and their applications are briefly discussed.

THE use of diamagnetic radical scavengers or ' spin traps ' has been evaluated in two recent reviews.[2,3] The scavengers so far employed have been nitroso-compounds and nitrones, both of which trap free radicals to give relatively stable nitroxide radicals; these may usually be detected and identified spectroscopically (e.s.r.).

One interesting scavenger, the phenolic nitrone (1) has been advocated by Pacifici and Browning as a means of differentiating between the participation in a reaction of oxygen-centred and carbon-centred free radicals.[4]

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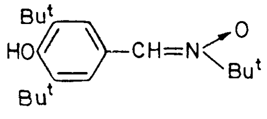
[1] Part VI, C. M. Camaggi, R. J. Holman, and M. J. Perkins, preceding paper.

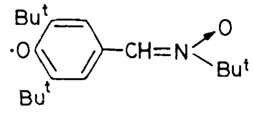
[2] M. J. Perkins, *Chem. Soc. Special Publ.*, No. 24, 1970, p. 97.

[3] E. G. Janzen, *Accounts of Chemical Research*, 1971, **4**, 31; see also C. Lagercrantz, *J. Chem. Phys.*, 1971, **75**, 3466.

[4] J. G. Pacifici and H. L. Browning, *J. Amer. Chem. Soc.*, 1970, **92**, 5231.

The former preferentially abstract hydrogen to give the phenoxyl (2); the latter give nitroxides, presumably by addition to the nitrone function. We have briefly reinvestigated this interesting bifunctional spin trap, and wish to comment on its use, and also to point out that very similar results may generally be obtained using equimolar mixtures of the benzylidene nitrone (3) and 2,4,6-tri-t-butylphenol (4).


(1)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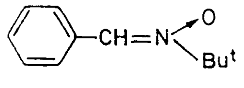
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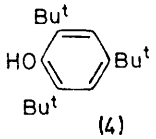

(4)

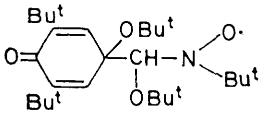
In most experiments with (1), the formation of only one stable radical (*i.e.* phenoxyl or nitroxide) was reported, and the present work was initially undertaken in order to examine the possibility of a phenomenological difference between the intramolecular competition involved in reactions of (1), and the intermolecular competition which occurs with mixtures of (3) and (4).

The scavengers were compared using several reaction systems, of which two will be discussed here as being representative of reactions in which the chemistry is fairly well understood.

t-Butoxyl radicals can be generated at, or near, room temperature by thermolysis of di-t-butyl peroxyoxalate,[5] and at such temperatures fragmentation to methyl radicals and acetone is relatively slow.[6] Decomposition of this peroxide in benzene containing a large excess of either (1), or (3) plus (4), gave the appropriate phenoxyl radical, together with a very low concentration of nitroxide. The nitroxides had splitting constants $a_N = 14\cdot3$; $a_H = 1\cdot8$ G [from (1)], and $a_N = 13\cdot9$; $a_H = 1\cdot8$ G [from (3)]. The latter corresponds to scavenging of an oxygen-centred radical, and not of methyl,[7] and the similarity of the splitting constants suggests that this is also the case for the nitroxide from (1).

Misleading results are obtained in the above systems if the concentration of scavenger is less than that of peroxide, and if a substantial fraction of the peroxide decomposes. Under these conditions the dominant e.s.r. signal is that of a nitroxide, phenoxyl having been formed and subsequently destroyed. The identity of the nitroxide from (1) under these conditions is uncertain. A possibility would be (5). In none of our experiments with (1) was evidence obtained for the formation of a diradical such as (6).

Azobisisobutyronitrile decomposes in solution to give cyanopropyl radicals, and in benzene, in the presence of either (1), or (3) plus (4), weak spectra of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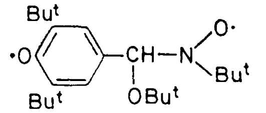

(6)

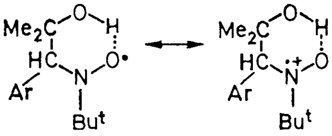
phenoxyl radicals were detected immediately after mixing. However, on standing, or on warming to 40—50°, these were rapidly replaced by intense spectra of the expected nitroxides [$a_N = 13\cdot8$; $a_H = 3\cdot1$ G from (3) [8] and $a_N = 13\cdot7$; $a_H = 3\cdot4$ G from (1) [4]].

Decomposition of the excess of azo-compound in the presence of pre-prepared phenoxyl or nitroxide led to the disappearance of the spectrum of the stable radical, consistent with rapid scavenging of cyanopropyl radicals by both species.

Until more quantitative data is available concerning scavenging rates by phenols, phenoxyls, nitrones, and nitroxides, more detailed discussion of these scavenging experiments would be out of order. However the qualitative parallel between reactions with (1) and those with mixtures of (3) and (4) did extend to other systems examined.

The decomposition of lauryl peroxide in the presence of high concentrations of scavenger gave phenoxyl radicals as well as nitroxide. Similar results with acetyl peroxide have been interpreted in terms of partial scavenging of aliphatic acyloxyl radicals.[4] However, at the concentrations required for detection of a phenoxyl (>*ca.* 0·1M-phenol), we feel that direct oxidation of the phenol by the peroxide cannot be discounted.

In the course of this work it was noted that the spectra of nitroxides believed to have been formed by scavenging of 2-hydroxy-2-propyl radicals (generated by hydrogen abstraction from isopropanol by butoxyl radicals or by photoexcited benzophenone) exhibited appreciably larger nitrogen and α-hydrogen splitting constants than were found with other nitrone spin-adducts, and also showed pronounced line-broadening at temperatures below 0 °C [$a_N = 14\cdot5$, $a_H = 3\cdot5$ G from (3), and $a_N = 14\cdot85$, $a_H = 4\cdot0$ G from (1). *Cf.* values for the cyanopropyl spin adducts given above]. These results can be accommodated by a contribution from


(7) (7a)

the hydrogen-bonded structure (7), in which the benzylic proton is properly orientated for hyperconjugative

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[5] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.

[6] C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, 1964, **86**, 3368.

[7] E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481.

[8] M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Japan*, 1967, **40**, 702, 703.

interaction; emphasis of the dipolar structure (7a) by hydrogen bonding is evident in the relatively large nitrogen coupling constant.

In summary, although the bifunctional spin trap affords an ingenious addition to the range of diamagnetic scavengers it seems to have little to recommend it over mixtures of the more accessible (3) and (4). Both systems can be used for visual differentiation of oxygen or carbon centred radical processes if sufficiently high concentrations of reagents are employed (blue phenoxyl, brown nitroxide), but only with the latter can the ratio of phenol to nitrone be varied in the scavenger system. Furthermore the width of the spectrum of the phenoxyl from (4) is narrower than that from (1), and its ^{13}C satellites do not interfere with weak nitroxide signals. Finally, it should be pointed out that for many purposes nitroso-compounds have advantages over nitrones as spin traps,[1] and that ' spin-adducts ' of, say, nitrosobutane with carbon-centred and oxygen-centred radicals are readily distinguished by their different nitrogen splittings (carbon-centred radicals give nitroxides with a_N *ca.* 7—15 G, oxygen-centred radicals give nitroxides with $a_N > 25$ G). On the other hand it must be acknowledged that nitrosobutane is not always an effective scavenger for oxygen-centred radicals.

EXPERIMENTAL

The general procedure followed that previously indicated[9] (see also ref. 4). Commercial tri-t-butylphenol was crystallised from ethanol. The benzylidene nitrone (3) was prepared as described previously.[10] The nitrone (1) was similarly prepared by condensation of t-butylhydroxylamine and 3,5-di-t-butyl-4-hydroxybenzaldehyde (*cf.* ref. 4).

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[9] G. R. Chalfont, A. Horsfield, and M. J. Perkins, *J. Amer. Chem. Soc.*, 1968, **90**, 7141.

[10] G. R. Chalfont, A. Horsfield, and M. J. Perkins, *J. Chem. Soc.* (*B*), 1970, 401.