Tetrahedron Letters,Vol.26,No.10,pp 1349-1352,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

SPIN-TRAPPING OF LIGATED BORYL RADICALS

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Amine- and phosphine-boryl radicals add to 2-methyl-2-nitrosopropane, 2,4,6-tri-t-butylnitrosobenzene, and phenyl-N-t-butylnitrone to give nitroxide spin-adducts and the application of these spin-trapping reactions as mechanistic probes is described.

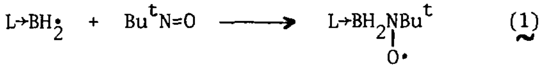
'Spin-trapping', the reaction of a short-lived radical with a diamagnetic scavenger to give a more persistent and thus more readily detectable adduct radical, has become established as an important technique for the study of homolytic reactions.[1]

As part of our investigations[2-4] of ligated boryl radicals $L{\rightarrow}BH_2^{\bullet}$, we have examined the spin-trapping of these species with 2-methyl-2-nitrosopropane (MNP), 2,4,6-tri-t-butylnitrosobenzene (TBN), and phenyl-*N*-t-butylnitrone (PBN) to give relatively long-lived nitroxides which are readily detectable by e.s.r. spectroscopy.

A deoxygenated benzene solution containing MNP (0.014 M) and trimethylamine-borane[5] (*ca.* 2 M) showed no e.s.r. spectrum in the dark at room temperature. However, after addition of di-t-butyl hyponitrite[6] (0.05 M added as a 1 M solution in benzene) which provides a thermal source of t-butoxyl radicals, the spectrum shown in the Figure appeared. The splitting pattern results from interaction of the unpaired electron with two non-equivalent ^{14}N nuclei, one ^{11}B nucleus, and two equivalent protons and we assign the spectrum to the nitroxide (1; $L = Me_3N$), formed as shown in equations (1)-(3). The blue colour of monomeric MNP persisted throughout these experiments. The spectral assignment was confirmed by generating the *B*-deuteriated nitroxide from $Me_3N{\rightarrow}BD_3$ and the e.s.r. parameters for all spin-adducts are collected in the Table.

$$Bu^tON{=}NOBu^t \longrightarrow 2Bu^tO^{\bullet} + N_2 \qquad (1)$$

$$Bu^tO^{\bullet} + L{\rightarrow}BH_3 \longrightarrow Bu^tOH + L{\rightarrow}BH_2^{\bullet} \qquad (2)$$



$$L{\rightarrow}BH_2^{\bullet} + Bu^tN{=}O \longrightarrow L{\rightarrow}BH_2N(O^{\bullet})Bu^t \quad (1) \qquad (3)$$

Support for reaction (3) as the source of nitroxide adducts was obtained by conducting the experiment in the presence of n-butyl bromide (1 M) when the spectrum of (1; $L = Me_3N$) was completely replaced by that of the n-butyl spin-adduct (2) at 298 K. Amine-boryl radicals are known[3] to abstract bromine atoms rapidly from alkyl bromides and, under the conditions of the experiment, halogen abstraction must take place much more rapidly than the trapping of $Me_3N{\rightarrow}BH_2^{\bullet}$ by MNP [eqns. (4) and (5)]. With n-butyl chloride under the same conditions only

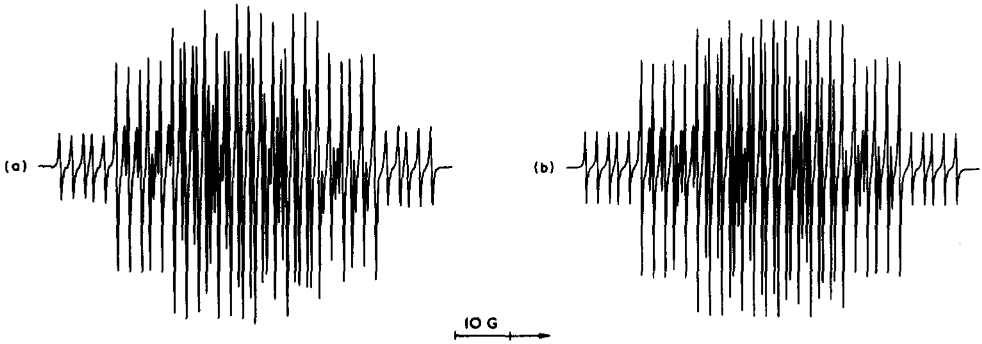


FIGURE: (a) E.s.r. spectrum of (1; L = Me_3N) at 294 K and (b) its computer simulation.

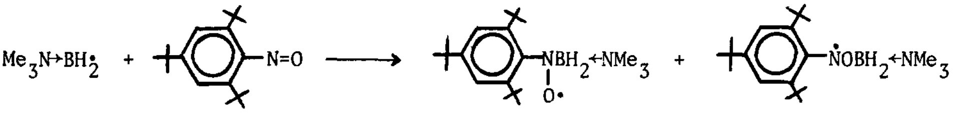
$$Me_3N{\rightarrow}B\dot{H}_2 + Bu^nBr \longrightarrow Me_3N{\rightarrow}BH_2Br + Bu^n\cdot \qquad (4)$$

$$Bu^n\cdot + Bu^tN{=}O \longrightarrow Bu^nN(\dot{O})Bu^t \quad (2) \qquad (5)$$

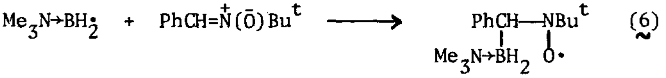
(1; L = Me_3N) was detected. Spectra of nitroxides of the type (1) were observed in similar experiments with $Et_3N{\rightarrow}BH_3$ and pyridine-borane at, or slightly above, room temperature (see Table). The pyridine-boryl radical is of interest as an isoelectronic counterpart of the benzyl radical.

E.s.r. spectra of the anionic nitroxides $H_3\bar{B}N(\dot{O})R$ (3) have been reported previously by Crozet and Tordo[7,8] (R = Bu^t or aryl) and by Perkins *et al.*[9] (R = 2,6-Br_2-4-$SO_3NaC_6H_2$), although it is possible that these nitroxides are formed by routes other than trapping of $H_3\bar{B}\cdot$ by the appropriate nitroso compound.[7] The nitroxide-nitrogen, boron, and β-proton splittings for (3) are similar to those obtained by us for the spin-adducts of the neutral ligated boryl radicals.

We have also observed e.s.r. spectra of nitroxide spin-adducts when $Me_3N{\rightarrow}B\dot{H}_2$ or $Me_3N{\rightarrow}B\dot{D}_2$ were generated in the presence of TBN[10] (0.005 M) or PBN[11] (0.007 M) [eqns. (6) and (7)]. TBN is known to function as an ambident spin-trap towards alkyl radicals;[10] primary radicals



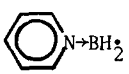
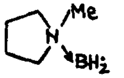
(4) (5) (6)



$$Me_3N{\rightarrow}B\dot{H}_2 + PhCH{=}\overset{+}{N}(\bar{O})Bu^t \longrightarrow \underset{Me_3N\rightarrow BH_2}{PhCH}{-}\underset{O\cdot}{N}Bu^t \quad (6) \qquad (7)$$

are reported to add exclusively to nitrogen to give nitroxides, secondary radicals add competitively to N and O to give mixtures of nitroxides and alkoxy(aryl)aminyl radicals, and tertiary radicals yield only the aminyl spin-adduct.[12] The trimethylamine-boryl radical adds competitively to N and O in TBN and at room temperature the spectrum of the oxy(aryl)aminyl adduct (5) was appreciably stronger than that of (4). Trialkylsilyl radicals add exclusively to the oxygen atom in TBN[10] and we have noted previously[2,3] a number of other similarities in

TABLE: E.S.R. PARAMETERS FOR NITROXIDE SPIN ADDUCTS IN BENZENE

Trapped radical	Spin trap	Temp. /K	g-Factor	Hyperfine splittings (G) [a]
$Me_3N{\to}BH_2^{\bullet}$	MNP	294	2.0064	12.3 (1N), 5.8 (1B), 10.2 (2H), 2.2 (1N)
	PBN [b]	341	2.0059	15.3 (1N), 4.3 (1B), 2.8 (1H)
	TBN [c,d]	304	2.0064	12.7 (1N), 7.3 (1B), 18.6 (2H)
	TBN [c,e]	304	2.0044	10.9 (1N)
$Me_3N{\to}BD_2^{\bullet}$	MNP	292	2.0064	12.3 (1N), 5.8 (1B), 1.5 (2D), 2.2 (1N)
$Et_3N{\to}BH_2^{\bullet}$	MNP	300	2.0064	12.7 (1N), 5.8 (1B), 11.3 (2H), 1.8 (1N)
	MNP	292	2.0063	12.4 (1N), 5.1 (1B), 8.4 (2H), 3.0 (1N)
$Pr^i_2EtN{\to}BH_2^{\bullet}$	MNP	292	2.0063	12.6 (1N), 6.4 (1B), 17.1 (2H), 1.4 (1N)
$PhCH_2NMe_2{\to}BH_2^{\bullet}$	MNP	292	2.0064	12.4 (1N), 5.9 (1B), 10.8 (2H), 2.0 (1N)
	MNP	292	2.0063	12.5 (1N), 5.8 (1B), 10.9 (2H), 1.8 (1N)
(8)	MNP	312	2.0061	15.4 (1N), 11.1 (2H)
$Et_3P{\to}BH_2^{\bullet}$	MNP	292	2.0063	13.5 (1N), 6.4 (1B), 15.1 (2H), 10.6 (1P)
$Bu^n_3P{\to}BH_2^{\bullet}$	MNP	292	2.0063	13.5 (1N), 6.5 (1B), 15.2 (2H), 9.8 (1P)

a Number of equivalent nuclei shown in parentheses. ^{11}B-Splittings are given; $(\gamma 10_B/\gamma 11_B) = 0.335$. *b* The spectrum of the $Me_3N{\to}BD_2^{\bullet}$ adduct showed narrower lines. *c* Splittings refer to the adduct of 3,5-dideuterio-TBN which afforded simpler spectra. *d* Parameters for (4). *e* Parameters for (5).

the reactivities of ligated boryl and silyl radicals.

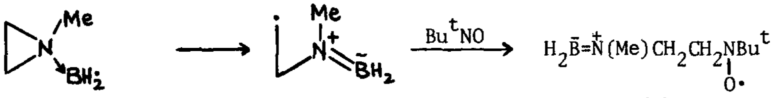
At room temperature, the hyperfine lines in the spectrum of (6) or of its *B*-deuteriated analogue were of unequal width and lines 2,7,10,15,18, and 23 were particularly broad, although for the $Me_3N{\to}BD_2^{\bullet}$ adduct the expected amplitude distribution was approached by 340 K. We attribute this lineshape effect to out-of-phase modulation of the boron and proton splittings [whilst a(N) remains unchanged], brought about by exchange between two approximately equally populated conformations of this sterically congested radical. The effects will be discussed in detail in a full paper.

Appropriately constituted amine-boryl radicals are known[2-4] to undergo rapid unimolecular β-scission or rearrangement and spin-trapping can be made to compete with these transformations. Thus, at 292 K a benzene solution containing $Bu^tON{=}NOBu^t$, $PhCH_2NMe_2{\to}BH_3$ (1.0 M), and MNP (0.014 M) afforded overlapping spectra of (1; L = $PhCH_2NMe_2$) and benzyl t-butyl nitroxide, the latter resulting from trapping of the benzyl radicals produced by β-scission of the amine-boryl radical [equation (8; R = $PhCH_2$)]. With $Bu^tNMe_2{\to}BH_3$ under similar conditions, only di-t-butyl nitroxide was detectable and β-scission of $Bu^tNMe_2{\to}BH_2^{\bullet}$ is now much more rapid than its

$$RNMe_2{\rightarrow}BH_2^{\bullet} \longrightarrow R^{\bullet} + Me_2\overset{+}{N}{=}\overset{-}{B}H_2 \qquad (8)$$

trapping by MNP. A similar experiment with $Pr^i{}_2NEt{\rightarrow}BH_3$ afforded only the spectrum of $Bu^tN(\dot{O})Pr^i$, but when the concentration of MNP was increased to 0.050 M the nitroxide (1; L = $Pr^i{}_2NEt$) was also detectable.

Only the spectrum of (1; L = $\overline{CH_2(CH_2)_3N}Me$) was observed in experiments with *N*-methylpyrrollidine-borane and MNP (0.014 M), but relief of angle strain in the *N*-methylaziridineboryl radical (7) leads to its rapid β-scission with ring-opening to give (8) and the spin-adduct (9) of this primary alkyl radical was the only nitroxide detectable in experiments with *N*-methylaziridine-borane at 310 K.



(9)

(7) (8) (9)

Phosphine-boryl radicals[2] can also be spin-trapped under similar conditions. For example, strong e.s.r. spectra of the corresponding nitroxides (1; L = R_3P) were observed from benzene solutions containing MNP (0.014 M), $Bu^tON{=}NOBu^t$ (0.05 M), and $Et_3P{\rightarrow}BH_3$ or $Bu^n{}_3P{\rightarrow}BH_3$ (*ca.* 0.8 M) at 292 K. The spectra of these adducts (see Table) were similar to those derived from the amine-boryls, except that the smaller nitrogen splitting shown by the latter adducts was replaced in the former by a ^{31}P splitting of *ca.* 10 G, in the range expected if the unpaired electron population of the P-3s orbital in (1; L = R_3P) is similar to the corresponding N_γ-2s population in (1; L = R_3N).

In conclusion, it is clear that spin-trapping studies will have an important role to play in future investigations of the chemistry of ligated boryl radicals and the utility of this technique will be greatly increased when rate coefficients for trapping of these boron-centred radicals become available.

References and notes

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5. The natural isotopic abundances of ^{11}B (I = 3/2) and ^{10}B (I = 3) are 80.2 and 19.8%, respectively. In some experiments amine-boranes containing 97.5 atom % ^{11}B were used in order to simplify the e.s.r. spectra (as in the Figure).
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12. In our hands, when the primary n-butyl radical was generated as shown in equation (4), a relatively small concentration of the spin-adduct to the oxygen atom in 3,5-dideuterio-TBN was detected at 300 K along with the nitroxide resulting from addition to nitrogen. In similar experiments with neopentyl bromide, the more bulky $Me_3C{-}CH_2^{\bullet}$ (isoelectronic with $Me_3N{\rightarrow}BH_2^{\bullet}$) afforded somewhat more of the alkoxy(aryl)aminyl adduct, although the spectrum of the nitroxide was still the stronger. We note, however, that interpretations of relative radical concentrations under steady-state conditions can be misleading and absolute rates of adduct formation are much more meaningful.

(Received in UK 2 January 1985)