Homolytic Reactions of Ligated Boranes. Part 5.[1] Spin-trapping and Other Addition Reactions of Ligated Boryl Radicals

Vernon P. J. Marti and Brian P. Roberts[*]

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H OAJ

The addition reactions of a variety of amine- and phosphine-boryl radicals ($L \rightarrow \dot{B}H_2$; $L = R_3N$ or R_3P) with 2-methyl-2-nitrosopropane (MNP), 2,4,6-tri-t-butylnitrosobenzene (TBN), and phenyl-N-t-butyl-nitrone (PBN) have been studied in benzene solution using e.s.r. spectroscopy. Spin-trapping of the boron-centred radicals by MNP and PBN affords nitroxides, while addition of $Me_3N \rightarrow \dot{B}H_2$ to the ambident TBN yields a mixture of the nitroxide and oxyaminyl adducts, with the latter predominating. Appropriately constituted amine-boryl radicals undergo β-N–C cleavage to give carbon-centred radicals in competition with their spin-trapping by MNP and PBN. In addition to providing mechanistic information, this competition has been used to measure the rate coefficient for spin-trapping of $Pr^i_2EtN \rightarrow \dot{B}H_2$ by MNP. At 314 K, k_{trap} is $ca.$ 1.6×10^8 dm³ mol⁻¹ s⁻¹ and thus amine-boryl radicals are trapped more efficiently than alkyl radicals. Attempts to scavenge $H_3N \rightarrow \dot{B}H_2$ were frustrated by the rapid reduction of the spin-traps by ammonia–borane, but this amine-boryl radical did undergo ready addition to alkyl cyanides and isocyanides, to 1,1-di-t-butylethylene, and to 2,6-di-t-butylpyridine as judged by e.s.r. spectroscopy. Addition to cyanides affords transient iminyl radicals $H_3N \rightarrow BH_2(R)C=N^{\bullet}$ which undergo subsequent β-scission at a rate which increases along the series $R = Et < Pr^i < Bu^t$ in parallel with the stabilisation of the departing alkyl radical $R^{\bullet}$.

Addition of carbon-centred radicals to unsaturated molecules is very important in organic chemistry.[2] The ligated boryl radicals $R_3N \rightarrow \dot{B}H_2$ and $R_3P \rightarrow \dot{B}H_2$ are isoelectronic with the substituted methyl radicals $R_3C\text{-}\dot{C}H_2$ and $R_3Si\text{-}\dot{C}H_2$, respectively, and as part of a programme designed to explore the chemistry of the boron-centred radicals we have investigated their addition to a number of types of unsaturated molecule using e.s.r. spectroscopy.

'Spin-trapping' of carbon-centred radicals by C-nitroso compounds and by nitrones, to give relatively persistent nitroxide adducts readily detectable by e.s.r. spectroscopy, has become established as an important tool in mechanistic free radical chemistry.[3] Spin-trapping of ligated boryl radicals can provide similarly useful information, as we have indicated in a preliminary communication,[4] and here we describe this work in full. E.s.r. studies of the addition reactions of the prototype amine-boryl radical[5] $H_3N \rightarrow \dot{B}H_2$ with nitriles, isocyanides, 1,1-di-t-butylethylene, and 2,6-di-t-butylpyridine are also reported.

Results and Discussion

The ligated boryl radicals were produced by hydrogen-atom abstraction from the corresponding ligated borane $L \rightarrow BH_3$, using photochemically or thermally generated t-butoxyl radicals [equation (1)].[6–8] In the spin-trapping experiments
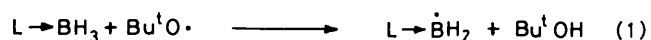
$$L \rightarrow BH_3 + Bu^tO^{\bullet} \longrightarrow L \rightarrow \dot{B}H_2 + Bu^tOH \quad (1)$$

with 2-methyl-2-nitrosopropane (MNP), 2,4,6-tri-t-butyl-nitrosobenzene (TBN), and phenyl-N-t-butylnitrone (PBN), the t-butoxyl radicals were generated by thermolysis of di-t-butyl hyponitrite (TBHN) in benzene solvent [equation (2)], whilst

$$Bu^tON=NOBu^t \xrightarrow{\Delta} 2Bu^tO^{\bullet} + N_2 \quad (2)$$
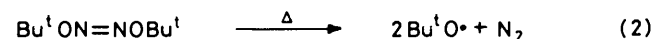
for reactions of $H_3N \rightarrow \dot{B}H_2$ with the other acceptors, $Bu^tO^{\bullet}$ was produced by u.v. photolysis of di-t-butyl peroxide (DTBP) [equation (3)] generally using t-butyl alcohol–dimethyl ether (4:1 v/v) solvent.
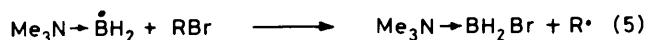
$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^{\bullet} \quad (3)$$
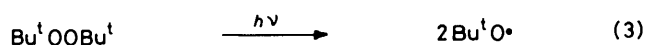
Naturally occurring boron consists of 80.8% ¹¹B (I 3/2) and 19.2% ¹⁰B [I 3; $\gamma(^{10}B)/\gamma(^{11}B)$ 0.335], but isotopically enriched ligated boranes containing 97.5 atom% ¹¹B were often used to facilitate the interpretation of e.s.r. spectra.

Addition to MNP.—Deoxygenated benzene solutions containing MNP (0.01—0.02M) and the ligated borane ($ca.$ 1M) showed no e.s.r. spectra in the dark at $ca.$ 300 K. However, after addition of TBHN in benzene (1M) to give a final initiator concentration of $ca.$ 0.05M, the spectrum of the appropriate ligated boryl nitroxide (1) became apparent [equation (4)].

$$L \rightarrow \dot{B}H_2 + Bu^tN=O \longrightarrow L \rightarrow BH_2N(\dot{O})Bu^t \quad (4)$$
$$(1)$$
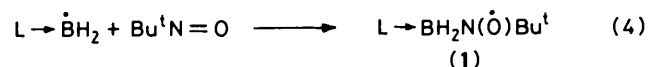
With trialkylamine- or trialkylphosphine-boranes, the blue colour of monomeric MNP persisted throughout these experiments. The e.s.r. parameters for the nitroxides (1) are collected in Table 1 and the spectrum of (1; $L = Me_3N$) has been reproduced in ref. 4.

Trialkylamine-boryl radicals are known[7] to abstract halogen very rapidly from alkyl bromides and when n-butyl bromide (1M) was present along with $Me_3N \rightarrow BH_3$, TBHN, and MNP (0.014M), only the e.s.r. spectrum of (2; $R = Bu^n$) was detectable at 298 K. Halogen abstraction [equation (5)] is thus much faster

$$Me_3N \rightarrow \dot{B}H_2 + RBr \longrightarrow Me_3N \rightarrow BH_2Br + R^{\bullet} \quad (5)$$

$$R^{\bullet} + Bu^tN=O \longrightarrow RN(\dot{O})Bu^t \quad (6)$$
$$(2)$$

than spin-trapping of the amine-boryl radical under these conditions. The nitroxide (2; $R = Me_3CCH_2$), which is iso-electronic with (1; $L = Me_3N$), was generated in a similar fashion from neopentyl bromide; its e.s.r. parameters (see Table

3) differ markedly from those [a(N) 13.44, a(2H) 4.33 G at room temperature] reported by Janzen and Lopp[9] and which we believe to be in error.

E.s.r. spectra of the anionic nitroxides $H_3\bar{B}N(\dot{O})R$ have been reported previously by Crozet and Tordo[10,11] (R = Bu^t or aryl) and by Perkins et al.[12] (R = 2,6-Br$_2$-4-SO$_3$NaC$_6$H$_2$), although it is not clear whether these nitroxides were formed by spin-trapping of $H_3B^{-\cdot}$.

With acyclic tertiary amine-boranes in which a secondary alkyl, tertiary alkyl, or benzylic group is attached to nitrogen, β-scission of the amine-boryl radical [equation (7)] was

$$R_3N \rightarrow \dot{B}H_2 \longrightarrow R\cdot + R_2N \rightleftharpoons BH_2 \qquad (7)$$

competitive with its spin-trapping. The relative concentrations of (1; L = R$_3$N) and (2), which is formed by trapping of the β-cleavage product R$^\cdot$ [equation (6)], depends on the structure of the co-ordinated amine[7] and the concentration of MNP. Interpretation of the overlapping spectra obtained in such experiments was often facilitated by the line narrowing which resulted from use of [^{2}H$_9$]MNP.[13] Figure 1a shows the e.s.r. spectrum obtained from PhCH$_2$NMe$_2$→BH$_3$ at 292 K with an MNP concentration of 0.014M and consists of a superposition of the spectra of (1; L = PhCH$_2$NMe$_2$) and (2; R = PhCH$_2$) [a(N) 15.2, a(2H) 7.6 G, g 2.0060]. Under similar conditions, only di-t-butyl nitroxide was detectable from Bu^{t}NMe$_2$→BH$_3$, indicating that β-scission of the amine-boryl is more rapid than that of its N-benzyl counterpart.

Only the spectrum of [1; L = $\overline{CH_2(CH_2)_3NMe}$] was observed in experiments with N-methylpyrrolidine–borane and MNP (0.014M), but relief of angle strain in the N-methyl-aziridine-boryl radical (3; R = Me) leads to its more rapid β-scission with ring opening to give (4), and the spin-adduct (5; R = Me) [a(N) 15.4, a(2H) 11.1 G, g 2.0061] of the latter was the only nitroxide detected in experiments with N-methyl-aziridine–borane at 312 K (see Figure 1b). This result provides strong evidence for the absence of routes to (1; L = R$_3$N) other than spin-trapping of tertiary amine-boryl radicals.

$$[\text{3}] \longrightarrow [\text{4}] \xrightarrow{\text{Bu}^t\text{N=O}} H_2B \rightleftharpoons N(R)CH_2CH_2NBu^t \quad (8)$$

(3)   (4)   (5)
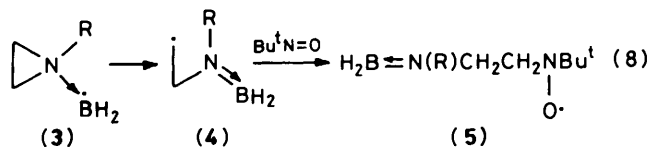
When similar experiments were attempted with aziridine–borane, a secondary amine-borane,[8] the sample rapidly lost the initial blue colour of monomeric MNP.* However, three overlapping spectra could be observed at 292 K whether the solution was blue or colourless, and these are attributed to Bu^{t}N(H)O$^\cdot$ [a(N) 13.6, a(1H) 11.6 G, g 2.0061], (5; R = H) [a(N) 15.8, a(2H) 12.2, a(2H) 0.3 G, g 2.0060], and (6), the spin-adduct of the unopened amine-boryl radical (3; R = H). Presumably (5; R = H) and (6) are formed by hydrogen abstraction from the corresponding hydroxylamines, rather than by spin-trapping, once the solution is colourless. In benzene solvent, a(N$_\alpha$) and a(2H$_\beta$) for (6) are both appreciably larger than the corresponding splittings for (1; L = Me$_3$N) and provide support for

(6)

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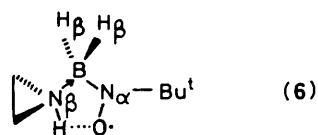
* Primary amine–boranes and ammonia–borane reacted even more rapidly with MNP and also reacted visibly with TBN. No adducts of amine-boryl radicals were detected.

Table 1. E.s.r. parameters for the spin adducts (1) obtained by addition of ligated boryl radicals L→$\dot{B}H_2$ to MNP in benzene

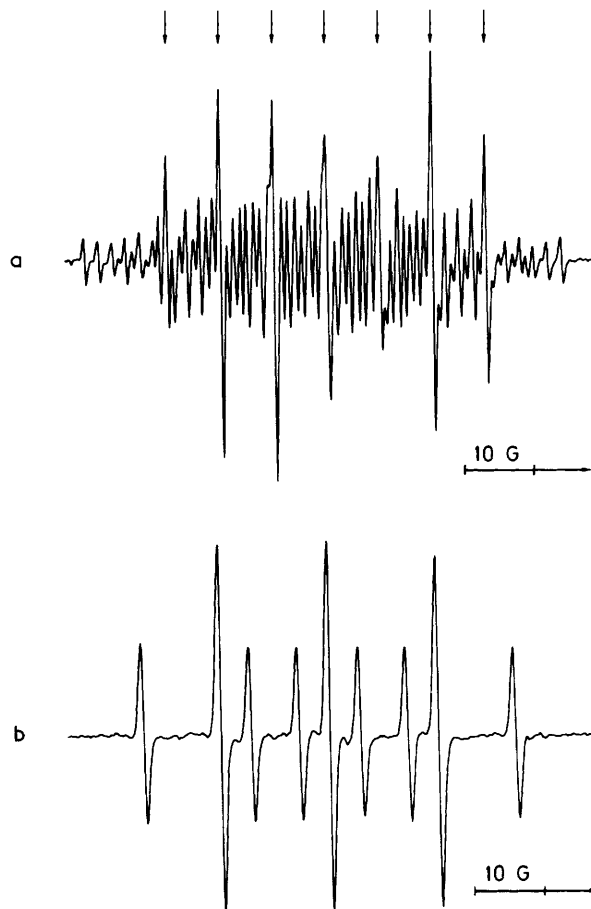| L	T/K	g Factor	a(N$_\alpha$)	a(^{11}B)	a(2H$_\beta$)	Others
			Hyperfine splittings (G)			
Me$_3$N	294	2.0064	12.3	5.8	10.2	2.2 (1N)
PhCH$_2$NMe$_2$	292	2.0064	12.4	5.9	10.8	2.0 (1N)
Et$_3$N	300	2.0064	12.7	5.8	11.3	1.8 (1N)
Pr$^i_2$NEt	292	2.0063	12.5	6.4	17.1	1.4 (1N)
$\overline{CH_2(CH_2)_3NMe}$	292	2.0063	12.5	5.8	10.9	1.8 (1N)
$\overline{CH_2CH_2NH}$	319	2.0059	14.4	6.3	16.4	0.8 (1N)
Pyridine	292	2.0063	12.4	5.1	8.4	3.0 (1N)
Et$_3$P	292	2.0063	13.5	6.4	15.1	10.6 (1P)
Bu$^n_3$P	292	2.0063	13.5	6.4	15.2	9.8 (1P)

Figure 1. a, Overlapping e.s.r. spectra of (1; L = PhCH$_2$NMe$_2$) and benzyl t-butyl nitroxide (line positions indicated by arrows) in benzene at 292 K. b, E.s.r. spectrum of (5; R = Me) obtained from N-methyl-aziridine–borane and MNP in benzene at 312 K

the preferred conformation illustrated for the former nitroxide. Intramolecular hydrogen bonding as shown for (6) should cause a shift of spin density from oxygen to nitrogen within the nitroxide function and lead to an increase in a(N$_\alpha$) and a reduction in g compared with (1; L = Me$_3$N).[14] The β-nitrogen atom is close to the nodal surface of the SOMO in (6), accounting for the relatively small value of a(N$_\beta$) and large value of a(2H$_\beta$) compared with (1; L = Me$_3$N), since the

Table 2. Solvent effects on the e.s.r. parameters for $L \rightarrow BH_2N(\dot{O})Bu^t$ when $L = Me_3N$ or aziridine

L	T/K	Solvent	g Factor	Hyperfine splittings (G)			
				$a(N_\alpha)$	$a(^{11}B)$	$a(2H_\beta)$	$a(N_\beta)$
Me_3N	291	100% C_6H_6	2.0064	12.3	5.8	10.1	2.2
	291	88% C_6H_6 + 12% Bu^tOH	2.0063	12.7	5.8	9.8	2.4
	293	95% C_6H_6 + 5% CD_3OD	2.0062	13.1	5.9	9.7	2.5
	292	52% C_6H_6 + 48% CD_3OD	2.0062	13.2	5.9	9.4	2.6
$\overline{CH_2CH_2NH}$	319	100% C_6H_6	2.0059	14.4	6.3	16.4	0.8
	320	88% C_6H_6 + 12% Bu^tOH	2.0059	14.4	6.3	16.4	0.8
	321	95% C_6H_6 + 5% CD_3OD	2.0059	14.5	6.4	16.2	0.8
	311	52% C_6H_6 + 48% CD_3OD	2.0059	14.5	6.4	16.0	1.0

Scheme.
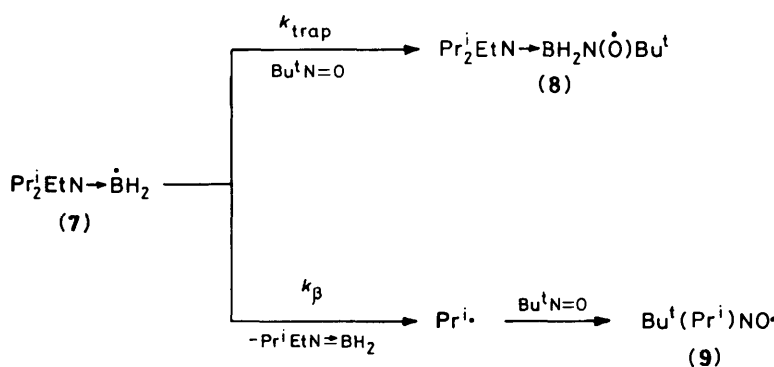
couplings to these β-nuclei should exhibit the normal $\cos^2\theta$ dependence for hyperconjugative spin transmission.[15] Support for this interpretation was obtained from the solvent dependence of the splittings for (6) and (1; $L = Me_3N$) which are given in Table 2. As the alcohol content of the solvent increases, $a(N_\alpha)$ for (1; $L = Me_3N$) increases whilst g decreases slightly, whereas for (6) these parameters do not change significantly since the propensity of the nitroxide function to enter into hydrogen bonding is now satisfied intramolecularly.

The trends in $a(2H_\beta)$ and $a(N_\beta)$ for the spin-adducts (1) of the tertiary amine-boryls can also be understood in terms of conformational preferences about the N_α–B bond. Thus, as the bulk of the amine ligand increases along the series $L = Me_3N < PhCH_2NMe_2 < Et_3N < Pr^i_2EtN$ there is a progressive increase in $a(2H_\beta)$ from 17.2 to 17.1 G accompanied by a decrease in $a(N_\beta)$ from 2.2 to 1.4 G (see Table 1). This indicates that steric compression between the N_α-t-butyl group and the bulky amine forces the latter to occupy a site closer to the nodal surface of the SOMO than the position favoured in the absence of steric constraints.

Rate of Spin-trapping by MNP.—The competition between β-scission of $Pr^i_2EtN \rightarrow \dot{B}H_2$ (7) and its spin-trapping by MNP was utilised to measure the relative rates of these two reactions (see Scheme). Provided that every isopropyl radical produced by β-scission of (7) is trapped by MNP and since decay of (8) and (9) may be neglected when nitroxide concentrations are very small, equation (9) may be derived.[16,17] In a series of

$$\{d[(8)]/d[(9)]\}_{t\rightarrow 0} = (k_{trap}/k_\beta)[MNP]_{t=0} \qquad (9)$$

experiments in benzene solvent at 314 K, spectra were repeatedly recorded at known times after the addition of TBHN, nitroxide concentrations were then plotted as a function of reaction time, and finally $[(8)]_t$ was plotted against $[(9)]_t$. With

a fixed concentration of MNP (0.55M), the zero-time slope of the latter plot was independent of the amine–borane concentration (0.33—1.33M). However, as predicted by equation (9), the zero-time slope was proportional to the concentration of MNP and from four separate runs with [MNP] in the range 0.18—0.55M we obtained (k_{trap}/k_β) 13.9 ± 1.5 dm^3 mol^{-1}.

We have previously studied the β-scission of (7) using a laser flash photolysis–e.s.r. technique and from experiments between 206 and 289 K in cyclopropane–t-pentyl alcohol–DTBP (3:1:1 v/v) solvent the kinetic data fitted equation (10), in which $R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}.[18] The value of k_β extrapolated to

$$\log_{10}(k_\beta/s^{-1}) = (12.5 \pm 0.5) - (32.7 \pm 2.0)/2.303RT \qquad (10)$$

314 K is 1.15×10^7 s^{-1} and, assuming little solvent dependence of this rate coefficient, we estimate k_{trap} to be 1.6×10^8 dm^3 mol^{-1} s^{-1} at 314 K in benzene. This rate coefficient can be compared with those obtained previously for trapping of primary[17] $(9.0 \times 10^6$ dm^3 mol^{-1} s$^{-1})$ and secondary[19] $(6.1 \times 10^6$ dm^3 mol^{-1} s$^{-1})$ alkyl radicals under similar conditions at 313 K. Spin-trapping of amine-boryl radicals is thus more rapid than the trapping of alkyl radicals, in accord with the higher nucleophilicity of the former and the stronger bonds which boron forms to electronegative elements (*i.e.* its metalloidal character).

No t-butyl ethyl nitroxide (2; $R = Et$) was detected in experiments with $Pr^i_2EtN \rightarrow BH_3$, implying a high degree of regioselectivity in the β-scission of (7) with preferential cleavage of the weaker N–C bond.
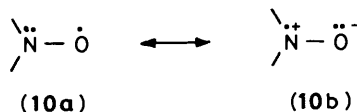
Electronic Structure of Ligated Boryl Nitroxides.—Boron is more electropositive than carbon and, at first sight, it is rather surprising that amine-boryl nitroxides should exhibit significantly smaller α-nitrogen splittings and slightly higher g-factors than those shown by related dialkyl nitroxides (see Table 3).

**Table 3.** E.s.r. parameters for substituted t-butyl nitroxides $X_3MN(\dot{O})Bu^t$

				Hyperfine splittings (G)			
X_3M	T/K	Solvent[a]	g Factor	$a(N_a)$	$a(nH_\beta)^b$	$a(M)$	Ref.
$Me_3N{\rightarrow}BH_2$	292	A	2.0064	12.3	10.2 (2)	5.8 (^{11}B)	c
$Me_3C\text{-}CH_2$	298	A	2.0062	15.3	9.2 (2)	4.4^d (^{13}C)	c
Me_3Si	ca. 178	B	2.0082	9.75		5.4 (^{29}Si)	e
$H_3\bar{B}$	298	C	2.0057	14.1	12.7 (3)	5.7 (^{11}B)	f
H_3C	ca. 298	A		15.25	11.3 (3)		g

[a] A = benzene; B = hexane; C = NN-dimethylformamide. [b] Number of β-protons given in parentheses. [c] This work. [d] Value for di-t-butyl nitroxide from G. F. Hatch and R. Kreilick, *Chem. Phys. Lett.*, 1971, **10**, 490; the coupling constant is negative. [e] Ref. 21. [f] Ref. 10. [g] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 1970, 395.

The unpaired electron in a nitroxide resides in an N–O π* orbital or, in valence bond terms, the nitroxide function may be represented as a hybrid of the structures (**10a** and **b**). Replacement of an N-alkyl group by a more electropositive ligated boryl moiety might be expected to favour (**10b**) and lead to an increase

$$\overset{\cdot\cdot}{\underset{/}{\overset{\backslash}{N}}} - \overset{\cdot}{O} \quad\longleftrightarrow\quad \overset{\cdot+}{\underset{/}{\overset{\backslash}{N}}} - \overset{\cdot\cdot}{O}^-$$

(**10a**)   (**10b**)

in $a(N)$ and to a decrease in g (because the spin–orbit coupling constant for nitrogen is smaller than that for oxygen), changes opposite from those observed. It thus appears that the $R_3N{\rightarrow}BH_2$ group must be a better π acceptor than an alkyl group and that this property predominates over its σ donor character when attached to the nitroxide function, to favour (**10a**) and bring about a shift of π spin density from nitrogen to oxygen. A trialkylsilyl group is a similar σ-donor–π-acceptor substituent (see Table 3).[20,21] The $R_3N{\rightarrow}B$ dative bond is relatively weak and the experimental observations may be accounted for by including structure (**11**) in the valence bond description of the nitroxide, that is the BH_2 group shares its Lewis acidity between L and the nitroxide nitrogen.

$$L: \quad \underset{Bu^t}{\overset{H_2B}{\underset{/}{\overset{\backslash\backslash}{N}}}} - O\cdot \quad\quad (11)$$
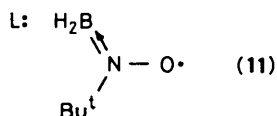
The H_3B group in $H_3\bar{B}N(\dot{O})Bu^t$ may also act as a weak π acceptor [see (**11**; L = H⁻)] since $a(N)$ is smaller than for $H_3CN(\dot{O})Bu^t$ (Table 3). However, the g-factor reported for the former is rather less than that of a dialkyl nitroxide suggesting that other factors are also important. It has been suggested[22] on the basis of molecular orbital calculations that the H_3B group in $H_3\bar{B}F$ acts as a stronger π acceptor than the CH_3 group in the isoelectronic H_3CF. We have argued previously[8] that the H_3B group in an aminyl-borane radical $R_2\dot{N}{\rightarrow}BH_3$ acts as a hyperconjugative π electron *donor* towards the attached nitrogen radical centre. The dominant substituent effect of a H_3B (or $L{\rightarrow}BH_2$, in general) group evidently depends on the nature of the centre to which it is attached and we note that the SOMO energy for a nitroxide moiety will be higher (and thus closer to the energy of the $\pi*H_3B$ group orbital) than that for an aminyl radical. Similar conclusions regarding the substituent effect of a trialkylsilyl group have been reached by Sakurai *et al.*[23]

Addition to TBN.—TBN is known to function as an ambident spin-trap towards alkyl radicals;[24] primary radicals are reported to add exclusively to nitrogen to give nitroxides,
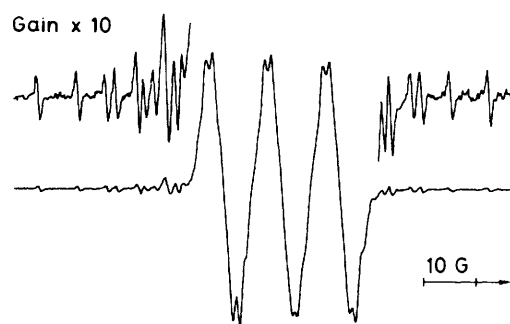

Gain x 10

10 G

Figure 2. E.s.r. spectra of the oxyaminyl radical (**12**) (three strong lines) and the nitroxide (**13**) obtained from $Me_3N{\rightarrow}BH_3$ (97.5 atom% ^{11}B) and TBN in benzene at 296 K

secondary radicals add competitively to N and O to give mixtures of nitroxides and aryl(alkoxy)aminyl radicals, and tertiary alkyl radicals yield only the oxyaminyl spin-adduct. Trialkylsilyl radicals also add exclusively to oxygen.[24] In some of our experiments 3,5-dideuterio-2,4,6-tri-t-butylnitrosobenzene ([$^2H_2$]TBN) was used in order to simplify the e.s.r. spectra of the spin-adducts.

At 296 K, a benzene solution containing $Me_3N{\rightarrow}BH_3$ (97.5 atom% ^{11}B, *ca.* 1.5M), [$^2H_2$]TBN (*ca.* 0.005M), and TBHN (*ca.* 0.05M) afforded overlapping spectra of two radicals (see Figure 2). The stronger spectrum consisting of three broad lines [$a(N)$ 10.9 G, g 2.0044] is assigned to the oxyaminyl radical (**12**) and the weaker, more complex spectrum is attributed to the nitroxide (**13**) [$a(N)$ 12.7, $a(^{11}B)$ 7.3, $a(2H)$ 18.6 G, g 2.0064]. Each line of the nitrogen triplet due to (**12**) is further split into

(**12**)   (**13**)
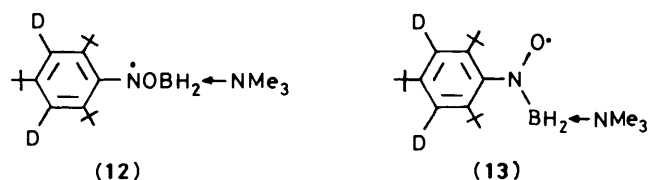
seven lines spaced by *ca.* 1 G as a result of coupling with two protons and one nitrogen and/or one boron-11 nucleus. In similar experiments with $Me_3N{\rightarrow}^{11}BD_3$ this complex fine structure was absent, confirming the contribution of $a(2H)$ to the appearance of the spectrum of (**12**).

For comparison, spin-trapping of the isoelectronic neopentyl radical $Me_3C\text{-}\dot{C}H_2$, generated by reaction (5), was investigated. At 300 K, a benzene solution of $Me_3N{\rightarrow}BH_3$ (*ca.* 1.2M), neopentyl bromide (*ca.* 1M), [$^2H_2$]TBN (*ca.* 0.005M), and TBHN (*ca.* 0.05M) gave rise to overlapping spectra of the nitroxide formed by trapping of neopentyl radicals [$a(N)$ 13.8, $a(2H)$ 18.4

(14)
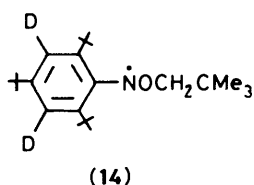
G, g 2.0061] and of the oxyaminyl radical (14) [a(N) 12.2, a(2H) 2.8 G, g 2.0044]. Although the concentration of (14) was less than that of the nitroxide adduct, this result does show that the primary (albeit relatively bulky) neopentyl radical adds competitively to N and O in TBN. A similar conclusion has been reached independently by Ingold and his co-workers[25] for the neopentyl radical generated by thermolysis of bis-t-butylacetyl peroxide.

Addition to PBN.—Alkyl radicals (R') add to PBN to give nitroxides of the type (15) the e.s.r. spectra of which are relatively insensitive to the nature of R'.[26,27] Ligated boryl radicals undergo corresponding addition to PBN to give (16), which afford rather richer spectra.


(15)   **(16)**
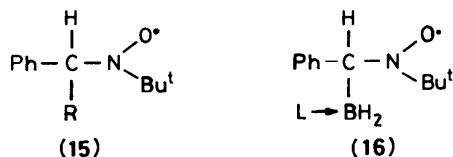
Between 291 and 336 K, a benzene solution containing $Me_3N{\rightarrow}BH_3$ (*ca.* 1.5M), PBN (*ca.* 0.007M), and TBHN (*ca.* 0.05M) afforded a spectrum assigned to (16; L = Me_3N) (see Table 4). Spectra obtained from $Me_3N{\rightarrow}BD_3$ were similar apart from a reduction in linewidth (from 1.2 to 1.0 G). At room temperature the 24 lines (the pairs of lines 8/9 and 16/17 are superimposed) in the spectrum of (16; L = Me_3N) are of unequal widths and lines 2,7,10,15,18, and 23 are especially broad (see Figure 3). At higher temperatures the expected amplitude distribution was approached, as shown in Figure 3b, and Figure 3c shows a computer simulation assuming all lines to have equal width. Experiments at 292 K in cyclopropane–benzene (1:1 v/v) or t-butylbenzene (which are less and more viscous than benzene, respectively) yielded spectra very similar to those obtained in benzene, indicating that slow tumbling of the radical and incomplete averaging of anisotropy do not influence the linewidths selectively. Differential line broadening was not apparent in the spectrum of (16; L = Et_3N) and attempts to trap amine-boryl radicals containing ligands less bulky than Me_3N were unsuccessful. Thus, in experiments with $Me_2NH{\rightarrow}BH_3$ (*ca.* 1.5M) at 291 K only the spectrum of $PhCH_2N(\dot{O})Bu^t$ was detected and with aziridine–borane only a spectrum ascribed to the spin-adduct of the carbon-centred radical (4; R = H) [a(N) 15.0, a(1H) 3.6 G, g 2.0060 at 304 K] was observed.

We attribute the selective line broadening in the spectrum of (16; L = Me_3N) to out-of-phase modulation of the boron and β-proton splittings, whilst the nitrogen splitting remains virtually unchanged, brought about by exchange between two approximately equally populated conformers of this sterically congested radical [see *e.g.* (17a and b)]. When exchange takes place at an 'intermediate' rate on the e.s.r. timescale, the extent of line broadening in the resulting, partially averaged, spectrum will depend on the difference in the line positions for the two conformers. As illustrated in Figure 4 for the low-field group of the nitrogen triplet [$M_1(N_a)$ = +1] with appropriately chosen values of $a(H_\beta)$ and $a(^{11}B)$, lines 2 and 7 shift most and will thus be broadest in the intermediate exchange region. Lines 3 and 6

Table 4. E.s.r. parameters for the nitroxides (16) obtained by addition of $L{\rightarrow}\dot{B}H_2$ to PBN in benzene

L	T/K	g Factor	a(N_a)	a(^{11}B)	a(H_β)	Others
Me_3N	341	2.0059	15.3	4.3	2.8	
Et_3N	307	2.0061	15.2	3.2	3.2	
Et_3P	305	2.0058	15.3	4.5	2.6	0.9 (1P), 0.6 (1H)
Et_3P[a]	305	2.0057	15.3	4.5	2.5	0.9 (1P)
Bu^n_3P	301	2.0058	15.2	4.7	2.3	1.0 (1P), 0.5 (1H)
(MeO)_3P	297	2.0058	15.1	3.6	3.3	b

[a] Derived from $Et_3P{\rightarrow}BD_3$ (see text). [b] No further splittings were resolvable (ΔB_{p-p} 1.5 G).


(17a)   **(17b)**   (11)
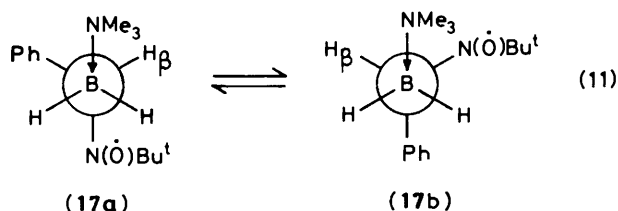
evidently shift little upon exchange and thus appear sharp, whilst lines 1 and 8 must shift to an intermediate extent. It did not prove possible to obtain separate spectra for the two conformers of (16; L = Me_3N) at lower temperatures in the slow-exchange region.

The absence of selective line broadening for the spin-adducts of $Et_3N{\rightarrow}\dot{B}H_2$ or the phosphine-boryl radicals is probably a consequence of the increased bulk of the ligands attached to boron, which leads one of the conformers analogous to (17a and b) to be strongly preferred.

The spectrum of (16; L = Et_3P) obtained from a benzene solution containing $Et_3P{\rightarrow}BH_3$ (*ca.* 0.7M), PBN (*ca.* 0.007M), and TBHN (*ca.* 0.05M) at 305 K was complex, but could be satisfactorily simulated on the basis of a(N) 15.3, a(1H) 2.6, and $a(^{11}B)$ 4.5 G, along with further splittings of 0.6 and 0.9 G each due to coupling with one spin-1/2 nucleus (see Figure 5). The spectrum of the corresponding radical derived from $Et_3P{\rightarrow}BD_3$ (97.5 atom% ^{11}B) and given in Figure 6 clearly shows that the larger of the two doublets results from coupling to ^{31}P, while the 0.6 G doublet must be assigned to one of the diastereotopic B-protons.

Addition of $H_3N{\rightarrow}\dot{B}H_2$ *to Nitriles.*—U.v. irradiation between 255 and 270 K of a $Bu^tOH–Me_2O$ solution containing ammonia–borane (*ca.* 1M), acetonitrile (*ca.* 1M), and DTBP (*ca.* 15% v/v) afforded an e.s.r. spectrum which we attribute to the iminyl radical (18) formed by addition of the ammonia-boryl radical to the nitrile [equation (12)]. The same radical was

$$H_3N{\rightarrow}\dot{B}H_2 \; + \; MeC{\equiv}N \; \longrightarrow \; H_3N{\rightarrow}BH_2(Me)C{=}N\cdot \quad (12)$$

(18)
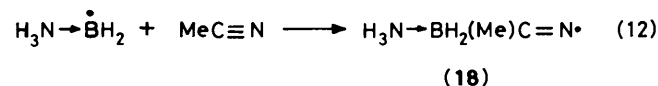
obtained between 210 and 250 K in $Bu^tOH–NH_3$ (4:1 v/v) solvent. The B-proton splitting was unresolved but contributed to the linewidth and in order to obtain simpler, more intense spectra most reactions were carried out using ^{11}B-enriched $H_3N{\rightarrow}BD_3$. Thus, addition of $H_3N{\rightarrow}\dot{B}D_2$ to [$^2H_3$]acetonitrile at 262 K gave rise to the spectrum of (19; R = CD_3) shown in Figure 7; at 258 K this radical decayed within the fall time of the spectrometer (0.1 s) when u.v. irradiation was interrupted.
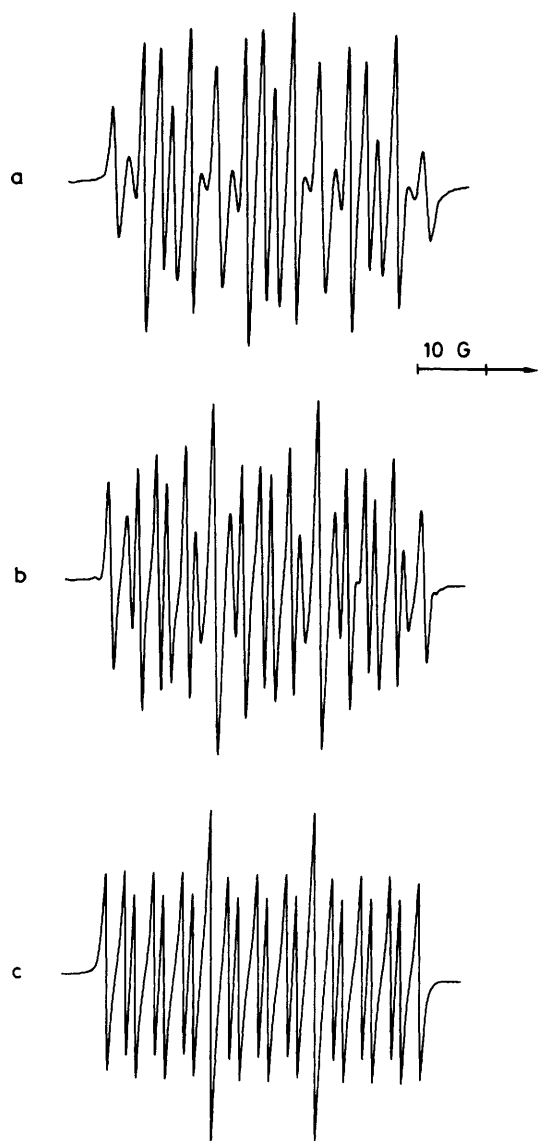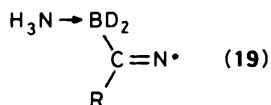
Figure 3. a, E.s.r. spectrum of the B,B-dideuterio analogue of (16; L = Me$_3$N) obtained from Me$_3$N→BD$_3$ (97.5 atom% [11]B) in benzene at 294 K. b, The same spectrum at 330 K. c, Computer simulation based on a(N) 15.20, a([11]B) 4.25, a(H) 2.78 G and a lorentzian linewidth of 0.63 G

$$H_3N \to BD_2$$
$$\underset{R}{\overset{\backslash}{C}}=N\cdot \quad (19)$$

Similarly, addition to ethyl cyanide afforded (19; R = Et) and no other radical was detected up to 270 K; the e.s.r. parameters of all iminyl adducts are collected in Table 5. In contrast, with isopropyl cyanide (ca. 1M) at 210 K a weak spectrum of the isopropyl radical was present alongside that of (19; R = Pr^i) and the intensity of the former spectrum increased at the expense of the latter as the temperature was raised to 270 K, implying that β-scission of the iminyl radical takes place [equation (13; R = Pr^i)]. The ease of β-cleavage reflects the

$$H_3N \to BD_2(R)C=N\cdot \longrightarrow R\cdot + H_3N \to BD_2CN \quad (13)$$

strength of the R–C$\overset{\cdot}{N}$ bond and only Bu$^{t\cdot}$ was detected between

R	T/K	g Factor	Hyperfine splittings (G)		
			a(N)	a([11]B)	a(nH$_\gamma$)
Me	261	2.0026	9.4	23.0	2.7 (3)
CD$_3$	260	2.0026	9.4	23.1	0.4 (3)^a
Et	266	2.0027	9.4	23.1	2.9 (2)
Pr^i	261	2.0028	9.4	23.1	2.8 (1)
c-C$_3$H$_5$	261	2.0028	9.6	21.9	1.4 (1)
1-Ad	260	2.0028	9.5	22.4	
Me^b	252	2.0026	9.9	22.6	2.7 (3)

^{a} Deuterium splitting (see Figure 7). ^{b} Data for the D$_3$B$^{\cdot-}$ adduct D$_3$B̄(Me)C=N$^\cdot$ from ref. 28; solvent Me$_2$O–Pe^{t}OH (1.3:1 v/v).

210 and 270 K in similar experiments with t-butyl cyanide. However, with 1-adamantyl cyanide (ca. 0.4M) or cyclopropyl cyanide (ca. 1M) no alkyl radicals resulting from β-scission of (19; R = 1-Ad or cyclo-C$_3$H$_5$) were detect alongside the iminyl adducts even at 270 K. 1-Adamantyl and cyclopropyl radicals are destabilised with respect to acyclic tertiary and secondary alkyl radicals, respectively. Furthermore, charge separation of the type illustrated in (20) could be important in the transition state and this would also disfavour β-scission when R is 1-adamantyl or cyclopropyl since the corresponding carbocations are highly destabilised.

$$R+$$
$$\overset{\cdot}{C}=\bar{N} \quad (20)$$
$$/$$
$$H_3N \to BD_2$$
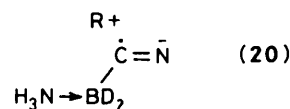
The simplest ligated boryl radical, namely the borane radical anion H$_3$B$^{\cdot-}$, also adds to alkyl cyanides to give iminyl adducts of the type H$_3$B̄(R)C=N$^\cdot$ (see Table 5).[28]

Reactions of H$_3$N→BH$_2$ *with Alkyl Isocyanides.*—The borane radical anion reacts with alkyl isocyanides (RNC) to displace the alkyl radical R$^\cdot$ and no intermediate imidoyl adduct RN=ĊBH$_3^-$ is detectable by e.s.r. spectrocopy.[28] A similar dealkylation is brought about by trialkylsilyl radicals, although now the intermediate adduct RN=ĊSiR$_3$ is readily detectable.[29] Alkyl radicals react much more sluggishly with isocyanides.[30] When the ammonia-boryl radical was generated in the presence of either methyl or t-butyl isocyanide (ca. 1M), only the spectrum of the appropriate alkyl radical was observable down to 250 K in Bu^{t}OH–Me$_2$O (4:1 v/v) solvent and any possible imidoyl intermediate [see equation (14)] must be too short-lived to detect.

$$H_3N \to BH_2 + RN=C \longrightarrow [H_3N \to BH_2\overset{\cdot}{C}=NR]$$
$$\longrightarrow R\cdot + H_3N \to BH_2CN \quad (14)$$
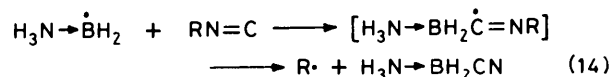
Addition of H$_3$N→BH$_2$ *to* 1,1-*Di-t-butylethylene and to* 2,6-*Di-t-butylpyridine.*—In common with trialkylsilyl radicals[28–31] the ammonia-boryl radical added readily to these two acceptors, as evidenced by e.s.r. spectroscopy. Thus, u.v. irradiation of a Bu^{t}OH–NH$_3$ (4:1 v/v) solution containing DTBP (ca. 15% v/v), H$_3$N→BD$_3$ (97.5 atom% [11]B; ca. 1M), and Bu$^t_2$C=CH$_2$ (ca. 1M) between 257 and 297 K afforded a spectrum which we attribute to the adduct (21). At 258 K, the spectroscopic parameters of this relatively persistent radical ($t_{\frac{1}{2}}$
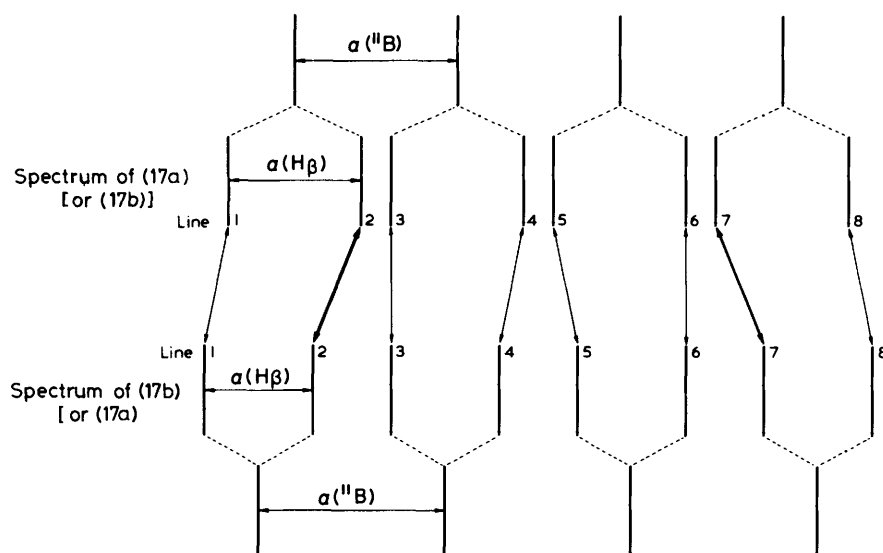
$$H_3N \to \overset{\cdot}{B}D_2 + Bu^t_2C=CH_2 \longrightarrow H_3N \to BD_2CH_2\overset{\cdot}{C}Bu^t_2 \quad (15)$$

$$(21)$$
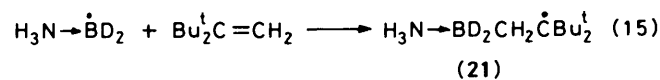
Figure 4. Stick diagram illustrating the way in which out-of-phase modulation of $a(^{11}B)$ and $a(H_\beta)$ would result in selective line broadening in the spectrum of (**16**; $L = Me_3N$). Only the first eight lines [corresponding to $M_I(N_a) = +1$] are shown

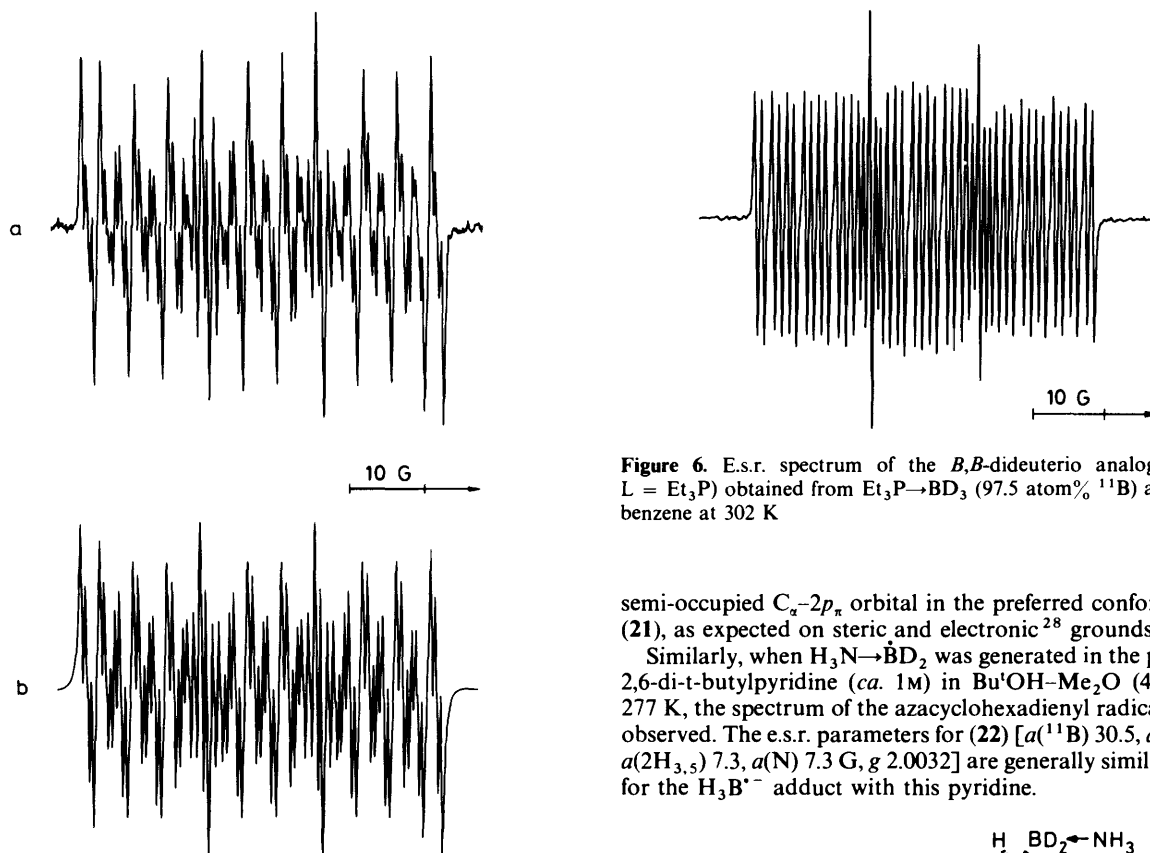**Figure 5.** a, E.s.r. spectrum of (**16**; $L = Et_3P$) obtained from $Et_3P\rightarrow BH_3$ (80.2 atom% ^{11}B) and PBN in benzene at 305 K. b, Computer simulation as a superposition of the ^{11}B- and ^{10}B-containing radicals based on the parameters given in Table 4 and a lorentzian linewidth of 0.40 G

Figure 6. E.s.r. spectrum of the *B,B*-dideuterio analogue of (**16**; $L = Et_3P$) obtained from $Et_3P\rightarrow BD_3$ (97.5 atom% ^{11}B) and PBN in benzene at 302 K

semi-occupied C_α–$2p_\pi$ orbital in the preferred conformation of (**21**), as expected on steric and electronic[28] grounds.

Similarly, when $H_3N\rightarrow BD_2$ was generated in the presence of 2,6-di-t-butylpyridine (*ca.* 1M) in Bu^tOH–Me_2O (4:1 v/v) at 277 K, the spectrum of the azacyclohexadienyl radical (**22**) was observed. The e.s.r. parameters for (**22**) [$a(^{11}B)$ 30.5, $a(1H)$ 41.7, $a(2H_{3,5})$ 7.3, $a(N)$ 7.3 G, g 2.0032] are generally similar to those for the $H_3B^{\cdot-}$ adduct with this pyridine.

for its first-order decay at 260 K is *ca.* 6.5 s) were $a(^{11}B)$ 24.7, $a(2H)$ 14.8 G, g 2.0026. The large boron and relatively small β-proton splitting confirm[28] that the B–C bond eclipses the
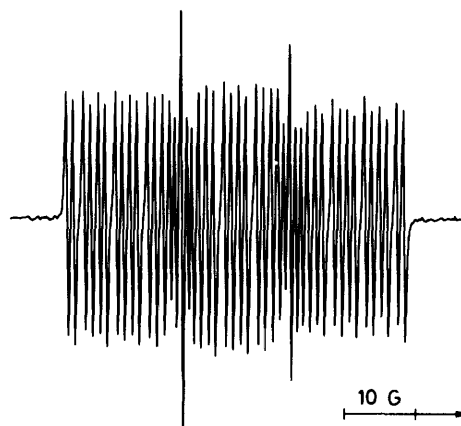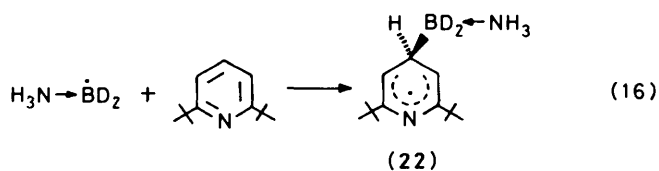
Experimental

E.s.r. Spectroscopy.—E.s.r. spectra were recorded using Varian E-109 or E-4 instruments operating at *ca.* 9.2 GHz. The techniques used for photochemical generation of transient free
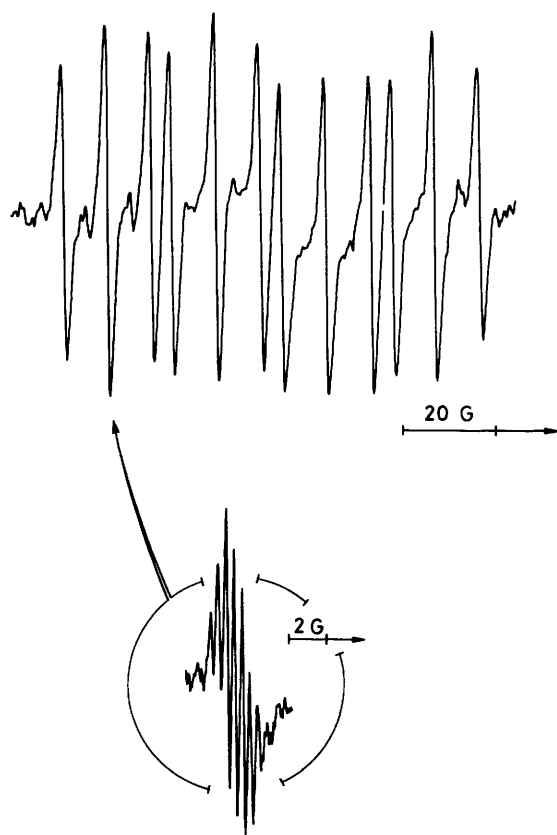
Figure 7. E.s.r. spectrum of the iminyl radical (19; R = CD$_3$) in Bu^{t}OH–Me$_2$O (4:1 v/v) at 262 K. The expansion of the second line under higher resolution shows the septet resulting from coupling to the CD$_3$ group

radicals have been described previously.[32] Samples were sealed in evacuated Suprasil quartz tubes which were relatively narrow bore (3 mm o.d. × 2 mm i.d.) on account of the high dielectric constants of the solvents employed.

For the spin-trapping experiments, a benzene solution containing the trap (MNP, TBN, or PBN) and the ligated borane was deaerated in the sample tube by purging with a fine stream of argon bubbles. After closure of the tube with a self-sealing rubber cap and checking for the absence of e.s.r. signals, a deaerated solution of TBHN in benzene was introduced by syringe, the sample was rapidly mixed by shaking, and returned to the spectrometer cavity. For the quantitative trapping experiments with MNP, the sample was made up under argon in the e.s.r. tube from stock solutions of the reagents which had been prepared under argon using deaerated benzene; this procedure obviated the need to purge the sample solution prior to recording spectra. The usual precautions to exclude light were taken when working with MNP.

Materials.—All procedures not involving water were carried out under an atmosphere of dry argon or nitrogen. N.m.r. spectra were obtained using a Varian XL-200 instrument. The solvent was C$_6$D$_6$ (^{1}H) or C$_6$H$_6$–C$_6$D$_6$ (^{11}B) with tetramethyl-silane internal standard (^{1}H) or BF$_3$–OEt$_2$ external standard (^{11}B).

Neopentyl bromide,[33] TBHN,[34] and 1,1-di-t-butylethylene[35] were prepared by published methods. MNP (Lancaster Synthesis), TBN (Aldrich), PBN (Lancaster Synthesis), and 2,6-di-t-butylpyridine (Aldrich) were used as received. [^{2}H$_2$]TBN was a gift from Dr P. Tordo. [^{2}H$_9$]MNP was prepared as

described by Holman and Perkins[13] from [^{2}H$_9$]Bu^{t}NH$_2$, itself prepared[36] from [^{2}H$_9$]Bu^{t}OD (Aldrich).

Pyridine–, di-isopropylethylamine–, and tri-n-butylphosphine–borane (Aldrich) were redistilled before use. Other tertiary amine–,[7] secondary amine–,[8] tertiary phosphine–,[6] and trialkyl phosphite–boranes[6] (including the ^{11}B-enriched compounds) were prepared by published methods or were available from previous work. Et$_3$P→^{11}BD$_3$ was prepared from Me$_3$N→^{11}BD$_3$[7] and triethylphosphine (Fluka) as described for the unlabelled compound;[37] δ(^{11}B) −41.5 (d of septets, $^1J_{B-P}$ 56.7, $^1J_{B-D}$ 14.1 Hz).

Isotopically normal ammonia–borane was obtained commercially (Alfa) and was used as received; enriched material was prepared as described below.[38]

Lithium aluminium hydride (2.85 g, 75 mmol) was stirred in dry 1,2-dimethoxyethane (DME) (50 cm^3) during dropwise addition of F$_3$B←OMe$_2$ (14.3 g, 125 mmol; 97.5 atom% ^{11}B) in DME (50 cm^3). After the addition was complete (1 h), the reaction mixture was held at 60 °C for a further 1 h. The diborane produced during this reaction was carried in a slow stream of argon into dry tetrahydrofuran (THF) (100 cm^3) cooled in a solid CO$_2$–acetone bath. Liquid ammonia (10 cm^3) was allowed to evaporate and the gas was passed into the stirred, cooled borane–THF solution. THF was removed under reduced pressure to give the crude product which was recrystallised from diethyl ether to yield H$_3$N→^{11}BH$_3$ (1.4 g); δ(^{11}B) (in THF) −21.6 (q, $^1J_{B-H}$ 95.4 Hz).

H$_3$N→^{11}BD$_3$ was prepared using the foregoing procedure but substituting LaAlD$_4$ (98 atom% D, Aldrich). The ^{11}B n.m.r. spectrum showed a broad singlet at δ −21.9.

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