A Probe for Homolytic Reactions in Solution. Part V.[1] Perdeuterionitrosobutane: an Improved Spin Trap

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The synthesis of the title compound is described, and its merits as a spin trap are outlined.

There has been considerable interest recently in the applications of *C*-nitroso-compounds and of nitrones as diamagnetic scavengers (' spin traps '[2]) for reactive free radicals.[3] These reactions lead to relatively stable nitroxide radicals, whose e.s.r. spectra are readily observed. Identification of the nitroxide by its spectrum then usually implies identification of the reactive radical.

2-Methyl-2-nitrosopropane (nitrosobutane) has proved particularly useful in this respect, and we recently outlined a simple synthesis of this compound from t-butylamine.[4] In an earlier paper [5] we had commented on the potential utility of fully deuteriated nitrosobutane as a spin trap. We now describe the application of the t-butylamine oxidation procedure to the synthesis of perdeuterionitrosobutane, and outline the advantages of this compound over its undeuteriated counterpart.

The synthesis utilised a standard Grignard method [6] to prepare [$^2H_9$]-t-butyl alcohol from hexadeuterioacetone and trideuteriomethyl iodide, though the procedure was modified slightly to improve product recovery. The butanol was converted into [$^2H_9$]-t-butylamine by a modified Ritter procedure,[7] in which the acidic reaction medium comprised monodeuterioacetic acid and dideuteriosulphuric acid, in order to minimise possible incorporation of protium by exchange in the intermediate t-butyl cation. (Although no attempt was made to remove exchangeable protium from the hydroxy-group of the alcohol, complete exchange of this should have resulted in only *ca.* 3% incorporation into the final t-butylamine.) The amine was isolated as its hydrochloride, from which it was liberated with alkali prior to oxidation with solid *m*-chloroperoxybenzoic acid, as previously described.[4] Although the i.r. and n.m.r. spectra of the nitrosobutane failed to reveal incorporation of protium, the mass spectrum indicated as much as 3% [^1H] in the product, possibly incorporated at the stage indicated above.

The merit of perdeuterionitrosobutane as a spin trap lies in the reduced magnitude of the hyperfine splitting which results from the presence of nine equivalent deuterium nuclei in the t-butyl group, in comparison with nine equivalent protons. Although splittings from the t-butyl protons are not normally resolved in the e.s.r. spectra of t-butyl nitroxides, they are sufficient to cause considerable line broadening, which limits the resolution of other small hyperfine splittings in the nitroxide spectra. An incidental consequence of the narrower line width in the spectra of the perdeuterio-t-butyl nitroxides is that a better signal-to-noise ratio should be achieved than when the undeuteriated scavenger is used under comparable conditions.

The improved resolution obtained in spectra of nitroxides derived from the deuteriated scavenger has been demonstrated in preliminary communications both from this laboratory,[1b] and, independently, from Jakobsen and Torssell.[8] The spectra shown here further illustrate this improvement. Figure 1 shows comparison spectra of t-butyl undecyl nitroxide obtained by scavenging undecyl radicals from lauryl

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[1] (*a*) Part IV, G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 401; (*b*) preliminary communication, R. J. Holman and M. J. Perkins, *Chem. Comm.*, 1971, 244.

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

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

[4] R. J. Holman and M. J. Perkins, *J. Chem. Soc.* (*C*), 1970, 2195.

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

[6] W. M. Cumming, I. V. Hopper, and T. S. Wheeler, ' Systematic Organic Chemistry,' 4th edn., Constable, London, 1950, p. 81.

[7] J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, 1948, **70**, 4048.

[8] H. J. Jakobsen and K. Torssell, *Tetrahedron Letters*, 1970, 5003.

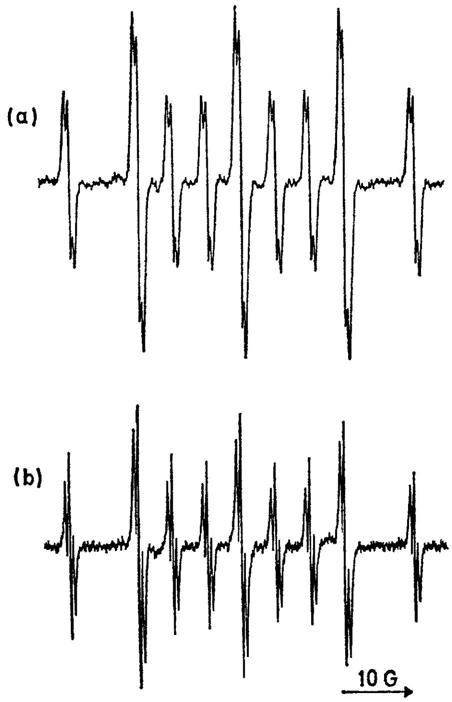

FIGURE 1 E.s.r. spectra of (a) n-$C_{11}H_{23}(Bu^t)NO\cdot$, and (b) n-$C_{11}H_{23}([^2H_9]Bu^t)NO\cdot$, recorded under comparable conditions

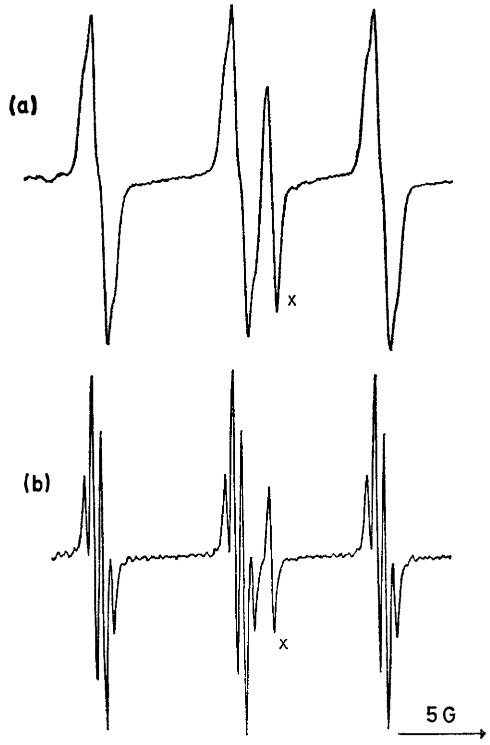

FIGURE 2 E.s.r. spectra of (a) $MeO\cdot CO(t\text{-}C_4H_9)NO\cdot$, and (b) $MeO\cdot CO([^2H_9]Bu^t)NO\cdot$, recorded under comparable conditions. In each spectrum the line marked × is the central line of the triplet due to t-butoxy t-butyl nitroxide

peroxide;[9] Figure 2 gives comparison spectra of t-butyl methoxycarbonyl nitroxide obtained by scavenging methoxycarbonyl radicals formed by hydrogen abstraction from methyl formate by butoxy-radicals.[1b] In the former case, deuteriation enhances the resolution of the splitting due to the β-methylene protons of the n-alkyl group. In the latter, long-range coupling across the carboxy-group is clearly revealed.[1b]

EXPERIMENTAL

$[^2H_9]$-*t-Butyl Alcohol.*—A solution of dry trideuteriomethyl iodide (24 g) in sodium-dried ether (80 ml) was slowly added to dry magnesium (4 g) under nitrogen, to produce the Grignard reagent (*cf.* ref. 6). To the rapidly stirred, ice-cooled solution was added dropwise a solution of hexadeuterioacetone (9·5 g) in dry ether (20 ml). The mixture was set aside overnight at room temperature, and the magnesium complex was then decomposed by slow addition of just sufficient 4N-sulphuric acid. (Any iodine which is liberated at this stage should be removed by addition of sodium thiosulphate; this produces some sulphur, which is removed in the subsequent distillation.) The ether layer was separated and the aqueous layer was subjected to repeated (×3) continuous extraction with ether to ensure complete removal of the butanol from the aqueous phase. The combined extracts were dried ($MgSO_4$). The bulk of the solution was then reduced in volume by about 50% by distillation through a short fractionating column equipped with a total reflux distillation head, and the remainder of the solution was distilled through a spinning-band column. The yield of $[^2H_9]$-t-butyl alcohol, b.p. 78°, was 12·5 g.

$[^2H_9]$-*t-Butylamine.*—Sodium cyanide (11 g) was gradually added to a well stirred mixture of dideuteriosulphuric acid (98%; 50 g) and monodeuterioacetic acid (25 ml). The stirred solution was then warmed to 50—60°, and a solution of the $[^2H_9]$alcohol (9 g) in monodeuterioacetic acid (25 ml) was added dropwise, the temperature being maintained at 50—60° throughout. Stirring was continued for a further 12 h at room temperature before the mixture was poured on ice (300 g) and neutralised with aqueous sodium hydroxide (15%; *ca.* 250 ml). The resulting mixture was extracted with ether (6 × 100 ml), and the combined extract was washed with aqueous 15% hydrochloric acid (2 × 10 ml), dried (K_2CO_3), and distilled to give $[^2H_9]$-t-butylformamide, b.p. 202° (6·2 g). The acid washings were evaporated to give a little (80 mg) $[^2H_9]$-t-butylamine hydrochloride.

The t-butylformamide (4·0 g) was then boiled under reflux with aqueous 30% potassium hydroxide (50 ml), the top of the reflux condenser being connected in series with two U-tubes, each of which was charged with aqueous 25% hydrochloric acid (25 ml). After 6 h, cooling of the condenser was discontinued, and the bulk of the solution was distilled into the U-tubes. The hydrochloric acid solutions were combined and evaporated to dryness under reduced pressure to leave white crystalline $[^2H_9]$-t-butylamine hydrochloride, m.p. 309° (3·15 g).

The foregoing procedure for the synthesis of $[^2H_9]$-t-butylamine is more convenient than the approach adopted in the one previous synthesis of this compound.[10]

Perdeuterionitrosobutane ($[^2H_9]$-2-*Methyl-2-nitrosopropane*).—To the foregoing amine hydrochloride (1·2 g) in a flask flushed with a slow stream of nitrogen was added

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

[10] H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 1965, 6421.

aqueous 10% potassium hydroxide (15 ml). The solution was eventually heated to liberate the last traces of amine. During these operations, the stream of nitrogen issuing from the flask was passed through a condenser loosely packed with a mixture of *m*-chloroperoxybenzoic acid (3 g) and sodium chloride (27 g) (*cf.* ref. 4). The blue nitroso-monomer was collected and purified as described for its undeuteriated counterpart.[4] The colourless dimer (0·36 g) had m.p. 82°. I.r. and n.m.r. spectroscopy showed no trace of incorporation of protium into the product. Mass spectral examination suggested that the material contained at least 70% of the [$^2H_9$]-compound with *ca.* 25% of the [$^2H_8$]-analogue.

Spectra.—These were obtained by the general procedure indicated previously.[9]

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