Spin Trapping by Use of Nitroso-compounds. Part V.[1] 2,4,6-Tri-t-butylnitrosobenzene: a New Type of Spin-trapping Reagent

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The utility of 2,4,6-tri-t-butylnitrosobenzene as a spin-trapping reagent has been examined, and two main advantages of its use have been clarified. 2,4,6-Tri-t-butylnitrosobenzene has two sites for spin trapping. Primary alkyl radicals normally attack the nitrogen atom of the nitroso-group to generate nitroxides. Tertiary alkyl radicals, however, attack the oxygen atom of the nitroso-group to form *N*-alkoxyanilino-radicals which are sufficiently stable for e.s.r. spectra to be recorded. Secondary alkyl radicals usually add both on the nitrogen and oxygen atoms to produce both the corresponding spin adducts, whose ratio varies with the structure of the radical trapped. Solutions of the nitroso-compound produce no detectable paramagnetic species during u.v. irradiation. The relation between the structure of a spin adduct and the spectral datum is discussed.

SPIN trapping is an e.s.r. technique developed for the indirect detection and identification of short-lived free radicals, and has recently received wide attention.[2-4] Reactive free radicals add easily to the diamagnetic scavengers (spin traps) to form stable radicals (spin adducts), whose e.s.r. spectra afford information about the structure of the initial free radicals trapped. Two kinds of spin trap, nitroso-compounds and nitrones, which are most commonly utilized, react with various kinds of free radical to yield relatively stable nitroxides. Previously we employed nitrosobenzene and 2-methyl-2-nitrosopropane as spin traps to detect and identify free-radical intermediates in nickel peroxide oxidations.[1a,5] Each of these spin traps has some advantages and some disadvantages.[2-4] Thus 2-methyl-2-nitrosopropane,[6] which is one of the best spin traps, is subject to photolysis to produce di-t-butyl nitroxide [7] whose spectrum may seriously overlap the most interesting region. The spectra of spin adducts of *N*-benzylidene-t-butylamine *N*-oxide,[8] one of the best alternative spin traps, produce some difficulties in that to identify a trapped radical unequivocally a reference spectrum must be prepared in another way. Few other nitroso-compounds [5,9] and nitrones [10] have been examined. Some

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[1] (*a*) Part IV, S. Terabe and R. Konaka, *J.C.S. Perkin II*, 1972, 2136; (*b*) preliminary communication, S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, 1971, **93**, 4306.

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

[3] M. J. Perkins, in 'Essays 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 E.s.r. Symposium (Japan), Sapporo, 1968, p. 44; Abstracts, The XXIInd Annual Meeting of the Chemical Society of Japan, Tokyo, 1969, p. 1711; (*b*) S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, 1969, **91**, 5655; (*c*) S. Terabe, K. Kuruma, and R. Konaka, *Chem. Letters*, 1972, 115.

[6] See, *e.g.*, (*a*) A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, 1968, **24**, 1623; (*b*) C. Lagercrantz and S. Forschult, *Nature*, 1968, **218**, 1247; K. Torssell, *Tetrahedron*, 1970, **26**, 2759; (*c*) M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395; (*d*) I. H. Leaver and G. C. Ramsay, *Tetrahedron*, 1969, **25**, 5669.

[7] Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron*, 1967, **23**, 4021.

[8] See, *e.g.*, (*a*) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481; (*b*) M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Japan*, 1967, **40**, 702, 703; 1970, **43**, 856, 860.

[9] See, *e.g.*, A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1966, 2115; J. W. Hartgerink, J. B. F. N. Engberts, Th. A. J. W. Wajer, and Th. J. de Boer, *Rec. Trav. chim.*, 1969, **88**, 481; R. Stammer, J. B. F. N. Engberts, and Th. J. de Boer, *ibid.*, 1970, **89**, 169; S. Forshult, C. Lagercrantz, and K. Torssell, *Acta Chem. Scand.*, 1969, **23**, 522; R. Konaka, S. Terabe, and K. Kuruma, Abstracts, The Xth E.s.r. Symposium (Japan), Osaka, 1971, p. 107.

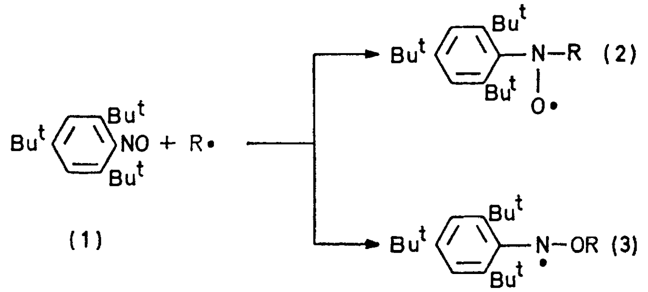
[10] See, *e.g.*, G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 401; M. Iwamura and N. Inamoto, ref. 8*b*.

new types of spin trap have also been reported[11,12] in the expectation that a variety of spin traps will be of use in applications to mechanistic studies.[2]

We now describe the utility of 2,4,6-tri-t-butylnitrosobenzene (1) as another type of spin trap and certain advantages of it compared with other spin traps. There were three reasons for its choice. (i) The nitroso-compound (1) exists completely in the active monomeric form in the solid state as well as in solution.[13] (ii) E.s.r. spectra of spin adducts were expected to be simpler than those from nitrosobenzene whose *ortho*- and *para*-hydrogen coupling constants are large. (iii) Steric effects would be revealed in spin-trapping reactions.

Various radicals were generated from various sources in the presence of 2,4,6-tri-t-butylnitrosobenzene (1) (0·01—0·005M) in benzene or in substrates themselves to give spin adducts. Radicals were mainly generated either by the abstraction of hydrogen atoms from substrates by t-butoxyl radicals (formed by the photolysis of di-t-butyl peroxide or the thermolysis of di-t-butyl peroxyoxalate) or by the abstraction of halogens from alkyl halides by tri-n-butylstannyl radicals.

It has been shown that the nitroso-compound (1) has two main advantages over other spin traps. The first is that the nitroso-compound (1) has two trapping sites, the nitrogen and oxygen atoms of the nitroso-group. The *N*-alkoxyanilino-radicals (3) can be distinguished from the nitroxides (2) by *g* values and nitrogen coupling constants. The anilino-radical (3) is sufficiently stable (for several hours) to observe its spectrum which shows the hyperfine splitting by the hydrogen atom attached to the carbon atom adjacent to the oxygen atom. It is, therefore, possible to distinguish between attacking secondary and tertiary alkyl radicals from the spectrum of the anilino-radical alone. The nitroxide (2) is, of course, much more stable than the anilino-radical (3). The second merit of using the nitroso-compound (1) is its stability even in solution, especially for photolysis. Thus, irradiation of a benzene solution containing the nitroso-compound (1) by a 1 kW high-pressure mercury lamp gave no detectable e.s.r. signal. This fact makes the nitroso-compound (1) available for many photoradical reactions.



The nitroxides obtained in these experiments are

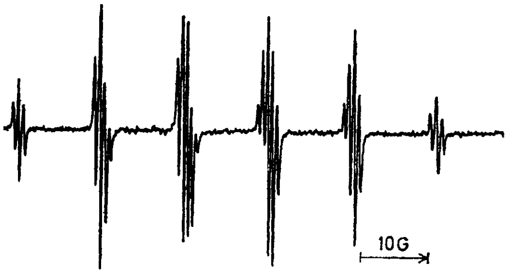


FIGURE 1 A typical spectrum of the nitroxide obtained by radical trapping with 2,4,6-tri-t-butylnitrosobenzene. This spectrum shows the adduct of methyl radical (5) generated by the reaction of methyl iodide with tri-n-butylstannane in benzene at room temperature. The smallest couplings are assigned to the two *meta*-hydrogens

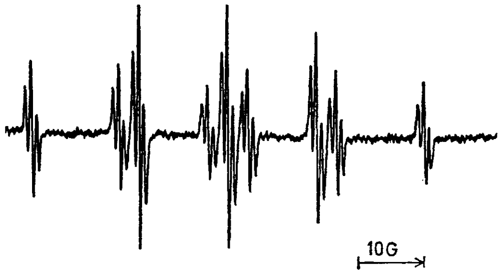


FIGURE 2 Spectrum of allyl 2,4,6-tri-t-butylphenyl nitroxide (13). The larger 1 : 2 : 1 triplet reveals coupling to the two equivalent β-hydrogens, and it is apparent that β-hydrogen coupling is larger than nitrogen coupling

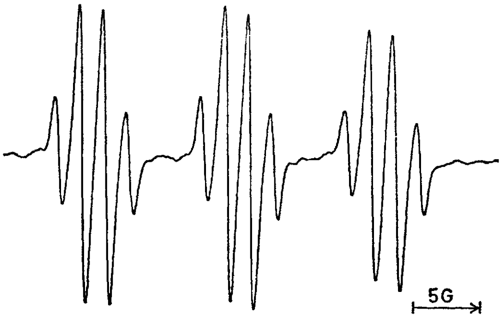


FIGURE 3 A typical *N*-alkoxyanilino-radical spectrum. This spectrum was observed on the irradiation of di-t-butyl peroxide in cyclohexane in the presence of 2,4,6-tri-t-butylnitrosobenzene. The coupling constant by the hydrogen atom on the carbon atom adjacent to the oxygen atom shows the same magnitude as *meta*-hydrogen coupling

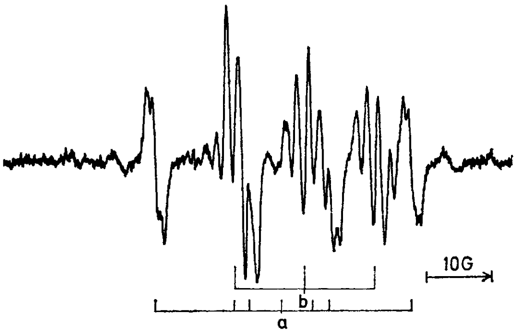


FIGURE 4 Spectrum of a mixture of both the nitroxide (25) and the anilino-radical (31) obtained by the irradiation of di-t-butyl peroxide in n-butyl alcohol. The nitroxide (a) has larger *g* value and nitrogen coupling constant than the anilino-radical (b). The line widths in the nitroxide spectrum are broadened by unresolved fine couplings

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

[12] B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Amer. Chem. Soc.*, 1971, **93**, 3290.

[13] R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 3611.

summarized in Table 1 along with radical sources, *g* values, and hyperfine splitting constants. The anilino-radicals observed are summarized in Table 2. The structures of spin adducts formed are reasonably deduced from their e.s.r. spectra. Some typical spectra are shown in Figures 1—4.

TABLE 1

Nitroxides [structure (2)] formed by the addition of various radicals to 2,4,6-tri-t-butylnitrosobenzene in benzene at room temperature

R	Radical source *	*g* Value	Hyperfine splitting constants (G)			
			a_N	$a_{m\cdot H}$	$a_{\beta\cdot H}$	Other
H(4)	T	2·0061	11·65	1·03		12·96(α-H)
Me(5)	*h*ν + DTBP T + MeI (Bu^{t}O·OCO)$_2$ *h*ν + (PhCMe$_2$O)$_2$	2·0060	13·03	0·81	12·33	
Et(6)	T + EtBr *h*ν + (Et$_3$Sn)$_2$	2·0060	13·46	0·83	17·99	
Pr^n(7)	T + Pr^{n}Br	2·0060	13·39	0·82	17·83	
Bu^n(8)	T + Bu^{n}Br *h*ν + DTBP + Bu$^n_3$P	2·0061	13·44	0·78	17·97	
[CH$_2$]$_{10}$·Me(9)	(Me·[CH$_2$]$_{10}$·CO$_2$)$_2$	2·0061	13·46	0·79	17·97	
[CH$_2$]$_2$·Ph(10)	T + Ph·[CH$_2$]$_2$·Br	2·0061	13·45	0·78	17·88	
[CH$_2$]$_2$·Cl(11)	T + Cl·[CH$_2$]$_2$·Br	2·0061	13·40	0·82	17·55	
CH$_2$·CHMe$_2$(12)	T + Me$_2$CH·CH$_2$Br	2·0061	13·57	0·78	18·27	
CH$_2$·CH:CH$_2$(13)	T + CH$_2$:CH·CH$_2$Br	2·0060	13·40	0·84	16·42	
CH$_2$·C≡CH(14)	T + CH≡C·CH$_2$Br	2·0062	13·14	0·85	15·50	
CH$_2$·COMe(15) †	*h*ν + Me$_2$CO	2·0060	13·47	0·82	14·93	
CH$_2$Ph(16) †	*h*ν + DTBP + PhMe (Bu^{t}O·OCO)$_2$ + PhMe	2·0061	13·62	0·83	14·75	
CH$_2$·OPh(17) †	*h*ν + DTBP + PhOMe	2·0064	12·23	0·82	9·85	
CH$_2$·OH(18) †	*h*ν + DTBP + MeOH *h*ν + PhCOPh + MeOH	2·0060	13·73	0·95	13·73	
Pr^i(19) ‡	T + Pr^{i}Br	2·0060	13·29	0·76	22·19	0·38(6γ-H)
CHMeEt(20) ‡	T + EtCHMeBr	2·0061	13·33	0·77	22·25	0·39(5γ-H)
CHMePh(21) † ‡	*h*ν + DTBP + PhEt	2·0060	13·59	0·89	18·72	
CHMe·[CH$_2$]$_3$·Me or CHEt·[CH$_2$]$_2$·Me(22) † ‡	*h*ν + DTBP + Me·[CH$_2$]$_4$·Me	2·0060	13·16	*a*	21·77	
CH(OH)Me(23) †	*h*ν + DTBP + EtOH	2·0060	12·60	0·96	14·40	0·19(12H) [b]
CH(OH)Et(24) † ‡	*h*ν + DTBP + Pr^{n}OH	2·0060	12·59	1·02	14·39	
CH(OH)Pr^n(25) † ‡	*h*ν + DTBP + Bu^{n}OH	2·0061	12·36	1·05	14·37	
Ph(26)	(PhCO$_2$)$_2$	2·0057	9·88	0·63		2·86(2H) [c] 2·61(1H) [c] 0·92(2*m*′-H)
SPh(27)	*h*ν + (PhS)$_2$	2·0066	16·29	0·85		

* T = Tri-n-butylstannane, DTBP = di-t-butyl peroxide. † In solution of substrate. ‡ Anilino-radical also observed (see Table 2).

[a] Not observed because of line broadening. [b] Assignment unknown. [c] Couplings by *o*′- and *p*′-H, but assignment not established.

TABLE 2

Anilino-radicals [structure (3)] formed by the addition of various radicals to 2,4,6-tri-t-butylnitrosobenzene in benzene at room temperature

R	Radical source *	*g* Value	Hyperfine splitting constants (G)		
			a_N	$a_{m\cdot H}$	$a_{R\cdot H}$
Pr^i(28)	See Table 1	2·0040	11·01	1·82	1·82(1H)
CHMeEt(29)	See Table 1	2·0041	10·91	1·66	1·66(1H)
Cyclohexyl(30) †	*h*ν + DTBP + cyclohexane	2·0040	10·95	1·79	1·79(1H)
CH(OH)Pr^n(31) †	See Table 1	2·0040	10·72	1·70	1·70(1H)
Bu^t(32)	T + Bu^{t}Br *h*ν + DTBP + (EtO)$_3$P	2·0040	10·26	1·90	
C(CN)Me$_2$(33)	[Me$_2$C(CN)N:]$_2$	2·0037	10·01	1·98	
SiEt$_3$(34)	*h*ν + DTBP + Et$_3$SiH	2·0040	10·33	1·96	
SnEt$_3$(35)	*h*ν + (Et$_3$Sn)$_2$	2·0040	9·98	1·95	
COPh(36)	*h*ν + DTBP + PhCHO	2·0036	10·53	2·07	

* See Table 1. † In solution of substrate.

Addition of Alkyl and Substituted Alkyl Radicals.—

Addition of 1-cyano-1-methylethyl radical generated from azobisisobutyronitrile to the nitroso-compound (1) afforded *N*-(1-cyano-1-methylethoxy)-2,4,6-tri-t-butyl anilino-radical (33) (Table 2). The structural assignment of this spin adduct has been described.[1b,14] E.s.r.

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[14] T. Hosogai, N. Inamoto, and R. Okazaki, *J. Chem. Soc.* (*C*), 1971, 3399.

spectra of *N*-alkoxy-*N*-alkylamino-radicals have been reported.[15]

Primary alkyl radicals reacted with the nitroso-compound (1) to form exclusively nitroxides (2) in the normal course of addition, and anilino-radicals (3) were not detected at all. Secondary alkyl radicals added at both nitrogen and oxygen atoms to give nitroxides (2) and anilino-radicals (3). The ratio of spin adducts may be related to steric interference around the radical centre in the radical trapped. Thus 1-hydroxypropyl radical produced by hydrogen abstraction from n-propyl alcohol by t-butoxyl radical yielded both the nitroxide (24) and the anilino-radical [3; R = CH(OH)Et] in an initial ratio of *ca.* 3 : 1, while 1-hydroxybutyl radical from n-butyl alcohol yielded both spin adducts (25) and (31) in an initial ratio of *ca.* 1 : 2 (see Figure 4). Only the nitroxide (23), however, was observed in the reaction of 1-hydroxyethyl radical. Tertiary alkyl radicals attacked the nitroso-group at the oxygen atom exclusively.

Most carbon-centred radicals reacted with the nitroso-compound (1) to give nitroxide (2) and/or anilino-radical (3). Photolysis of di-t-butyl peroxide in chloroform or in methylene dichloride in the presence of the nitroso-compound (1) did not yield any paramagnetic species. This indicates that although hydrogen atoms should be abstracted easily from chloroform or methylene dichloride by t-butoxyl radical, the radicals formed may not be scavenged by the nitroso-compound (1). However, perfluoroalkyl radicals are trapped readily.[16] The nitroxide (5) resulting from the β-scission of t-butoxyl radical was recognized when hydrogen abstraction by t-butoxyl radical proceeds relatively slowly (see Table 1).

The photolysis of di-t-butyl peroxide in isopropyl alcohol produced the e.s.r. spectrum of 2,4,6-tri-t-butylphenyl nitroxide (4) in high concentration together with a weak signal possibly assigned to the anilino-radical (3; R = CMe_2OH). The spectral data of the latter spin adduct, however, could not be determined because of the superposition of the strong signal of the nitroxide (4). Formation of the hydrogen atom adduct has been reported on spin trapping by use of 2-methyl-2-nitrosopropane instead of the nitroso-compound (1) in a similar reaction,[6c] while the nitroxide formed by the trapping of the 1-hydroxy-1-methylethyl radical was referred to in the photolytic reduction of benzophenone in isopropyl alcohol.[6d] Structural assignment of the latter nitroxide seems not to be unequivocal. The formation of the former spin adduct may be the result of either hydrogen-atom transfer from the 1-hydroxy-1-methylethyl radical to the nitroso-group [6c] or intramolecular proton transfer in the 1-hydroxy-1-methylethyl adduct followed by elimination of acetone.[17]

Propargyl nitroxide (14) was the sole adduct obtained on the reduction of propargyl bromide with tri-n-butylstannane, though the product study of the reduction of propargyl chloride with the same reagent at 65 °C showed that propyne and allene were produced in the ratio of 5·9 : 1.[18] The failure to observe the propadienyl–radical adduct may be due to its instability and/or to its slow addition to the nitroso-group compared with the propargyl radical.

Additions of Radicals other than Alkyl Radicals.—Phenyl radical generated by the photolysis or thermolysis of dibenzoyl peroxide added readily to the nitroso-compound (1) to give 2,4,6-tri-t-butyldiphenyl nitroxide (26). The nitrogen coupling constant (9·88 G) is smaller than those of alkyl phenyl nitroxides (10·4—12·3 G),[1a,5a,b] and close to the value for diphenyl nitroxide ($a_{\rm N} = 9{\cdot}77$ G).[19] The three hydrogens at the *ortho*- and *para*-positions in alkyl phenyl nitroxides are generally equivalent as described previously.[1a] These three hydrogens in the nitroxide (26), however, are not equivalent. Perhaps the two *ortho*-hydrogens are not equivalent because of the significant steric hindrance to free rotation of the phenyl group. Phenoxyanilino-radicals (3; R = Ph) were not detected in this reaction.

Photolysis of diphenyl disulphide in the presence of the nitroso-compound (1) gave a spectrum of a triplet (1 : 1 : 1) of triplets (1 : 2 : 1) whose *g* value and nitrogen coupling constant are larger than other nitroxides in Table 1. The structural assignment of this spin adduct (27) is supported by the fact that t-butyl alkylthio- and phenylthio-nitroxides [6d,20] show larger *g* values and nitrogen coupling constants than alkyl t-butyl nitroxides. The *S*-nitroxide (27) was very unstable and could only be observed during irradiation. The spectrum decayed rapidly when the light source was removed.

The formation of only the anilino-radical (36) from benzoyl radical is interesting, because acyl radicals have been known to produce stable nitroxides by addition to nitroso-compounds.[6a] The above observation suggests that the benzoyl radical is as large as tertiary alkyl radicals.

No spin adduct was obtained on the oxidation of carbazole and *N*-methylaniline with nickel peroxide, in which the presence of nitrogen radical intermediates has been shown previously.[1a,5b]

Triethylsilyl and triethylstannyl radicals exclusively added at the oxygen atom to the nitroso-compound (1) as did the tertiary alkyl radicals [see (34) and (35) in Table 2]. Steric hindrance in the addition may force these radicals to give only the anilino-radicals. The strong O–Si and relatively strong O–Sn bonds [21] make it possible to form anilino-radicals. In addition, only a few silyl nitroxides are known.[22]

The absence of the tri-n-butylstannyl–radical adducts

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[15] W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, 1971, **93**, 5582.

[16] R. Konaka and S. Terabe, Abstracts, The Xth E.s.r. Symposium (Japan), Osaka, 1971, p. 110.

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

[18] R. M. Fantazier and M. L. Poutsma, *J. Amer. Chem. Soc.*, 1968, **90**, 5490.

[19] E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, 1967, **32**, 3853.

[20] I. H. Leaver, G. C. Ramsay, and E. Suzuki, *Austral. J. Chem.*, 1969, **22**, 1891.

[21] R. A. Jackson, *Adv. Free Radical Chem.*, 1969, **3**, 231.

[22] R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, 1971, **93**, 5901.

in spin trapping studies of the reduction of alkyl halides with tri-n-butylstannane may imply that the rate of

$$\mathrm{Bu^n{}_3Sn\cdot + RX \longrightarrow Bu^n{}_3SnX + R\cdot} \qquad (1)$$

$$\mathrm{Bu^n{}_3Sn\cdot + (1) \longrightarrow Ar\dot{N}{-}OSnBu^n{}_3} \qquad (2)$$

$$\mathrm{R\cdot + Bu^n{}_3SnH \longrightarrow RH + Bu^n{}_3Sn\cdot} \qquad (3)$$

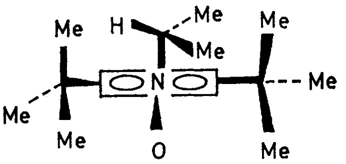
$$\mathrm{R\cdot + (1) \longrightarrow ArN(O\cdot){-}R} \qquad (4)$$

$$\mathrm{Ar = 2,4,6\text{-}Bu^t{}_3\cdot C_6H_2}$$

reaction (1) is much faster than that of reaction (2), and that reaction (4) proceeds at a rate at least comparable with that of reaction (3). These findings are consistent with the results of kinetic studies by Carlsson and Ingold[23] that reaction (3) is the rate-controlling step for the chain propagation in reductions of alkyl bromides and iodides with alkylstannanes.

In spin-trapping studies of alkyl radicals produced by reduction of alkyl halides by tri-n-butylstannane, each alkyl halide was mixed with the nitroso-compound (1) in benzene as a control test, and a search for paramagnetic species by e.s.r. was performed, but no radical species could be observed.

Hyperfine Splitting Constants and Structural Assignment.—Of interest is the finding that the order of magnitude of the β-hydrogen couplings in the nitroxides observed is secondary > primary > methyl for the initial radicals trapped (see Table 1), in contrast to that found in the usual nitroxides.[24,25] β-Hydrogen couplings in alkyl phenyl nitroxides, for example, are 10·4, 8·3, and 2·1 G when alkyls are methyl, ethyl, and isopropyl, respectively.[24] β-Hydrogen coupling is known to depend on its relative orientation to the p_z-orbital containing the odd electron[26] and it is considered that the conformation of an alkyl group is largely governed by steric repulsion between the phenyl group and the *N*-alkyl group in alkyl phenyl nitroxides.[25] Thus the preferred dihedral angle between the C_β–H bond and the p_z-orbital in alkyl phenyl nitroxides has the largest value in isopropyl phenyl nitroxide, leading to the smallest value for the β-hydrogen coupling as expected from the $\cos^2\theta$ law.[26] In the case of alkyl 2,4,6-tri-t-butylphenyl nitroxides, however, the orientation of β-hydrogen atoms may be substantially affected by the non-bonded interaction between the *N*-alkyl groups and the two *ortho*-t-butyl groups. Steric hindrance from the two *ortho*-t-butyl groups would constrain the N–O bond to twist at about 90° from the plane of the phenyl group. The large nitrogen coupling (13·0—13·7 G) compared with that of alkyl phenyl nitroxides (10·4—12·3 G)[1a] convincingly demonstrates the above view. Such a steric situation is best understood by inspection of molecular models consisting of atomic models having dimensions proportional to van der Waals radii. Such a model of isopropyl nitroxide (19) indicates that the dihedral angle between the C_β–H bond and the axis of the p_z-orbital on the nitrogen atom comes very close to 0° as shown in structure (I). The fact that the largest β-hydrogen coupling constant observed appears in isopropyl nitroxide (19) supports the above consideration. In the case of the nitroxide (6) the average dihedral angle predicted is 30° which is consistent with the observed β-hydrogen couplings.



(I)

Distinction among nitroxides (6)—(10) is difficult (see Table 1). However, in nitroxides (11)—(18) the methylene group shows different β-hydrogen couplings. The differences of the β-hydrogen coupling constants in these series of nitroxides seem to reflect mainly the electronegativity effect of the substituent on the β-carbon atom rather than a change of the relative conformation of the β-methylene group to the nitroxyl group. This tendency could be investigated more closely by a study of the temperature-dependence of the e.s.r. spectra of these nitroxides.[16]

In the case of secondary alkyl–radical adducts the electronegativity effect is also probably an important factor influencing the β-hydrogen coupling constant. Thus, the secondary alkyl nitroxides (19), (21), and (23) can be successfully distinguished by the difference in the β-hydrogen coupling constants, but distinction between nitroxides (19) and (20), or among (23), (24), and (25) is almost impossible from spectra of the nitroxides alone. However, the observed ratios of nitroxides (2) and anilino-radicals (3) are also available for identification as described above. The e.s.r. spectra of the anilino-radicals (33)—(36) were little different (Table 2).

Unfortunately it seems that 2,4,6-tri-t-butylnitrosobenzene (1) is not a good spin trap for radicals other than alkyl. However, for alkyl radicals it is better than other spin traps because the spectrum of the spin adduct is more susceptible to variation in the nature and structure of the radical trapped. Further, the nitroso-compound (1) has good prospects for applications to photoradical reactions owing to its stability towards photolysis.

EXPERIMENTAL

E.s.r. Spectra.—General experimental procedures have been described.[1a] An inverted U-type mixing cell[27] was used for all experiments. In halogen abstractions, benzene solution (*ca.* 1 ml) containing 0·02—0·001M-2,4,6-tri-t-butylnitrosobenzene (1) and 0·5M-alkyl halide was mixed

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with a benzene solution (*ca.* 1 ml) containing 0·5M-tri-n-butylstannane at room or somewhat higher (60 °C) temperatures. For hydrogen abstractions, *ca.* 2 ml of a substrate containing 0·01—0·005M-nitroso-compound (1) and di-t-butyl peroxide (0·2 ml) was irradiated *in situ* in the cavity of the spectrometer at 250 ± 10 nm. For photolysis or thermolysis of azobisisobutyronitrile (at 365 ± 10 nm or at 60 °C), dilauroyl peroxide (at 250 ± 10 nm or at 70 °C), hexaethyldistannane (at 310 ± 10 nm for the generation of triethylstannyl radical and at 250 ± 10 nm for the generation of ethyl radical), dicumyl peroxide (at 250 ± 10 nm), diphenyl disulphide (at >310 nm), di-t-butyl peroxyoxalate (at room temperature), and dibenzoyl peroxide (at 80 °C), benzene solutions (*ca.* 2 ml) of 0·005M-nitroso-compound (1) and 0·01—0·1M of the radical source were used. Benzophenone (0·005M in benzene) and acetone (neat) were irradiated at 365 ± 10 and 250 ± 10 nm, respectively. For irradiation, the output from a Shimazu–Bausch and Lomb high-intensity grating monochromator with a high-pressure mercury lamp source was focused on the sample with a quartz lens.

Spectra were recorded 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 non-polar substrates at room temperature. The determination of hyperfine splitting constants and *g* values has been given,[1a] and the values listed in Tables 1 and 2 were averages of at least three measurements. Spectral simulation was not carried out because the simple spectra did not require it.

Reagents.—Most of the compounds used were commercial, and purified by crystallisation or distillation if necessary. Alkyl halides were passed through a column of active aluminium oxide immediately before use. The nitroso-compound (1) was prepared by the oxidation of 2,4,6-tri-t-butylaniline with *m*-chloroperbenzoic acid.[13] Di-t-butyl peroxide distilled at reduced pressure gave one peak on g.l.c., and di-t-butyl peroxyoxalate was obtained by the method of Bartlett *et al.*[28] Tri-n-butylstannane was prepared by the reaction of hexa-n-butyldistannoxane with polymethylhydrosiloxane.[29] Hexaethyldistannane was supplied by Professor Y. Sato of Nagoya City University.

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