Spin Trapping by Use of Nitroso-compounds. Part VI.[1] Nitrosodurene and Other Nitrosobenzene Derivatives

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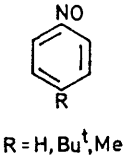
The utility of nitrosodurene (4). 2.4.6-trimethoxynitrosobenzene (5). 2.4.6-trimethoxycarbonylnitrosobenzene (6). 2.4.6-trichloronitrosobenzene (7). and pentafluoronitrosobenzene (8) as spin traps has been examined. and nitrosodurene has proved to be particularly useful. Various kinds of free radicals can be successfully scavenged by nitrosodurene to produce relatively stable nitroxides whose e.s.r. spectra are as simple as those obtained from 2-methyl-2-nitrosopropane. although line widths are slightly broader. Nitrosodurene is as stable towards photolysis as 2.4.6-tri-t-butylnitrosobenzene. Some characterisation of spin adducts of nitrosodurene from spectral data is discussed. A few examples of spin adducts to other nitroso-compounds are shown. The results of preliminary experiments with 2.3.5.6-tetrakis(trideuteriomethyl)nitrosobenzene are also briefly described.

SPIN trapping[2] has been studied by several groups of workers in recent years.[2-4] In this technique relatively stable nitroxides (spin adducts) formed by the addition of reactive radicals to appropriately constructed nitroso-compounds or nitrones (spin traps) are readily observed by e.s.r. spectroscopy. Detection and identification of the reactive radical can usually be achieved by the identification of the nitroxide from its e.s.r. spectrum. We recently utilised this method to identify free-radical intermediates in nickel peroxide oxidations where nitrosobenzenes (1) and 2-methyl-2-nitrosopropane (2) were employed.[5]

2-Methyl-2-nitrosopropane and phenyl *N*-t-butylnitrone are known to be useful spin traps in this technique, but each has some merits and demerits for spin trapping.[2-4] In previous papers [1,6] we have reported that 2,4,6-tri-t-butylnitrosobenzene (3) is a new type of spin trap and has some advantages over other spin traps, especially with respect to its stability towards photolysis. The present investigation was undertaken to develop more useful spin traps. Nitrosodurene (4), 2,4,6-trimethoxynitrosobenzene (5), 2,4,6-trimethoxycarbonylnitrosobenzene (6), 2,4,6-trichloronitrosobenzene (7), and pentafluoronitrosobenzene (8) were explored. In preliminary experiments it has been shown that nitrosodurene is a particularly useful spin trap. The main advantages of nitrosodurene as a spin trap lie in the simplicity of the spectra of spin adducts comparable to those from 2-methyl-2-nitrosopropane and in the stability towards photolysis comparable to that of 2,4,6-tri-t-butylnitrosobenzene.[1] Nitroso-compounds (5), (6), and (8), which gave no paramagnetic species on irradiation with visible or u.v. light in solutions, are also useful spin traps, especially for photoradical reactions. E.s.r. spectra of spin adducts of the nitroso-compounds (5)—(7) are as simple as those of the nitroso-compound (3), but are not so simple as those to nitrosodurene (4).

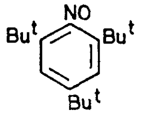
Nitrosodurene (4).—Nitrosodurene prepared by the method of Smith and Taylor[7] is a colourless dimer in the crystalline state, and a 0·005M-benzene solution is almost colourless at room temperature. This indicates that most of the nitrosodurene exists in the dimeric form even in solution. In fact, when the solution is warmed a light green colour appears, suggesting that the dimer dissociates substantially above room temperature. Nitrosodurene is readily soluble in chloroform and methylene chloride and is slightly soluble in aromatic hydrocarbons and alcohols. However, sufficient concentrations (0·02—0·005M) for spin trapping were readily obtained in most solvents at room temperature. Benzene solutions (0·01M) were irradiated by light from a 1 kW high-pressure mercury-lamp but no detectable paramagnetic species were formed.



(1)

Bu^tNO

(2)



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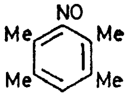

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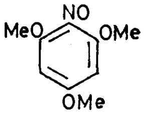

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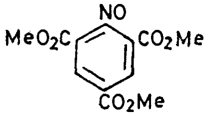

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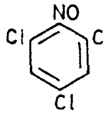

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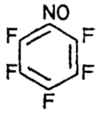

(8)

Nitrosodurene reacted with various kinds of free radicals at room temperature to form nitroxide spin-adducts in concentrations high enough for their e.s.r. spectra to be obtained, although only a very small part of the nitrosodurene was considered to exist in the active monomeric form for spin trapping at room temperature. The nitroxides observed in this study are listed in Table 1 together with radical sources, *g*-values, and hyperfine splitting constants. Reactive radicals were largely generated by the halogen abstraction by organostannyl radicals and by the hydrogen abstraction by the

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[1] Part V, S. Terabe and R. Konaka, *J.C.S. Perkin II*, 1973, 369.

[2] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31.

[3] M. J. Perkins, in 'Essay on Free-Radical Chemistry,' ed. R. O. C. Norman, *Chem. Soc. Special Publ.*, 1970, **24**, 97.

[4] C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

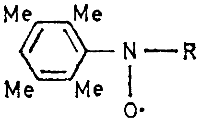
[5] (*a*) R. Konaka and S. Terabe, Abstracts, The VIIth ESR Symposium (Japan), Sapporo, 1968, p. 44; Abstracts, The XXIInd Annual Meeting of the Chemical Society of Japan, Tokyo, 1969, p. 1711; S. Terabe and R. Konaka, *J. Amer. Chem. Soc.* 1969, **91**, 5655; (*b*) S. Terabe and R. Konaka, *J.C.S. Perkin II*. 1972, 2163; (*c*) S. Terabe, K. Kuruma, and R. Konaka, *Chemistry Letters*, 1972, 115.

[6] S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, 1971, **93**, 4306.

[7] L. I. Smith and F. L. Taylor, *J. Amer. Chem. Soc.*, 1935, **57**, 2370, 2460.

TABLE 1

Nitroxides formed by addition of various radicals to nitrosodurene in benzene at room temperature



R	Radical source *	g-Value	Splitting constants (G)		
			a_N	$a_{\beta-H}$	Other
Me (9)	T + MeI $h\nu$ + DTBP	2·0060	13·70	12·17	0·34 (p-H) ‡
Et (10)	T + EtBr $h\nu$ + $(Et_3Sn)_2$	2·0061	13·68	10·97	
$CH_2\cdot[CH_2]_9\cdot Me$ (11)	$(Me\cdot[CH_2]_{10}\cdot CO_2\cdot)_2$	2·0061	13·56	10·64	0·51 $\left\{\begin{matrix}\gamma\text{-}CH_2\\ p\text{-}H\end{matrix}\right\}$ ‡
$CH_2\cdot CH_2Ph$ (12)	T + $PhCH_2\cdot CH_2Br$	2·0060	13·59	10·87	
$CH_2\cdot CH{:}CH_2$ (13)	T + $CH_2{:}CH\cdot CH_2Br$	2·0060	13·57	10·20	
$CH_2\cdot C{\equiv}CH$ (14)	T + $CH{\equiv}C\cdot CH_2Br$	2·0060	13·57	9·70	
CH_2Ph (15)	$h\nu$ + DTBP + PhMe	2·0061	13·61	7·93	
CH_2OPh (16)	$h\nu$ + DTBP + PhOMe	2·0062	12·00	4·84	0·31 (7H) [a]
CH_2OH (17) †	$h\nu$ + DTBP + MeOH	2·0059	13·91	7·71	
Pr^i (18)	T + Pr^{i}Br	2·0061	13·72	6·92	
$\overline{CH\cdot[CH_2]_4\cdot CH_2}$ (19)	$h\nu$ + DTBP + $\overline{CH_2\cdot[CH_2]_4\cdot CH_2}$	2·0060	13·57	6·93	0·14 [a,b]
CHMePh (20)	$h\nu$ + DTBP + PhEt	2·0060	13·80	3·77	
CHEtPh (21)	$h\nu$ + DTBP + PhPr^n	2·0059	14·04	7·60	
$CHPh_2$ (22)	$h\nu$ + DTBP + Ph_2CH_2	2·0060	13·74	1·43 ‡	[c]
$C_{14}H_{11}$ (23) [d]	$h\nu$ + DTBP + $C_{14}H_{12}$ [d]	2·0059	14·46	5·23	
$CHCl_2$ (24) †	$h\nu$ + DTBP + CH_2Cl_2	2·0068	11·13	1·14 ‡	3·01 (2Cl). [c]
CH(OH)Me (25) †	$h\nu$ + DTBP + EtOH	2·0059	13·86	6·88	
CH(OH)Et (26) †	$h\nu$ + DTBP + Pr^{n}OH	2·0060	13·75	3·99	
Bu^t (27)	T + Bu^{t}Br	2·0060	13·60		0·17 [a,e]
$C(CN)Me_2$ (28)	$[Me_2C(CN)N{:}]_2$	2·0061	13·14		0·18 [a,f]
CMe_2Ph (29)	$h\nu$ + DTBP + PhPr^i	2·0064	13·69		
CCl_3 (30)	$h\nu$ + DTBP + $CHCl_3$ $h\nu$ + $(Et_3Sn)_2$ + CCl_4	2·0071	10·73		1·31(3Cl)
$C(OH)Me_2$ (31) †	$h\nu$ + DTBP + Me_2CHOH $h\nu$ + $Ph_2C{:}O$ + Me_2CHOH	2·0059	14·13		
COPh (32)	$h\nu$ + DTBP + PhCHO	2·0069	7·24		
OBu^t (33)	$h\nu$ + DTBP	2·0054	25·18		
SMe (34)	$h\nu$ + $(MeS\cdot)_2$	2·0068	16·48		
SPr^n (35)	$h\nu$ + $(Pr^nS\cdot)_2$	2·0068	16·82		
SPh (36)	$h\nu$ + $(PhS\cdot)_2$	2·0065	16·01		
Ph (37)	$h\nu$ + BPO $Ph_3CN{:}NCPh$	2·0057	10·11		2·78 (o'-. p'-H) 0·95 (m'-H)
C_6H_4OH-p (38)	$h\nu$ + DTBP + PhOH Ni-PO + PhOH	2·0050	11·80		3·25, 2·75 (o'-H) [g] 0·83 (m'-H, OH)

* T = Tri-n-butylstannane, DTBP = di-t-butyl peroxide, BPO = benzoyl peroxide, Ni-PO = nickel peroxide. † In solution of the substrate. ‡ Could be determined by using 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene.

[a] Assignment was unknown. [b] Each of 6 lines further split into 38 lines. [c] Further small splittings were observed, but the analysis was not successful. [d] $C_{14}H_{11}$ = 9,10-Dihydroanthracen-9-yl, $C_{14}H_{12}$ = 9,10-dihydroanthracene. [e] Each of 3 lines further split into 16 lines. [f] Each of 3 lines further split into 12 lines. [g] Two *ortho*-protons are not equivalent.

t-butoxyl radical. Mixing of nitrosodurene with alkyl halides in solutions as control experiments yielded no e.s.r. signal.

The e.s.r. spectrum of the methyl-radical adduct (9) (Figure 1) consists of a triplet (1 : 1 : 1) of quartets (1 : 3 : 3 : 1). This spectrum indicates that the hyperfine splitting in the spin adduct other than that due to nitrogen is characteristic of the scavenged methyl radical, and that the 2,3,5,6-tetramethylphenyl system gives no resolvable splitting. This spectral feature is similar to that of the nitrodurene anion-radical in acetonitrile [8] and dimethylformamide,[9] although in dimethylformamide partially resolved proton hyperfine splitting has been revealed.[9b] No resolvable splitting due to the phenyl ring suggests that spin delocalisation due to the phenyl ring in the nitroxide (9) is as slight as that in nitrodurene anion-radical, and that the nitroxyl group twists along the ring-carbon–nitrogen bond from the plane of the phenyl ring. This view is supported by

FIGURE 1 E.s.r. spectrum of 2,3,5,6-tetramethylphenyl methyl nitroxide (9) in benzene

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[8] D. H. Geske and J. L. Ragle, *J. Amer. Chem. Soc.*, 1961, **83**, 3532; D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *ibid.*, 1964, **86**, 987.

[9] (*a*) I. Bernal and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1964, **86**, 1671; (*b*) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **41**, 699.

the relatively large nitrogen splitting constant (13·70 G) of the nitroxide (9) compared with that of methyl phenyl nitroxide (11·0 G).[10] The rather broad lines in Figure 1, however, suggest small hyperfine splittings from some of the protons in the phenyl ring moiety, and, in fact, in some cases, *e.g.*, the nitroxides (16), (19), (22), (24), (27), and (28), partial resolution of splittings due to some protons in the tetramethylphenyl group was recognised (see Figure 2). In addition, the hyperfine splitting (0·34 G) by the *para*-proton in the nitroxide (9) became apparent when 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene (see Experimental section) was used instead of nitrosodurene (see also Figure 3). Such small values of *para*-proton splitting constants have been noticed in many *ortho*-alkylaryl t-butyl nitroxides.[11,12] Nitrogen splitting constants (13·1—14·5 G) in 2,3,5,6-tetramethylphenyl alkyl nitroxides (Table 1) are substantially larger than those (12·2—13·6 G) [1,6] in 2,4,6-tri-t-butylphenyl alkyl nitroxides. *meta*-Proton splitting constants (0·8—1·0 G) [1,6] in 2,4,6-tri-t-butylphenyl alkyl nitroxides, which are comparable to those in phenyl alkyl nitroxides,[5] are remarkable, but no splitting due to the *meta*-methyl group in 2,3,5,6-tetramethylphenyl alkyl nitroxides were observed. The same relationship has been seen between those coupling constants in nitrodurene and 2,4,6-tri-t-butylnitrobenzene anion-radicals.[8]

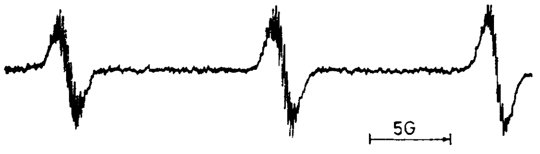

FIGURE 2 E.s.r. spectrum of 2,3,5,6-tetramethylphenyl t-butyl nitroxide (27) in benzene

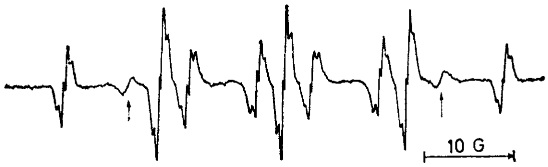

FIGURE 3 E.s.r. spectrum of 2,3,5,6-tetrakis(trideuteriomethyl)-phenyl undecyl nitroxide in benzene. Lines indicated by arrows are due to an unknown impurity

All tertiary alkyl radicals employed in this study added to nitrosodurene at the nitrogen atom to produce nitroxides, and no evidence was obtained for the formation of the anilino-radical. On the other hand, in spin trapping with 2,4,6-tri-t-butylnitrosobenzene tertiary alkyl radicals added exclusively at the oxygen atom of the nitroso-group.[1,6] The above observation may imply that the *N*-alkoxy-2,3,5,6-tetramethylanilino-radical is too reactive to be observed by e.s.r.

All alkyl-radical adducts shown in Table 1 except the nitroxides (16), (24), and (30) have similar *g*-values and nitrogen splitting constants. Slightly larger nitrogen splitting constants of 1-hydroxyalkyl-radical adducts are probably due to a solvent effect because these nitroxides were measured in the substrate itself. The larger *g*-values of the nitroxides (24) and (30) are thought to be due to the chlorine atom, and the smaller nitrogen splitting constants of the nitroxides (16), (24), and (30) are probably due to the electronegativity effect of the phenoxy-group or of the chlorine atom (see Figure 4).

The most characteristic feature in e.s.r. spectra of 2,3,5,6-tetramethylphenyl alkyl nitroxides is the variation of the β-hydrogen splitting constant depending on the structure of the radical trapped as seen in Table 1. For example, the discrimination among the nitroxides (20)—(22) is apparent from β-hydrogen splitting constants, although corresponding t-butyl nitroxides were hardly distinguishable by their spectra.[13] These results strongly suggest that phenyl *N*-2,3,5,6-tetramethylphenylnitrone would be a good spin trap. The magnitude of β-hydrogen splitting is mainly governed by the dihedral angle between the p_z-orbital on nitrogen and the C_β–H bond of the *N*-alkyl group provided that the spin density on nitrogen is constant.[14] It is known that usually in phenyl alkyl nitroxides and in t-butyl alkyl nitroxides, the bulkier the substituent on the β-carbon atom, the smaller the β-hydrogen splitting.[5b,15] This is probably due to the nonbonded interaction between the *N*-alkyl group and the phenyl or t-butyl group.[15] A reverse relationship, in contrast, has been found for 2,4,6-tri-t-butylphenyl alkyl nitroxides, and this is ascribed to both the twisting of the nitroxyl group about the axis lying in the plane of the ring and the dominant steric hindrance of the *ortho*-t-butyl group.[1,6] In 2,3,5,6-tetramethylphenyl alkyl nitroxides, the situation is intermediate between these two extreme cases. The nitroxyl group is twisted out of the plane of the ring but the steric repulsion between the *N*-alkyl group and the *ortho*-methyl group is not so significant as in 2,4,6-tri-t-butylphenyl alkyl nitroxides. The *ortho*-methyl group, the oxygen atom of the nitroxyl group, and π-electrons on the ring would comparably contribute to the conformation of the *N*-alkyl group. In some cases, the

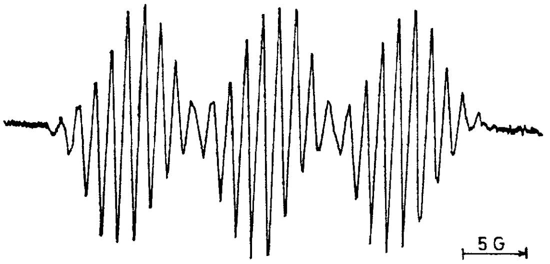

FIGURE 4 E.s.r. spectrum of 2,3,5,6-tetramethylphenyl trichloromethyl nitroxide (30) in benzene

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[10] G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3283.

[11] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481; A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1970, 1277.

[12] J. A. Pedersen and K. Torssell, *Acta Chem. Scand.*, 1971, **25**, 3151; see also, H. J. Jakobsen and K. Torssell, *Tetrahedron Letters*, 1970, 5003.

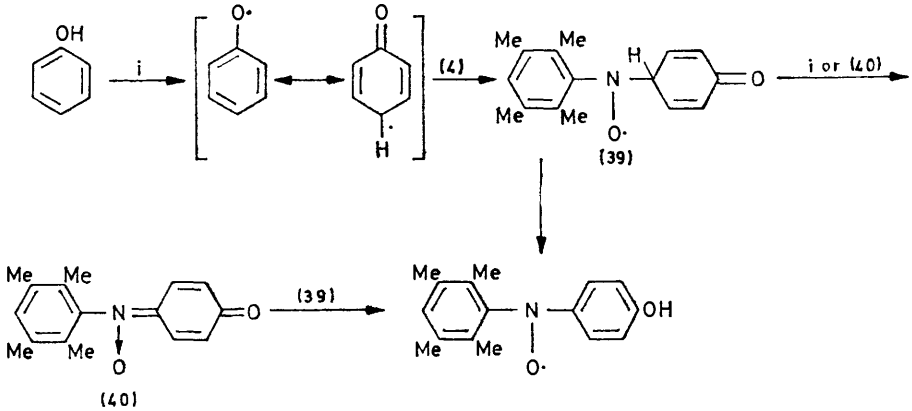
[13] E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481.

[14] C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535; D. H. Geske, *Progr. Phys. Org. Chem.*, 1967, **4**, 125.

[15] E. G. Janzen, *Topics Stereochem.*, 1971, **6**, 177.

effect of the *ortho*-methyl group is probably exerted on the conformation of the β-carbon atom through the γ-position or even more distant parts of the *N*-alkyl group. This steric circumstance is well illustrated by the examination of molecular models.

In the spectra of diphenylmethyl and dichloromethyl adducts (22) and (24), the β-hydrogen splitting constants could not be distinguished from ring methyl splittings because of many partially resolved lines. These splittings could be determined by the use of 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene instead of nitrosodurene (see Table 1). The pronounced difference between splitting constants of β-hydrogens in the nitroxides (22) and (23) is noteworthy, because it suggests the 9,10-dihydroanthracen-9-yl group has significantly different steric requirements from the diphenylmethyl group.



SCHEME i, $Bu^tO\cdot$ or nickel peroxide

It is easy to discriminate benzoyl, t-butoxy, thioalkoxy, and thiophenoxy adducts (32)—(36) from tertiary-alkyl adducts (27)—(31) by their spectra, because of essential differences in *g*-values and nitrogen splitting constants. The nitroxides (33)—(36) are unstable at room temperature, and can be observed only during the continuous generation of radicals. The decay of the thiophenoxy-nitroxide (36) was followed after removal of the irradiation. First-order decay kinetics with a 3·4 s half-life at room temperature could be observed.

Of particular interest is the observation of the nitroxide (31) in the photolysis of di-t-butyl peroxide or benzophenone in isopropyl alcohol in the presence of nitrosodurene. It was confirmed by another experiment that the latter spectrum was not due to the α-hydroxybenzhydryl-radical adduct. That is, the spectrum mentioned above could not be observed during the photolysis of benzophenone or di-t-butyl peroxide in the presence of diphenylmethanol in benzene. 2-Methyl-2-nitrosopropane [16] and the nitroso-compound (3) [1] could not trap 1-hydroxy-1-methylethyl radical, but produced the hydrogen-atom adducts which may have arisen from hydrogen transfer to the nitroso-compounds [16] or from intramolecular proton transfer in the primary spin adducts,[17] although the successful trapping of the radical by 2-methyl-2-nitrosopropane was reported in another study.[18]

Spin trapping with nitrosodurene in the oxidation of phenol with the t-butoxyl radical or nickel peroxide gave the nitroxide which showed the 48 line-spectrum analysed as shown in Table 1. The structural assignment was confirmed by using 2,4,6-trideuteriophenol and 3,5-dideuteriophenol instead of phenol. Further, addition of a drop of deuterium oxide to the reaction mixture replaced the quartet with 0·83 G spacings by the triplet having same spacings. The results obtained established that the nitroxide was 2,3,5,6-tetramethylphenyl 4-hydroxyphenyl nitroxide (38), which would be formed by the route shown in the Scheme. No evidence was obtained for the formation of the nitroxide (39). No attempt was made to detect the nitrone (40). However, *N*-phenyl-*p*-benzoquinoneimine *N*-oxide has been obtained in the oxidation of phenol with nickel peroxide in the presence of nitrosobenzene.[5b,c]

We conclude that nitrosodurene is an excellent spin trap because of (1) the simplicity of the e.s.r. spectra of the nitroxides formed, (2) its stability to photolysis, (3) the ready discrimination of the radicals trapped, and (4) the apparent high efficiency of spin trapping which means strong e.s.r. signals in most cases. The main disadvantage of nitrosodurene as a spin trap is the broadness of the absorption lines, but this can be much reduced by using 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene instead of nitrosodurene as shown in some examples described above. The deuteriated nitrosodurene can be easily obtained (see Experimental section). The lability of alkoxyl radical adducts to nitroso-compounds is a general characteristic. Alkoxyl and benzoyloxyl radicals * can be trapped by nitrones to give stable spin adducts,[13] but the identification of spin adducts is not

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* The claim [13] that nitrones trap acetoxyl radicals before they decarboxylate is a doubtful one [see ref. 3 and A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1971, 701].

[16] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395.

[17] P. B. Ayscough, R. C. Sealy, and D. E. Woods, *J. Phys. Chem.*, 1971, **75**, 3454.

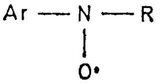
[18] I. H. Leaver and G. C. Ramsey, *Tetrahedron*, 1969, **25**, 5669.

unambiguous.[13] *N*-2,3,5,6-tetramethylphenylnitrone and methyl *N*-2,3,5,6-tetramethylphenylnitrone have proved to be other excellent spin traps for alkoxyl radicals in preliminary experiments,[19] because spin adducts of these radicals, *e.g.*, those of methoxyl, ethoxyl, phenoxyl, and acetoxyl radicals, which were independently prepared by spin trapping with nitrosodurene, are stable and can be easily discriminated by the large difference in β-hydrogen coupling constants. The same result may be expected for thioalkoxyl radicals.

2,4,6-*Trimethoxynitrosobenzene* (5).—This nitroso-compound (5) was prepared by a method which is similar to the synthesis of nitrosodurene; we could not however obtain this compound in a pure form (see Experimental section). The nitroso-compound (5) which is a colourless dimer in the crystalline state dissociates into a light green monomeric form to a considerable extent in solution. It is insoluble in most aliphatic and aromatic hydrocarbons, slightly soluble in alcohols, and soluble in methylene chloride, chloroform, and *o*-dichlorobenzene. The u.v. irradiation of 0·005M-*o*-dichlorobenzene solution gave no e.s.r. signals. A few examples of spin adducts to this nitroso-compound are listed in Table 2 together with spin adducts of other nitroso-compounds (6)—(8).

TABLE 2

Nitroxides formed by the addition of radicals to substituted nitrosobenzene at room temperature



$$\mathrm{Ar{-}\underset{\displaystyle O^{\bullet}}{\underset{|}{N}}{-}R}$$

Ar	R	Solvent	g-Value	Hyperfine splitting constants (G)				
				a_N	$a_{o,p}$	a_m	a_β	a_γ
2,4,6-$(MeO)_3C_6H_2$	$C(CN)Me_2$ [a] (41)	[f]	2·0062	13·07		0·71		0·36
2,4,6-$(MeO)_3C_6H_2$	$CH_2{\cdot}[CH_2]_9{\cdot}CH_3$ [b] (42)	CH_2Cl_2	2·0061	13·44		0·62	9·95	0·62
2,4,6-$(MeO)_3C_6H_2$	CF_3 [c] (43)	CH_2Cl_2	2·0066	10·24		0·70	8·78	
2,4,6-$(MeOCO)_3C_6H_2$	$C(CN)Me_2$ [a] (44)	C_6H_6	2·0062	13·46		0·91		0·32
2,4,6-$(MeOCO)_3C_6H_2$	CF_2CF_3 [c] (45)	C_6H_6	2·0066	10·05		0·78		0·78
2,4,6-$(MeOCO)_3C_6H_2$	$CF(CF_3)_2$ [c] (46)	C_6H_6	2·0064	10·98		0·79		1·57 [h]
2,4,6-$Cl_3C_6H_2$	$C(CN)Me_2$ [a] (47)	C_6H_6	2·0064	12·37		0·70		0·35
2,4,6-$Cl_3C_6H_2$	CF_2CF_3 [c] (48)	C_6H_6	2·0068	9·71		0·61	13·23	1·29
C_6F_5	$C(CN)Me_2$ [a] (49)	C_6H_6	2·0064	12·67	1·04 [i]	0·52 [i]		0·26
C_6F_5	$C(CN)Ph_2$ [d] (50)	C_6H_6	2·0064	12·32	0·99	0·50		
C_6F_5	OBu^t [e] (51)	[g]	2·0056	19·54	3·69 [j] 2·85 [k]	0·76		

[a] Generated from azobisisobutyronitrile. [b] Generated from lauroyl peroxide. [c] Generated by the photolyses of perfluoroalkyl iodides. [d] Generated by the oxidation of diphenylacetonitrile with nickel peroxide. [e] Generated by the photolysis of di-t-butyl peroxide. [f] C_6H_6–CH_2Cl_2 (1 : 1). [g] Perfluoro(methylcyclohexane). [h] The six γ-fluorines are not completely equivalent. [i] Tentatively assigned (see text). [j] Doublet. [k] Triplet.

The 1-cyano-1-methylethyl radical adds to the nitroso-compound (5) to give the spectrum of the nitroxide (41), in which the heptet having 0·36 G spacings was assigned to two methyl groups of the trapped radical, but not to the *ortho*-methoxy-protons for the following reasons. First, it has been reported [12] that the hyperfine splitting due to the *ortho*-methoxy-protons of the 2,6-dimethoxyphenyl t-butyl nitroxide is very small (0·04 G). Second, the γ-hydrogen splitting was also observed in the undecyl nitroxide (42) which was obtained by the thermolysis of lauroyl peroxide. Only *meta*-hydrogens from the phenyl ring show hyperfine splittings as in the nitroxides derived from the nitroso-compound (3).

The nitroso-compound (5) seems a good spin trap for the following reasons. The spectrum of the spin adduct is fairly simple. Compound (5) is stable towards photolysis. Line widths of the nitroxides are narrow. The main disadvantage is its insolubility in many solvents.

2,4,6-*Trismethoxycarbonylnitrosobenzene* (6).—The nitroso-compound (6) was obtained by the oxidation of the corresponding amine with 45% performic acid. It is a colourless dimer in the pure crystalline state; compound (6) however containing the corresponding nitrobenzene as a minor product forms blue crystals. It is assumed that the nitroso-compound is almost completely in the monomeric form in solution. The light blue solution of the nitroso-compound (6) (0·005M) gave a weak e.s.r. spectrum which remained unchanged when the solution was irradiated by u.v. light. The spectrum was analysed as follows: g = 2·0061, a_N = 6·96 G (1N), a_H = 10·76 G (1H), a_H = 1·03 G (2H), and a_H = 0·19 G (6H). The structure of the radical could not be clarified. This contamination was not serious for spin-trapping experiments because its concentration was very low.

The e.s.r. spectrum of the nitroxide (44) which was obtained in the thermal decomposition of azobisisobutyronitrile in the presence of the nitroso-compound (6) is shown in Figure 5. Line widths in the spectrum of the nitroxide (44) are narrower than those of (41) and (47) although all three spectra are similar. The heptet with 0·32 G spacings was assigned to methyl hydrogens in the 1-cyano-1-methylethyl group because the hyperfine splitting due to the methyl hydrogen in the methoxycarbonyl group was not recognised in other spin adducts of the nitroso-compound (6). Pentafluoroethyl and heptafluoroisopropyl radicals produced by photolyses of the corresponding iodides were also trapped. The β-fluorine splitting is discussed elsewhere [20] in regard to its angular dependence.

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[19] T. Mizuta and R. Konaka, unpublished data.

[20] S. Terabe and R. Konaka, *Bull. Chem. Soc. Japan*, 1973, **46**, 825.

The nitroso-compound (6) resembles the nitroso-compound (5) in the e.s.r. spectra of its spin adducts; it is considered to be a better spin trap however than the nitroso-compound (5) with respect to solubility and line widths.

2,4,6-*Trichloronitrosobenzene* (7).—This compound forms colourless crystals and dissociates into the blue monomeric form in solution to a considerable extent. The e.s.r. spectrum obtained by the thermolysis of azobisisobutyronitrile in the presence of the nitroso-compound (7) is similar to that of the nitroxide (41) as mentioned above. This observation suggests a failure to resolve the chlorine splitting. A similar failure to resolve chlorine splitting in the spectrum of 2,4,6-trichlorophenyl t-butyl nitroxide has also been noted.[12]

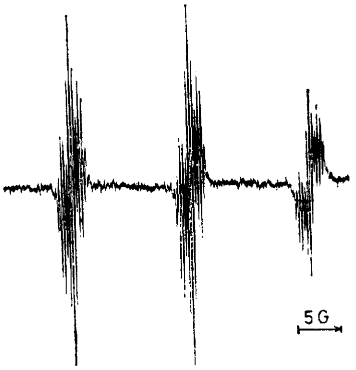

FIGURE 5 E.s.r. spectrum of 2,4,6-trimethoxycarbonylphenyl 1-cyano-1-methylethyl nitroxide (44) in benzene

The u.v. irradiation of a benzene solution of the nitroso-compound (7) gave a very complex spectrum having a g-value of 2·0060 and a nitrogen splitting constant of 9·57 G. The analysis of this spectrum was not successful, but it is assumed that this radical will be assigned to bis-(2,4,6-trichlorophenyl) nitroxide produced by the photolysis of the nitroso-compound (7).

Pentafluoronitrosobenzene (8).—This compound is blue, which indicates that it exists in the monomeric form even in the crystalline state. It produced no paramagnetic species on irradiation by u.v. light in benzene or in perfluoro(methylcyclohexane).

The e.s.r. spectrum of the nitroxide (49) consists of a triplet of multiplets composed of 21 lines. A complete analysis of the spectrum and assignment of splitting constants was difficult, but tentative assignments are listed in Table 2; it is coincidental that the fluorine atoms have the same splitting constants in pentafluorophenyl t-butyl nitroxide.[12] The larger nitrogen splitting constant for the nitroxide (49) compared with that (11·3 G) [21] for phenyl 1-cyano-1-methylethyl nitroxide may imply that the nitroxyl group is considerably twisted out of the plane of the phenyl ring because of the rather large steric requirement of the fluorine atom.

The nitroxide (51), whose spectrum showed that a fluorine atom among the *ortho*- and *para*-fluorine atoms was magnetically different from the other two, was observed only during the photolysis of di-t-butyl peroxide in the presence of the nitroso-compound (8). When the irradiation was stopped, decay of the nitroxide (51) obeyed first-order kinetics (the half-life is 52 s at room temperature). The sole observation of the nitroxide (51) suggests that either the t-butoxyl radical was scavenged before its decomposition to the methyl radical and acetone or the methyl radical could not effectively be trapped by the nitroso-compound (8). Attempts to trap a few alkyl radicals with the nitroso-compound (8) revealed that its efficiency was low. In some cases absorption lines were too broad for the *meta*-fluorine splitting to be resolved.

EXPERIMENTAL

E.s.r. Spectra.—The general experimental procedure has previously been described.[1,5b] The concentration of nitroso-compound used was 0·02—0·005M. All spectra were recorded at room temperature on a Varian V-4502-15 X-band spectrometer with 100 kHz magnetic field modulation in a flat quartz cell for polar substrates or in a cylindrical quartz cell for nonpolar substrates. Hyperfine splitting constants and g-values in the Tables are averages of at least three measurements.

Reagents.—Most of the compounds used were commercially available; the preparation and purification of others have been given previously.[1,5b] Nitrosodurene (4),[7] 2,4,6-trichloronitrosobenzene (7),[22] and pentafluoronitrosobenzene (8) [23] were prepared by known methods.

2,4,6-*Trimethoxynitrosobenzene* (5) was obtained by a method which is similar to the preparation of nitrosodurene.[7] 1,3,5-Trimethoxybenzene was mercuriated with mercury(II) acetate, followed by nitrosation with nitrosyl chloride to give colourless crystals. The crude product was recrystallised from methanol, m.p. 169°. This was not analytically pure (Found: C, 52·35; H, 5·5; N, 6·8. Calc. for $C_9H_{11}NO_4$: C, 54·8; H, 5·6; N, 7·1%), but further recrystallisation was not effective. N.m.r. ($CDCl_3$): τ 3·97 (s, 2H), 6·07 (s, 9H), and 4·10 and 6·28 (both absorptions were singlets having *ca.* 10% intensity of adjacent absorption lines).

2-*Acetamido*-1,3,5-*benzenetricarboxylic Acid.*—2,4,6-Trimethylacetanilide [24] (23 g, 0·13 mol) and potassium permanganate (160 g) in water (800 ml) were heated at *ca.* 80° for 4 h, and the reaction mixture was filtered. The filtrate was evaporated to 100 ml and neutralised with concentrated hydrochloric acid; the crude product separated. The pure compound (10·5 g, 30%) was obtained by recrystallisation, from aqueous ethanol, m.p. > 300° (Found: C, 49·4; H, 3·45; N, 5·4. Calc. for $C_{11}H_9NO_7$: C, 49·45; H, 3·4; N, 5·25%).

2,4,6-*Trismethoxycarbonylaniline.*— 2-Acetamido-1,3,5-benzenetricarboxylic acid (10·5 g, 0·039 mol) was deacetylated with concentrated hydrochloric acid in methanol. Crude 2-aminobenzene-1,3,5-tricarboxylic acid was methylated with diazomethane in ether, and recrystallised from methanol–carbon tetrachloride to give pure 2,4,6-trismethoxycarbonylaniline (3·0 g, 29%), m.p. 200° (Found: C, 53·85; H, 4·5; N, 5·1. Calc. for $C_{12}H_{13}NO_6$: C, 53·95;

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[21] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1966, 2115.

[22] R. R. Holmes and R. P. Bayer, *J. Amer. Chem. Soc.*, 1960, **82**, 3454.

[23] G. M. Brooke, J. Burdon, and J. C. Tatlow, *Chem. and Ind.*, 1961, 832.

[24] R. Biedermann and A. Ledoux, *Ber.*, 1875, **8**, 58.

H, 4·9; N, 5·25%); n.m.r. ($CDCl_3$): τ 1·38 (s, 2H), 1·45 (broad s, 2H), and 6·12 (s, 9H).

2,4,6-*Trismethoxycarbonylnitrosobenzene* (6) was prepared by the oxidation of the corresponding aniline with 45% performic acid in methylene chloride at 0°. The crude nitroso-compound containing unchanged aniline and the corresponding nitrobenzene was purified by making use of the differential solubilities of the three compounds in methanol and ether. Thus the aniline was hardly soluble in methanol while the other two were soluble. The nitrobenzene was slightly soluble in ether, but the nitrosobenzene was soluble. The nitrosobenzene (6) was recrystallised from methanol, m.p. 113° (Found: C, 51·2; H, 4·05; N, 5·1. Calc. for $C_{12}H_{11}NO_7$: C, 51·25; H, 3·95; N, 5·0%). N.m.r. ($CDCl_3$): τ 1·48 (s, 2H), 6·02 (s, 3H), and 6·12 (s, 6H).

1,2,4,5-*Tetrakis*(*trideuteriomethyl*)*benzene* was prepared by a modification of the method of Hirota and Ueda [25] where *p*-xylene was deuteriated with deuterium oxide in the presence of nickel, platinum, or palladium catalyst. Durene (11 g), commercial 5% palladium–carbon (10 g), and deuterium oxide (25—40 g) were charged in a sealed tube, and heated at 120° for 7—10 days. Partially deuteriated durene was recovered from the reaction mixture by extraction with ether followed by evaporation of ether, and was further deuteriated using new palladium–carbon and deuterium oxide reagents. The experiment was repeated three times after which the quantity of unchanged hydrogen in the deuteriated durene (9 g) was determined by n.m.r. spectroscopy, dimethyl sulphone (τ 7·01, s) being used as an internal reference in deuteriochloroform: methyl hydrogen (τ 7·81, quintet), 0·04 H (0·3% of total methyl H in durene); ring hydrogen (τ 3·03, s), 1·7 H (75% of total ring H in durene). The deuteriated durene obtained was referred to as 1,2,4,5-tetrakis(trideuteriomethyl)benzene for convenience in this study, although only 15% of the ring hydrogen was replaced by deuterium.

2,3,5,6-*Tetrakis*(*trideuteriomethyl*)*nitrosobenzene* was prepared from the deuteriated durene in the same way [7] as nitrosodurene.

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[25] K. Hirota and T. Ueda, *Bull. Chem. Soc. Japan*, 1962, **35**, 228.