Homolytic Reactions of Ligated Boranes. Part 3.[1] Electron Spin Resonance Studies of Radicals derived from Dialkylamine–Boranes

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Liquid-phase e.s.r. studies show that photochemically generated t-butoxyl radicals abstract hydrogen from secondary amine–boranes $R_2NH\rightarrow BH_3$ to give the corresponding amine–boryl radical $R_2NH\rightarrow\dot{B}H_2$ as the kinetically controlled product. Depending on the nature of the *N*-alkyl groups, the amine–boryl may undergo β-scission or may rapidly abstract hydrogen from the parent amine–borane to give the isomeric aminyl–borane radical $R_2\dot{N}\rightarrow BH_3$ which is thermodynamically more stable. Deuterium labelling experiments exclude 1,2-hydrogen atom migration as the mechanism of the isomerisation. The less electrophilic cyclopropyl radical reacts with $R_2NH\rightarrow BH_3$ to yield the aminyl–borane directly by abstraction of hydrogen from nitrogen. In the reactions with t-butoxyl radicals, intermediate amine–boryl radicals may be intercepted by halogen atom transfer from alkyl bromides or by addition to 2-methyl-2-nitrosopropane; with one amine–borane, $Bu^t(Pr^i)NH\rightarrow BH_3$, the amine–boryl radical was detected directly by e.s.r. spectroscopy. The e.s.r. spectra of the aminyl–borane radicals indicate appreciable hyperconjugative delocalisation of the unpaired electron onto the BH_3 group. *Ab initio* and/or semi-empirical molecular orbital calculations for $H_3N\rightarrow\dot{B}H_2$, $H_2\dot{N}\rightarrow BH_3$, and their *N*-methylated derivatives support the conclusions reached by experiment.

In Part 2[1] we reported that t-butoxyl radicals rapidly abstract hydrogen from boron in a trialkylamine–borane to yield the corresponding ligated boryl radical (1), the structure and reactivity of which can be investigated using e.s.r. spectroscopy. Similarly, ammonia-borane undergoes hydrogen abstraction from boron to give the 'inorganic ethyl' radical (1; R = H) and no evidence was found for competing attack at the NH_3 group to yield the aminyl–borane radical $H_2\dot{N}\rightarrow BH_3$.[2] The magnitudes and temperature dependencies of the boron and proton hyperfine splittings for (1) show that the radical centre is distinctly pyramidal, in contrast with the isoelectronic primary alkyl radicals which are close-to-planar at C_α.[1,2]

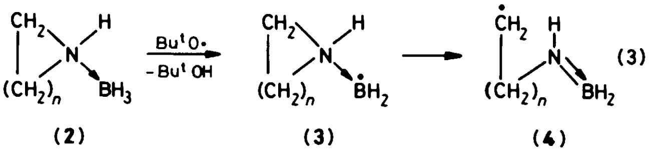
In many ways, the chemical reactivity of (1) resembles that of a silyl radical more closely than that of the isoelectronic alkyl radical, in accord with the 'diagonal' relationship between boron and silicon in the Periodic Table.[1,2] However, whereas alkylsilyl radicals do not undergo ready β-scission, the amine-boryls (1) do [equation (2)] and much more readily than the isoelectronic alkyl radicals.[1]

In this paper we describe an e.s.r. study of the reactions of photochemically generated t-butoxyl and cyclopropyl radicals with a number of secondary amine–boranes, $R_2NH\rightarrow BH_3$.

The reactions of Bu'O• with aziridine- and azetidine-boranes (2; *n* = 1 or 2) have been examined previously[1,3,4] and shown to lead ultimately to carbon-centred radicals (4), formed by the ring-opening β-scission of intermediate amine-boryl radicals [equation (3)].

$$Bu^tO\cdot + R_3N\rightarrow BH_3 \longrightarrow \underset{(1)}{R_3N\rightarrow\dot{B}H_2} + Bu^tOH \qquad (1)$$

$$R_3N\rightarrow\dot{B}H_2 \longrightarrow R\cdot + R_2N\!=\!BH_2 \qquad (2)$$



(2) (3) (4)

We have also reported[1] that the e.s.r. spectrum of the tertiary amine-boryl radical (1; R = Me) may be detected from polycrystalline trimethylamine–borane after its exposure to ^{60}Co γ-rays at 77 K. In contrast, γ-irradiated $Me_2NH\rightarrow BH_3$ or $Me_3N\rightarrow BH_3$ doped with $Me_2NH\rightarrow BH_3$ display a spectrum provisionally assigned[1,5] to the dimethylaminyl–borane radical $Me_2\dot{N}\rightarrow BH_3$ rather than to the isomeric dimethylamine-boryl radical $Me_2NH\rightarrow\dot{B}H_2$, although the precise route by which the nitrogen-centred species is formed in the rigid matrices remains to be elucidated.

Results

E.s.r. spectra were recorded during continuous u.v. irradiation of static liquid samples positioned directly in the microwave cavity of the spectrometer.[6] The usual primary radical source was di-t-butyl peroxide [DTBP; equation (4)] and the reactions

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \qquad (4)$$

of t-butoxyl radicals with the amine–boranes were examined in mixed solvent systems, generally oxirane–cyclopropane, t-butyl alcohol–dimethyl ether, or t-butyl alcohol–t-pentyl alcohol.

Photolysis of DTBP (40% v/v) in the presence of pyrrolidine–borane [(2; *n* = 3); *ca.* 1M] at *ca.* 260 K in Bu'OH–Pe'OH (4:1 v/v) gave rise to the e.s.r. spectrum shown in Figure 1a. This spectrum cannot be assigned to the carbon-centred radical (4; *n* = 3) nor is it as expected for the amine–boryl (3; *n* = 3), but it can be satisfactorily computer-simulated (Figure 1b) on the basis of *a*(3H) 45.2, *a*(4H) 33.6, *a*(^{14}N) 16.7, and *a*(^{11}B) 11.3 G and we therefore assign the spectrum to the pyrrolidinyl–borane radical (5).

In similar experiments, e.s.r. spectra which we ascribe to the corresponding aminyl–borane radicals (6) were obtained during u.v. irradiation of DTBP (15—20% v/v) in the presence of $Me_2NH\rightarrow BH_3$, $Et_2NH\rightarrow BH_3$, or $Pr^i_2NH\rightarrow BH_3$ using oxirane–cyclopropane as solvent (see Table 1). The natural abundances of ^{11}B (*I* 3/2) and ^{10}B (*I* 3) are 80.2 and 19.8%, respectively, but in most experiments amine–boranes

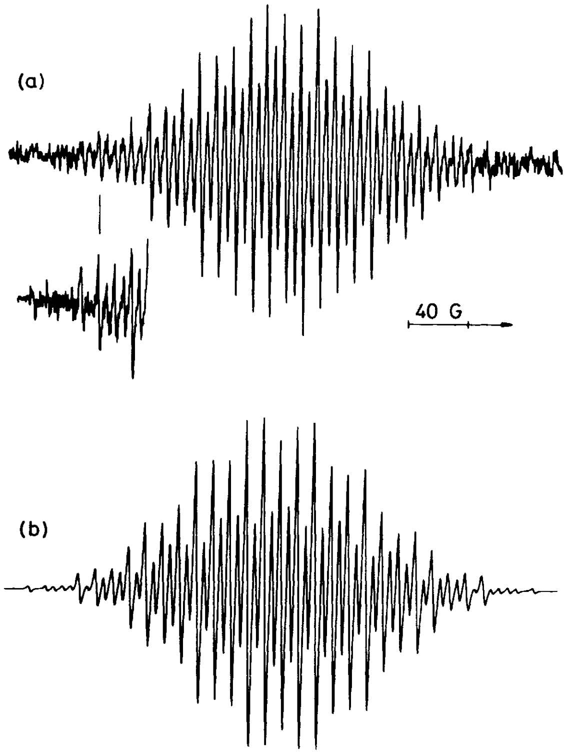


Figure 1. (a) E.s.r. spectrum of the pyrrolidinyl-borane radical obtained during u.v. irradiation of DTBP and pyrrolidine-borane (97.5 atom % ^{11}B) in Bu^tOH-Pe^tOH (4:1 v/v) at 258 K. (b) Computer simulation based on the coupling constants given in Table 1; the linewidth is 1.8 G and the lineshape is Lorentzian

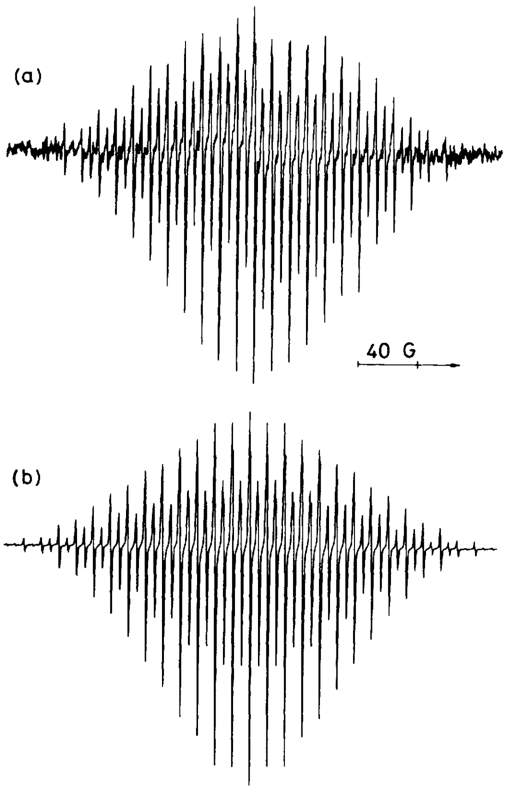
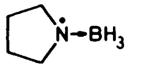


Figure 2. (a) E.s.r. spectrum of the dimethylaminyl-borane radical obtained during u.v. irradiation of DTBP and dimethylamine-borane (97.5 atom % ^{11}B) in oxirane-cyclopropane (2.5:1 v/v) at 168 K. (b) Computer simulation (including second-order effects) based on the coupling constants given in Table 1; the linewidth is 0.8 G and the lineshape is 50% Lorentzian (50% Gaussian)



(5)

$R_2\dot{N}\rightarrow BH_3$

(6)

enriched in ^{11}B (97.5 atom%) were used in order to facilitate analysis of the e.s.r. spectra. The spectrum of (**6**; R = Me) is shown in Figure 2 along with a computer simulation obtained using the e.s.r. parameters given in Table 1. A large second-order splitting of *ca.* 1 G was readily resolvable on the more intense lines and is clearly apparent in the complete spectrum (Figure 2). Detection of these second-order effects confirms the presence of the 46.4 G hyperfine coupling to three equivalent protons. With dimethylamine-borane (*ca.* 1M), no evidence for the presence of the isomeric amine-boryl radical $Me_2NH\rightarrow\dot{B}H_2$ could be found even at the lowest accessible temperature [150 K in oxirane-cyclopropane (2.5:1 v/v)]. When irradiation was interrupted at 170 K, the e.s.r. spectrum of (**6**; R = Me) decayed within the fall-time of the spectrometer (*ca.* 0.1 s).

The radicals (**5**) and (**6**; R = Me) were also generated from amine-boranes enriched in ^{10}B (97.0 atom %) in order to provide further support for the proposed assignments. Although the spectra obtained were less intense than their ^{11}B counterparts such that many of the lines were not detectable above the noise, both could be adequately simulated by assuming a ^{10}B splitting 0.335 $[=\gamma(^{10}B)/\gamma(^{11}B)]$ times the proposed ^{11}B splitting.

The splitting from the two isopropyl methine protons was not resolvable in the spectrum of (**6**; R = Pr^i) and, to confirm our assignment, the bisperdeuterioisopropyl analogue was generated. The spectrum of the latter was essentially superimposable on that of the protio radical, apart from some narrowing of the lines. For comparison with (**6**; R = Et or Pr^i), the previously unreported tertiary alkyl radicals $Et_2\dot{C}CH_3$ and $Pr^i_2\dot{C}CH_3$ were generated by established methods, respectively bromine abstraction from 3-bromo-3-methylpentane using triethylsilyl radicals[7] and the reaction of photochemically generated ethoxy radicals (from EtOOEt) with the mixed phosphite $Pr^i_2MeCOP(OEt)_2$.[8] Their e.s.r. parameters are included in Table 1.

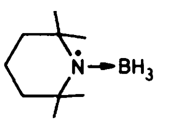
Although the spectrum of the corresponding dialkylaminyl-borane radical was observed during photolysis of DTBP in the presence of $Bu^tMeNH\rightarrow BH_3$ between 170 and 250 K, significantly different results were obtained with $Bu^tPr^iNH\rightarrow BH_3$ (*ca.* 0.3M) in which the hydrogen attached to nitrogen is sterically more protected. At the lowest accessible temperature [151 K in oxirane-cyclopropane (2.5:1 v/v)] a 1:1:1:1 quartet of binomial triplets was observed alongside a relatively weak spectrum of the t-butyl radical. We assign the former spectrum to the amine-boryl radical $Bu^tPr^iNH\rightarrow\dot{B}H_2$ [$a(^{11}B)$ 45.4, $a(2H_\alpha)$ 12.7 G, g 2.0024], β-scission of which gives rise to $Bu^{t\bullet}$. At higher temperatures, the spectrum of the amine-boryl radical was weaker, that of $Bu^{t\bullet}$ was stronger, and a third spectrum became apparent. Although this third spectrum was too weak to analyse with certainty, its general form was as expected for the aminyl-borane $Bu^tPr^i\dot{N}\rightarrow BH_3$.

Reaction of t-butoxyl radicals with 2,2,6,6-tetramethylpiperidine-borane did not afford the aminyl-borane (**7**), but rather a spectrum assigned to the carbon-centred radical (**9**)

Table 1. E.s.r. parameters for aminyl–borane radicals and related species

Radical	Solvent[a]	T/K	g Factor[b]	Hyperfine splittings (G)			
				$a(^{14}N)$	$a(^{11}B)$	$a(3H_\beta)$[c]	$a(nH_\beta)$[d]
$Me_2\dot{N}\rightarrow BH_3$	A	175	2.0039[e]	17.4	11.6	46.4	23.2 (6)
$Et_2\dot{N}\rightarrow BH_3$	A	199	2.0043	17.1	11.7	48.1	14.5 (4)
$Pr^i_2\dot{N}\rightarrow BH_3$	A	201	2.0043	17.8	11.9	49.0	$\leqslant$0.5 (2)
(5)	B	260	2.0043	16.7	11.3	45.2	33.6 (4)
(7)	C	268	2.0043	16.7	11.2	46.5	
(13)	C	270	2.0043	17.4	11.6	49.9	34.7 (4)
$Bu^t(Me)\dot{N}\rightarrow BH_3$	A	175	2.0042	17.5	11.7	46.9	23.5 (3)
$Me_3C^\bullet$[f]	D	203	2.0026[e]			22.74	22.74 (6)
$Et_2\dot{C}Me$	E	187	2.0027			22.8	17.6 (4)[g]
$Pr^i_2\dot{C}Me$	E	194	2.0027[e]			23.4	7.6 (2)[h]
$(CH_2)_4\dot{C}Me$[f]	D	256	2.0027			22.24	32.90 (4)
$Me_3N^{\bullet+}$[i]	F	300	2.0036[e]	20.55		28.56	28.56 (6)
$(CH_2)_4\dot{N}Me^+$[j]	G	120		16		28	42.5 (4)

[a] A = Oxirane–cyclopropane (2.5:1 v/v); B = Bu^tOH–Pe^tOH (4:1 v/v); C = benzene–Pe^tOH (5:1 v/v); D = methylcyclopentane; E = cyclopropane; F = water; G = frozen CCl_3F. [b] Second-order splittings not resolved unless otherwise stated. [c] Values of $a(BH_3)$ for the aminyl–borane radicals; $a(CH_3)$ for the other radicals. [d] Remaining β-protons, values of n given in parentheses. [e] Second-order splittings resolved, g-factor corrected to second order. [f] Data from H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575. [g] $da(4H_\beta)/dT = +7.0$ mG K^{-1}. [h] $da(2H_\beta)/dT = +16.6$ mG K^{-1}; $a(12H_\gamma)$ 0.45 G. [i] Data from R. W. Fessenden and P. Neta, *J. Phys. Chem.*, 1972, **76**, 2857. [j] Data from G. W. Eastland, D. N. R. Rao, and M. C. R. Symons, *J. Chem. Soc.. Perkin Trans. 2*, 1984, 1551.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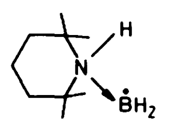
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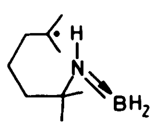
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[$a(6H_\beta)$ 23.0, $a(2H_\beta)$ 18.0, $a(2H_\gamma)$ 1.0 G, g 2.0027 at 243 K in oxirane–cyclopropane (1:1 v/v)] was observed, presumably arising from ring-opening β-scission of the initially formed amine–boryl radical (**8**).

Deuterium Labelling.—We considered three possible mechanisms for the formation of aminyl–borane radicals by reaction of $Bu^tO^\bullet$ with secondary amine–boranes: direct abstraction of hydrogen from nitrogen, intramolecular 1,2-hydrogen atom shift in a first-formed amine–boryl radical, or an intermolecular reaction of the amine–boryl which results in its overall isomerisation.

Reaction of t-butoxyl radicals with *N*-deuteriated pyrrolidine–borane (*ca.* 1M) in Bu^tOD–Me_2O (4:1 v/v) at 258 K gave rise to an e.s.r. spectrum which was completely superimposable on that of (**5**) obtained from the undeuteriated amine–borane in Bu^tOH–Me_2O. The spectrum is sufficiently different from that predicted for mono-*B*-deuteriated (**5**), by assuming that one *B*-proton splitting is replaced by a deuteron splitting of 0.154 ($= \gamma_D/\gamma_H$) in magnitude, for us to be confident that the *B*-deuteriated aminyl–borane is not formed from the *N*-deuteriated amine–borane. The pathway involving a 1,2-hydrogen atom shift can thus be discounted.

Direct abstraction of hydrogen from nitrogen is unlikely to be the route to the aminyl–boranes, since aziridine–borane (**2**; n = 1),[3,4] azetidine–borane (**2**; n = 2),[1] and 2,2,6,6-tetramethylpiperidine–borane all give products which originate from the corresponding amine–boryl radical *via* its rapid irreversible β-scission and no trace of the isomeric aminyl–boranes could be detected.* Furthermore, reaction of $Bu^tO^\bullet$ with $Bu^tPr^iNH\rightarrow BH_3$ gives $Bu^tPr^iNH\rightarrow\dot{B}H_2$ at low temperatures (see before). This leaves an intermolecular pathway for rapid conversion of $R_2NH\rightarrow\dot{B}H_2$ to $R_2\dot{N}\rightarrow BH_3$ as the most likely route to the latter radical.

Competitive Reactions.—In order to probe further the mechanism of formation of (**5**) and (**6**), we have investigated the reaction of $Bu^tO^\bullet$ with dialkylamine-boranes in the presence of various compounds with which $R_3N\rightarrow\dot{B}H_2$ and $H_3N\rightarrow\dot{B}H_2$ are known[1–4] to react.

Alkyl Halides.—Both $R_3N\rightarrow\dot{B}H_2$ (R = Me or Et) and $H_3N\rightarrow\dot{B}H_2$ rapidly abstract a halogen atom from alkyl chlorides or bromides under the conditions of our e.s.r. experiments.[1–4,10] It seems likely[1] that the absolute reactivities of the amine–boryls towards alkyl halides are broadly similar to those of trialkylsilyl radicals and the rate coefficient for abstraction of bromine from 1-bromopentane by $Et_3Si^\bullet$ is 5.4×10^8 dm^3 mol^{-1} s^{-1} at 300 K; 1-chloropentane is considerably less reactive and the corresponding rate coefficient for chlorine abstraction is 3.1×10^5 dm^3 mol^{-1} s^{-1} at 300 K.[11]

Photolysis of DTBP in the presence of $Me_2NH\rightarrow BH_3$ (*ca.* 1M) and Pr^nCl (1M) afforded only the spectrum of (**6**; R = Me) at 175 K and the n-propyl radical was not detectable. Under similar conditions, only (**6**; R = Me) was detectable with Bu^tCl (1M), but with Pr^nBr (1M) an intense spectrum of $Pr^{n\bullet}$ was observed and that of (**6**; R = Me) was barely discernible. With pyrrolidine-borane (1M) and Pr^nCl (1M) in t-butyl alcohol–dimethyl ether (4:1 v/v) at 260 K, again only the aminyl-borane (**5**) was detected, but this was replaced by $Pr^{n\bullet}$ in the presence of Pr^nBr.

At 173 K in oxirane–cyclopropane (2.5:1 v/v) with a fixed concentration of $Me_2NH\rightarrow BH_3$ (1.00M), the value of $[(6)]/[Pr^{n\bullet}]$ was inversely proportional to $[Pr^nBr]$ and with a fixed concentration of n-propyl bromide (0.30M), the value of $[(6)]/[Pr^{n\bullet}]$ was directly proportional to $[Me_2NH\rightarrow BH_3]$. These results strongly indicate that the relative radical concentrations during continuous u.v. irradiation are deter-

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* It might be argued that the N–H bonds in these amine–boranes are either particularly strong or sterically protected and thus that the relative reactivities of N–H and B–H groups are anomalous. However, DH°(C–H) for cyclobutane (404 kJ mol^{-1}) is not appreciably greater than that for cyclopentane (395 kJ mol^{-1}),[9] suggesting that the relative reactivities of N–H and B–H groups in (**2**; n = 2) and (**2**; n = 3) should not be very dissimilar.

mined by a competition between the reactions (6) and (7) of the amine–boryl radical $Me_2NH{\rightarrow}\dot{B}H_2$ formed initially by reaction (5). Provided that hydrogen abstraction from $Me_2NH{\rightarrow}BH_3$ by $Pr^{n\bullet}$ is unimportant at low temperature under the experimental conditions, that (**6**) does not react with Pr^nBr, and that the rate coefficients for self- and cross-reactions of (**6**) and $Pr^{n\bullet}$ are similar (encounter-controlled[12]), equation (8) should hold and a value of 0.7 ± 0.1 was obtained for (k_1/k_2) at 173 K from a plot of $[(\mathbf{6})]/[Pr^{n\bullet}]$ against $[Me_2NH{\rightarrow}BH_3]/[Pr^nBr]$. Photolysis of diheptanoyl peroxide in the presence of $Me_2NH{\rightarrow}BH_3$ (*ca.* 1M) at 195 K afforded only the the spectrum of the n-hexyl radical and that of (**6**; R = Me) was undetectable, showing that primary alkyl radicals do not abstract hydrogen from the amine–borane under these conditions. We conclude that reaction (6) is very rapid, accounting for our inability to detect $Me_2NH{\rightarrow}\dot{B}H_2$ directly.

Competition experiments were carried out with mixtures of Pr^nBr and Bu^tBr under conditions such that (**6**; R = Me) was undetectable and, making the usual[1] assumptions, $Me_2NH{\rightarrow}\dot{B}H_2$ was found to abstract bromine 1.3 times more rapidly from Bu^tBr than from Pr^nBr at 260 K in t-butyl alcohol–dimethyl ether (4:1 v/v). This relative reactivity is very close to that found previously for other amine–boryl radicals[1,10] under similar conditions and lends strong support to the proposal that (**6**) is formed indirectly from $Me_2NH{\rightarrow}BH_3$ *via* $Me_2NH{\rightarrow}\dot{B}H_2$.

$$Bu^tO^\bullet + Me_2NH{\rightarrow}BH_3 \longrightarrow Me_2NH{\rightarrow}\dot{B}H_2 + Bu^tOH \qquad (5)$$

$$Me_2NH{\rightarrow}\dot{B}H_2 + Me_2NH{\rightarrow}BH_3 \xrightarrow{k_1} Me_2\dot{N}{\rightarrow}BH_3 + Me_2NH{\rightarrow}BH_3$$
$$(\text{or } Me_2N{\doteq}BH_2 + H_2) \qquad (6)$$

$$Me_2NH{\rightarrow}\dot{B}H_2 + Pr^nBr \xrightarrow{k_2} Me_2NH{\rightarrow}BH_2Br + Pr^{n\bullet} \qquad (7)$$

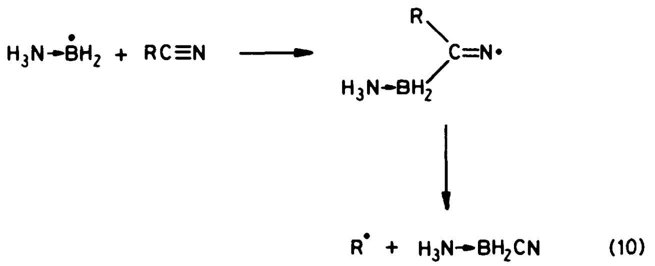
$$[(\mathbf{6})]/[Pr^{n\bullet}] = (k_1/k_2)[Me_2NH{\rightarrow}BH_3]/[Pr^nBr] \qquad (8)$$

Addition Reactions.—We have shown previously[10] that generation of $H_3N{\rightarrow}\dot{B}H_2$ in the presence of 1,1-di-t-butylethylene results in the detection of the relatively long-lived adduct (**10**) and, similarly, addition of $H_3N{\rightarrow}\dot{B}H_2$ or $R_3N{\rightarrow}\dot{B}H_2$ to nitriles is readily observable by e.s.r. spectroscopy [equation (10)].[1,10] However, these addition reactions appear to be relatively slow and proved unable to compete with isomerisation of $Me_2NH{\rightarrow}\dot{B}H_2$ to $Me_2\dot{N}{\rightarrow}BH_3$.

Spin trapping of amine–boryl radicals by addition to nitroso compounds or to nitrones is more efficient and we have reported[13] that trapping of $Pr^i_2EtN{\rightarrow}\dot{B}H_2$ with 2-methyl-2-nitrosopropane (MNP) (0.05M) is competitive with β-scission of the amine–boryl at 292 K [equation (11; R = Et)]. Although $Me_2NH{\rightarrow}BH_3$ rapidly reduced MNP monomer in a reaction of uncertain mechanism, reduction was slower when more bulky groups were attached to nitrogen and the blue colour of monomeric MNP (initially 0.05M) was still apparent after 15—20 min in the presence of $Pr^i_2NH{\rightarrow}BH_3$ (*ca.* 0.3M) in benzene at 294 K. When di-t-butyl hyponitrite[14] (TBHN) (*ca.* 0.05M) was also present in this solution to provide a thermal source of t-butoxyl radicals, the e.s.r. spectra of two nitroxides were observed [in addition to the spectrum of $Bu^tON(\dot{O})Bu^t$ which is always present in such experiments]. These nitroxides are readily identifiable as $Pr^iN(\dot{O})Bu^t$ and (**11**; R = H) [a(N^1) 14.2, $a(N^2) \leqslant 0.5$, $a(^{11}B)$ 6.4, a(2H) 17.8 G, g 2.0060 at 307 K] and their detection provides further evidence for the intermediacy of $R_2NH{\rightarrow}\dot{B}H_2$ in the ultimate formation of $R_2\dot{N}{\rightarrow}BH_3$ from the reaction of t-butoxyl radicals with $R_2NH{\rightarrow}BH_3$. The e.s.r. parameters for (**11**; R = H) suggest[10] that N^2 is close to the nodal plane of the SOMO [see (**12**)] and intramolecular hydrogen bonding may be responsible for this conformational preference. No evidence was found for trapping of the aminyl–borane (**6**; R = Pr^i).

Reaction of Cyclopropyl Radicals with Secondary Amine–Boranes.—Photolysis of diheptanoyl peroxide in the presence of pyrrolidine–borane at 260 K afforded only the spectrum of the n-hexyl radical and (**5**) was not detected. The spectrum of $Me^\bullet$ was observed at *ca.* 260 K during u.v. irradiation of a sample containing pyrrolidine–borane (*ca.* 1M), methyl bromide (*ca.* 1M),

$$H_3N{\rightarrow}\dot{B}H_2 + Bu^t_2C{=}CH_2 \longrightarrow \underset{(\mathbf{10})}{Bu^t_2\dot{C}CH_2BH_2{\leftarrow}NH_3} \qquad (9)$$



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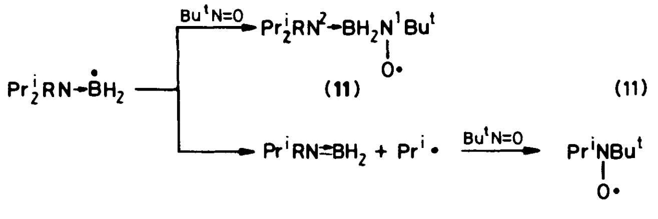

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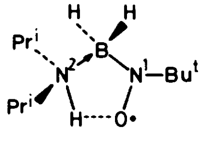
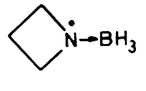


(**12**)

and DTBP; only a very weak spectrum of (**5**) might possibly have been present, suggesting that even methyl radicals do not abstract hydrogen rapidly from the NH group of pyrrolidine–borane under these conditions. In support of this conclusion, u.v. irradiation of diacetyl peroxide (*ca.* 0.5M) in the presence of dimethylamine–borane (*ca.* 1M) in oxirane–cyclopropane (2.5:1 v/v) at 174 K afforded only the spectrum of the methyl radical.

U.v. irradiation of bis(cyclopropylformyl) peroxide leads to the production of cyclopropyl radicals and any intermediate cyclopropylformyloxyl radical is apparently too short-lived to enter into bimolecular reactions [equation (12)].[15] Since cyclopropyl radicals should be much less electrophilic than Bu^{t}O$^\bullet$ but be significantly more reactive in hydrogen abstraction than primary alkyl radicals,[15] we have examined the reactions of cyclo-C$_3$H$_5$$^\bullet$ with secondary amine–boranes. Photolysis of bis(cyclopropylformyl) peroxide in the presence of pyrrolidine–borane in Bu^{t}OH–Pe^{t}OH (1:1 v/v) at 276 K or in the presence of dimethylamine–borane in oxirane–cyclopropane (2.5:1 v/v) at 175 K afforded e.s.r. spectra of (**5**) and (**6**; R = Me), respectively, although these were less intense than when derived from reactions of Bu^{t}O$^\bullet$.* However, product radicals different from those obtained from reactions of Bu^{t}O$^\bullet$ were derived from other amine–boranes. Thus, with 2,2,6,6-tetramethylpiperidine–borane in benzene–Pe^{t}OH (5:1 v/v) at 268 K a spectrum was obtained which we ascribe to the aminyl–borane (**7**) (see Table 1) and (**9**) was not detected. Similarly, in the same solvent at 270 K, azetidine–borane (**2**; *n* = 2) gave a spectrum which we assign to the azetidinyl–borane radical (**13**), and the carbon-centred radical (**4**; *n* = 2) obtained by reaction[1] with Bu^{t}O$^\bullet$ under the same conditions was not detectable.

$$\text{cyclo-}C_3H_5C(O)OOC(O)\,\text{cyclo-}C_3H_5 \xrightarrow{h\nu} 2\,\text{cyclo-}C_3H_5{}^\bullet + 2CO_2 \qquad (12)$$



(13)

U.v. irradiation of a solution containing bis(cyclopropylformyl) peroxide, Me$_2$NH→BH$_3$ (1.6M), and Pr^{n}Br (0.5M) at 178 K afforded almost exclusively the spectrum of (**6**; R = Me); the weak spectrum of Pr$^{n\bullet}$ also present {[(**6**)]/[Pr$^{n\bullet}$] *ca.* 20} probably reflects a small amount of hydrogen abstraction from boron by cyclopropyl radicals. When the diacyl peroxide was replaced by DTBP under otherwise identical conditions, the value of [(**6**)]/[Pr$^{n\bullet}$] was 2.1.

We conclude that the cyclopropyl radical reacts with secondary amine–boranes predominantly by hydrogen abstraction from nitrogen to yield *directly* the aminyl–borane without the intermediacy of an amine–boryl radical. It is also clear that aminyl–borane radicals react only slowly, if at all, with alkyl bromides to form alkyl radicals.

Hydrogen Gas Evolution.—When DTBP was photolysed in the presence of most secondary amine–boranes, a gas, shown to be dihydrogen by its Raman spectrum, was evolved and the effervescence was much brisker in experiments with amine–boranes which gave rise to aminyl–borane radicals. Hydrogen evolution occurred at a similar rate in protic and aprotic solvent systems. With dimethylamine–borane in the presence of n-propyl bromide at low temperatures, when (**6**; R = Me) was undetectable because $Me_2NH\rightarrow\dot{B}H_2$ was rapidly scavenged by the alkyl halide, evolution of hydrogen did not take place to a noticeable extent.

Several possibilities exist for hydrogen-forming reactions of aminyl–borane radicals and of the other species produced in these samples. Self-reaction of aminyl–boranes to give hydrogen and an aminoborane [equation (13)] is undoubtedly highly exothermic (see Discussion section) and represents a viable alternative to the counterparts of diffusion-controlled combination and disproportionation reactions undergone by the isoelectronic alkyl radicals.

Some hydrogen might also be produced in the isomerisation reaction of $R_2NH\rightarrow\dot{B}H_2$ with $R_2NH\rightarrow BH_3$ [see equation (6)] and the analogous hydrogen-atom transfer from $R_2\dot{N}\rightarrow BH_3$ [reaction (14)] is also feasible. The latter reaction constitutes a catalytic chain pathway for elimination of hydrogen from $R_2NH\rightarrow BH_3$ and thus cannot be proceeding rapidly at low temperatures, because sample lifetimes were not unusually short, but it may become more important at higher temperatures. Unassisted β-scission of (**6**) to give a free hydrogen atom and an aminoborane is also possible at higher temperatures.

$$2R_2\dot{N}\rightarrow BH_3 \longrightarrow 2R_2N\overset{+}{=}\overset{-}{B}H_2 + H_2 \qquad (13)$$

$$R_2\dot{N}\rightarrow BH_3 + R_2NH\rightarrow BH_3 \longrightarrow R_2N\overset{+}{=}\overset{-}{B}H_2 + H_2 + R_2\dot{N}\rightarrow BH_3 \qquad (14)$$

Discussion

The secondary amine–borane $R_2NH\rightarrow BH_3$ is isoelectronic with the alkane $R_2CH–CH_3$. t-Butoxyl radicals abstract hydrogen from isobutane (Me_2CHCH_3) to give the t-butyl radical ($Me_2\dot{C}CH_3$) *ca.* 50 times more rapidly at 170 K than they react to give the isobutyl radical ($Me_2CH\dot{C}H_2$),[16] which is less stable than the tertiary radical by *ca.* 20 kJ mol^{-1}.[9,17]

t-Butoxyl radicals react with secondary amine–boranes by hydrogen abstraction from boron to give amine–boryl radicals initially. However, only with Bu^{t}Pr^{i}NH→BH$_3$ was the amine–boryl detectable directly by e.s.r. spectroscopy. With the other amine–boranes investigated, if the amine–boryl does not undergo rapid irreversible β-scission to give a carbon-centred radical or is not scavenged by alkyl bromide or Bu^{t}N=O, then intermolecular isomerisation to the aminyl–borane takes place. It appears that $R_2\dot{N}\rightarrow BH_3$ is more stable thermodynamically than the isomeric $R_2NH\rightarrow\dot{B}H_2$ although the latter is formed more rapidly by reaction of Bu^{t}O$^\bullet$ with $R_2NH\rightarrow BH_3$, presumably because of polar effects which operate in the transition states for hydrogen atom abstraction: the electrophilic alkoxyl radical preferentially abstracts hydrogen from the electron-rich BH$_3$ group[1] rather than from the electron-deficient NH group. However, the amine–boryl radical is itself nucleophilic and, under our conditions, subsequently abstracts hydrogen rapidly from the NH group of $R_2NH\rightarrow BH_3$ to give the more stable aminyl–borane [*e.g.* equation (6)]. Also indicated in equation (6) is the possibility that $R_2NH\rightarrow\dot{B}H_2$ may react by hydrogen-atom transfer to

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* The cyclopropyl radical was not detectable in these experiments. Photolysis of the diacyl peroxide alone in oxirane–cyclopropane solvent gave rise to overlapping spectra of the cyclopropyl and oxiranyl radicals, the latter presumably generated by hydrogen transfer from oxirane to the cyclopropyl radical. In accord with this interpretation, the relative concentration of oxiranyl increased and that of cyclopropyl was smaller at higher temperatures.

$R_2NH\rightarrow BH_3$ since, as discussed later, the β-NH bond in the amine–boryl radical is probably very weak. With $Bu^tPr^iNH\rightarrow BH_3$ at low temperatures, steric protection of the NH group presumably prolongs the lifetime of the amine–boryl radical and permits detection of its e.s.r. spectrum. The relatively small β-proton splitting (unresolved, $\Delta B_{p\text{-}p}$ 5.5 G) for $Bu^tPr^i\text{-}NH\rightarrow\dot{B}H_2$ compared with the 11.0 G splitting observed[2] for $H_3N\rightarrow\dot{B}H_2$, implies that H_β occupies a position close to the nodal surface of the SOMO in the preferred conformation of the former radical, as would be expected on steric grounds.

It is not surprising that isomerisation of $R_2NH\rightarrow\dot{B}H_2$ to $R_2\dot{N}\rightarrow BH_3$ does not occur by an intramolecular 1,2-hydrogen atom shift, since the energy barriers associated with such pathways appear to be prohibitively large.[18] The calculated barriers for 1,2-hydrogen atom shift in $CH_3O^{\bullet}$ and $H_3\overset{+}{N}\text{–}\dot{C}H_2$ are 151 and 176 kJ mol^{-1}, respectively.[19,20]

The results obtained with the less electrophilic cyclopropyl radicals provide strong support for our interpretation of the reactions of t-butoxyl radicals with $R_2NH\rightarrow BH_3$. Thus, whilst t-butoxyl radicals react at the BH_3 group of 2,2,6,6-tetramethylpiperidine–borane to give (**8**) and thence the carbon-centred radical (**9**), cyclopropyl radicals react by abstraction from the NH group to give the aminyl–borane (**7**) which is probably more stable than (**8**). Similarly, whilst $Bu^tO^{\bullet}$ abstracts from the BH_3 group of azetidine–borane, the more nucleophilic cyclopropyl radical attacks the electron-deficient NH group instead.

The only detectable radical product from the reaction of $Bu^tO^{\bullet}$ with ammonia–borane was $H_3N\rightarrow\dot{B}H_2$ and no spectrum attributable to $H_2\dot{N}\rightarrow BH_3$ was observable.[2] Since $Me_2NH\rightarrow\dot{B}H_2$ abstracts hydrogen very rapidly from dimethylamine–borane, even at low temperatures, this result strongly suggests that the prototype amine–boryl $H_3N\rightarrow\dot{B}H_2$ is thermodynamically more stable than aminyl–borane $H_2\dot{N}\rightarrow BH_3$ and it is likely that equilibrium concentrations of the two isomers will be present under the e.s.r. conditions.

Halogen Abstraction by Amine–Boryl Radicals.—Initial formation of $Me_2NH\rightarrow\dot{B}H_2$ in the reaction of $Bu^tO^{\bullet}$ with dimethylamine–borane is further supported by the experiments in which an alkyl halide was included in the sample. Although $H_3N\rightarrow\dot{B}H_2$, $Me_3N\rightarrow\dot{B}H_2$, and $Et_3N\rightarrow\dot{B}H_2$ all abstract chlorine from alkyl chlorides under e.s.r. conditions,[1,10] the corresponding reaction of $Me_2NH\rightarrow\dot{B}H_2$ is too slow to compete with its intermolecular isomerisation to $Me_2\dot{N}\rightarrow BH_3$. However, alkyl bromides are much more reactive towards amine–boryl radicals and, as shown in Table 2, the selectivity with which $Me_2NH\rightarrow\dot{B}H_2$ abstracts bromine from t-butyl and n-propyl bromides is very similar to the selectivity exhibited by other amine–boryl radicals. As concluded previously,[1] this low selectivity implies a high absolute reactivity, similar to that of $H_3B^{\bullet-}$ but greater than that of $H_2\dot{B}CN^-$ and $R_3P\rightarrow\dot{B}H_2$.

Comparisons between $R_2\dot{N}\rightarrow BH_3$, $R_2\dot{C}\text{–}CH_3$, *and* $R_2\dot{N}\text{–}CH_3{}^+$.—The e.s.r. spectra (Table 1) of these isoelectronic radicals enable their electronic configurations and conformations to be compared.

For $Me_2\dot{N}\rightarrow BH_3$, $a(BH)$ is double $a(CH)$ (within the linewidth) which must reflect the greater extent of hyperconjugative delocalisation of the unpaired electron into the BH_3-π group orbital than into the corresponding CH_3 orbital, as a result of the closer energetic matching of the former with the N-$2p_\pi$ orbital.[5] The β-proton splitting for a π radical containing the $H_\beta X\dot{M}$ fragment should be given by the usual Heller–McConnell relationship[21] [equation (15)], where the dihedral

$$a(H_\beta) = (A_{MXH} + B_{MXH}\cos^2\theta)\rho_M^\pi \qquad (15)$$

angle θ is defined in (**14**), ρ_M^π is the π spin density on M, and A_{MXH} and B_{MXH} are constants with the former close to zero. If the A terms are neglected, it follows that (B_{NBH}/B_{CCH}) is 2.0 for $Me_2\dot{N}\rightarrow BH_3$ since rotation about both the C–N and B–N bonds should be unrestricted ($\overline{\cos^2\theta} = 0.5$).

Table 2. Relative reactivities of t-butyl and n-propyl halides towards halogen atom abstraction by ligated boryl radicals ($L\rightarrow\dot{B}H_2$)

L	Halogen	Solvent[a]	T/K	k_{Bu^tHal}/k_{Pr^nHal}	Ref.
H^-	Br	A	203	1.2	*b*
	Cl	A	203	2.4	*b*
CN^-	Br	A	203	5.1	*b*
H_3N	Br	B	261	1.5	*c*
	Cl	B	261	4.6	*c*
Me_3N	Br	B	261	1.5	*c*
	Cl	B	261	5.0	*c*
Et_3N	Br	C	246	1.2	*d*
Me_2NH	Br	B	260	1.3	This work
Bu^n_3P	Br	D	240	5.6	*e*

[a] A = $Me_2O\text{–}Pe^tOH$ (1.3:1 v/v); B = $Bu^tOH\text{–}Me_2O$ (4:1 v/v); C = cyclopropane–tetrahydrofuran (3:1 v/v); D = cyclopropane. [b] J. R. M. Giles and B. P. Roberts, *J. Chem. Soc.. Perkin Trans. 2*, 1982, 1699; 1983, 743. [c] Ref. 10; V. P. J. Marti, Ph.D. Thesis, London, 1985. [d] Ref. 1. [e] Part 1, J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1717.

Taking B_{CCH} for the isoelectronic t-butyl radical to be 58.6 G, the corresponding value of ρ_C^π is 0.78.[22] The value of ρ_N^π for $Me_2\dot{N}\rightarrow BH_3$ is difficult to estimate accurately, but it is probably less than 0.78 on account of the substantial unpaired electron delocalisation onto the BH_3 group. The value of $a(N)$ for $Me_2\dot{N}\text{–}CH_3{}^+$ is greater than that for $Me_2\dot{N}\rightarrow BH_3$, reflecting an increase in the efficiency of π–σ spin-polarisation for the positively charged species as well as the probably smaller π spin density at nitrogen in the aminyl–borane.

The small differences in $a(BH)$ for the aminyl–boranes listed in Table 1 probably parallel small changes in ρ_N^π, whilst the much larger differences in $a(CH_\beta)$ result from changes in the value of $\cos^2\theta$ averaged over the populated conformations about the C_β–N bond. By comparison with $a(CH)$ and $a(BH)$ for $Me_2\dot{N}\rightarrow BH_3$ and using equation (15) (neglecting A), it is possible to estimate $\bar{\theta}$* for the other aminyl–boranes and thus to deduce their preferred conformations. For pyrrolidinyl–borane $\bar{\theta}$ is 30.5°, close to the value expected for a quasi-planar five-membered ring. The idealised preferred conformations of $Et_2\dot{N}\rightarrow BH_3$ and $Pr^i_2\dot{N}\rightarrow BH_3$ are shown along with the calculated values of $\bar{\theta}$ in (**15**) and (**16**), respectively, and those of the isoelectronic alkyl radicals $Et_2\dot{C}\text{–}CH_3$ and $Pr^i_2\dot{C}\text{–}CH_3$ deduced by analogous arguments are shown in (**17**) and (**18**). The conformational preferences of the aminyl–boranes are greater than those of the alkyl radicals, as evidenced by the smaller values of $a(CH_\beta)$ shown by the former.

Conformational energies of alkyl radicals appear to be determined by a delicate balance between the needs to minimise steric repulsions and to maximise stabilising hyperconjugative interactions. The greater conformational preferences shown by the aminyl–boranes are consistent with the steric demands of the BH_3 group being greater than those of CH_3 and/or $H_\beta\text{–}C\dot{M}$ hyperconjugation being more stabilising than $C_\beta\text{–}C\dot{M}$ hyperconjugation when M = C but less stabilising when M = N. Such a trend in the strength of hyperconjugative interactions as M becomes more electronegative would accord with the explanation offered for the difference in conformational

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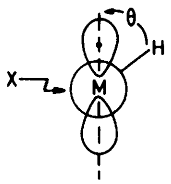
* Actually arccos $(\overline{\cos^2\theta})^{\frac{1}{2}}$.

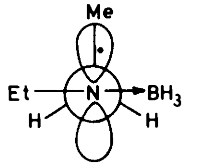
Table 3. Optimised geometries and total energies obtained from GAUSSIAN 82 calculations using a 6-31G** basis set

Radical/molecule	Geometry[a]	Energy (hartrees)[b] UHF	UMP2[c]	UMP3[c]
$H_3N\rightarrow\dot{B}H_2$ (**21**)	BN 1.662, BH 1.200, NH^1 1.005, NH^2 1.003, HBN 107.63, HBH 120.68, H^{1}NB 112.05, H^{2}NB 110.28, H^{1}NH^2 107.99, H^{2}NH^2 108.12	−81.986 169 757	−82.257 162 157	−82.282 000 694
$H_3N\rightarrow\dot{B}H_2$ (**22**)	BN 1.679, BH 1.199, NH^1 1.003, NH^2 1.003, HBN 107.99, HBH 121.00, H^{1}NB 110.66, H^{2}NB 111.01, H^{1}NH^2 107.92, H^{2}NH^2 108.20	−81.984 134 852	−82.254 860 915	−82.279 774 792
$H_2\dot{N}\rightarrow BH_3$ (**23**)	BN 1.585, BH^1 1.224, BH^2 1.206, NH 1.004, HNB 123.10, HNH 113.33, H^{1}BN 101.13, H^{2}BN 106.97, H^{1}BH^2 112.16, H^{2}BH^2 116.06	−81.990 907 884	−82.251 263 126	−82.280 896 098
$H_2N\overset{\rightarrow}{=}BH_2$	BN 1.388, BH 1.193, NH 0.994, HBN 119.46, HNB 123.04	−81.499 209 564[d]	−81.765 198 230[d]	−81.785 953 463[d]
$H^\bullet$		−0.498 232 909	−0.498 232 909	−0.498 232 909

[a] Bond lengths in Å, bond angles in degrees. Optimised values without taking account of electron correlation are given. [b] 1 hartree = 2 625.5 kJ mol^{-1}. [c] Single-point calculations using the UHF-optimised geometries. [d] Spin-restricted calculations for the singlet state.

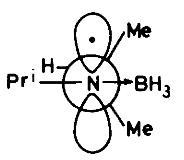


(**14**)



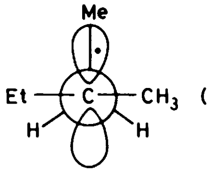
(**15**)

$\bar{\theta}$ = 57° (199 K)



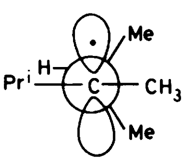
(**16**)

$\bar{\theta}$ = 84-90° (201 K)



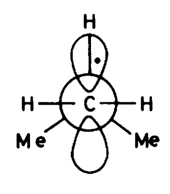
(**17**)

$\bar{\theta}$ = 52° (187 K)

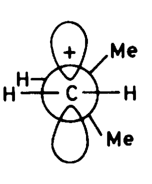


(**18**)

$\bar{\theta}$ = 66° (194 K)



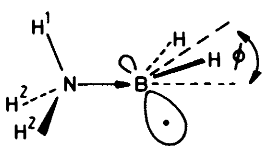
(**19**)



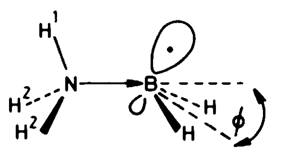
(**20**)

preferences of the isobutyl radical and of the corresponding carbocation [(**19**) and (**20**)].[17]

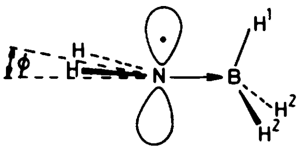
Molecular Orbital Calculations.—In order to gain further insight into the properties of the radicals derived from amine–boranes, we have carried out MO calculations using the spin-unrestricted Hartree–Fock (UHF) method at both *ab initio* (GAUSSIAN 82; 6-31G** basis set[23]) and semi-empirical (MNDO[24]) levels. In the *ab initio* studies, geometries were optimised without taking account of electron correlation, but this was included as second- or third-order Møller–Plesset corrections (MP2 or MP3) to the energies in subsequent single-point calculations at the UHF-optimised geometries.



(**21**)



(**22**)



(**23**)

The structures (**21**)—(**23**) were optimised within C_s symmetry and the results are collected in Table 3; calculation of vibrational frequencies showed that (**21**) and (**23**) represent local minima on the $BNH_5^\bullet$ potential energy surface. When electron correlation (MP3) is included, the staggered structure (**21**) is more stable then (**22**) by 5.8 kJ mol^{-1}† and the computed out-of-plane angles (ϕ) are 52.3 and 51.2°, respectively. For such highly pyramidal (close to 'tetrahedral') structures the predicted ^{11}B hyperfine splittings would be much greater than the experimental values[2] obtained for the ammonia–boryl radical in polar environments (42 G in solution at *ca.* 270 K and 46 G in polycrystalline $H_3N\rightarrow BH_3$ at *ca.* 120 K, corresponding to *ca.* 6% unpaired electron population of the B-2*s* orbital).

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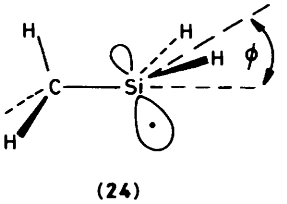
† Throughout, quoted energy differences do not include zero-point vibrational contributions.

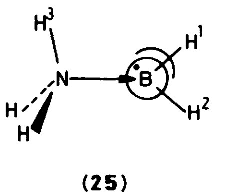
Although the time-averaged value of ø could be less than its equilibrium value, it appears that solvation and association may perturb the structure of this polar radical [the calculated dipole moment of (**21**) is 5.69 D] in condensed phases.

The inversion transition state separating (**21**) and (**22**) was located 14.2 kJ mol^{-1} (MP3) above (**21**) and was close to planar at boron (ø 3.8° below the N–B bond).

Calculations for the isoelectronic ethyl radical show that the equilibrium structure is almost planar at C_α but very easily distorted, such that the amplitude of the 'out-of-plane' bending vibration will be large under all conditions and strongly coupled to the internal rotation mode.[25,26] The methylsilyl radical (**24**) is calculated to be strongly pyramidal at silicon (ø 49.3°) with a computed inversion barrier of 29.7 kJ mol^{-1}.[27]



(24)



(25)

The C_s structure (**25**) in which the atoms $H^1H^2BNH^3$ are constrained to be coplanar was also investigated and found to be less stable than (**21**) by 14.2 kJ mol^{-1} (MP3). However, (**25**) is not a true minimum on the potential energy surface and shows one imaginary vibrational frequency associated principally with out-of-plane motion of H^1 and H^2. Next, the H^2BNH^3 grouping was constrained to be planar with the two remaining NH protons arranged symmetrically above and below this plane; H^1 was moved out of the plane by 0.5° and its position was then optimised freely against the symmetrical NH_3 group. In contrast with the result apparently found for the ethyl radical,[26] H^1 did not return to the plane but ended up 46.1° out-of-plane in a structure which is 13.9 kJ mol^{-1} (MP3) more stable than (**25**).

The aminyl-borane radical (**23**) is calculated to be nearly planar at nitrogen (ø 6.4°) and more stable than (**21**) by 12.4 kJ mol^{-1} at the UHF level, but inclusion of electron correlation (MP2 or MP3) corrections reversed this order making ammonia-boryl slightly more stable (by 2.9 kJ mol^{-1} at MP3). The different extents of pyramidalisation at the radical centres in (**21**) and (**23**) are in accord with expectations based on the electronegativity differences between the three-co-ordinate atoms and their attached ligands.[28]

Both (**21**) and (**23**) are predicted to be thermodynamically unstable with respect to $H_2N\rightleftharpoons BH_2$ and H·; the MP3 energy changes associated with the β-scissions (16) and (17) are −5.7 and −8.6 kJ mol^{-1}, respectively. In contrast, the ethyl

$$H_3N\rightarrow\dot{B}H_2 \longrightarrow H_2N\rightleftharpoons BH_2 + H\bullet \qquad (16)$$

$$H_2\dot{N}\rightarrow BH_3 \longrightarrow H_2N\rightleftharpoons BH_2 + H\bullet \qquad (17)$$

radical is more stable than $H_2C{=}CH_2$ + $H^\bullet$ by 162 kJ mol^{-1}.[29] The instability of ammonia–boryl and aminyl–borane appears to be attributable mainly to the large difference between N→B and $N\rightleftharpoons B$ bond energy terms.[1] The activation energies (MP3) for reactions (16) and (17) were calculated to be 90.7 and 4.5 kJ mol^{-1}, respectively, and the relative barrier heights parallel the spin densities on the β-hydrogens as reflected in the magnitudes of $a(H_\beta)$ for $H_3N\rightarrow\dot{B}H_2$ (11.0 G)[1] and $Me_2\dot{N}\rightarrow BH_3$ (46.4 G). A small activation energy for B–H cleavage in aminyl–boranes is not unexpected, since such radicals would be intermediates in the (unknown) S_H2 displacement[30] of $H^\bullet$ from BH_3 by $R_2N^\bullet$. Overall displacement of $R^\bullet$ from R_3B by $Me_2N^\bullet$ proceeds very rapidly and no intermediate aminyl-borane $Me_2\dot{N}\rightarrow BR_3$ has ever been detected.[31]

In agreement with previous estimates[19,20] of barriers to intramolecular 1,2-hydrogen atom migrations and in accord with our experimental observations, the activation energy for such rearrangement of (**21**) to (**23**) was calculated to be large (89.2 kJ mol^{-1} at MP3).

Semi-empirical MNDO-UHF calculations were also carried out for (**21**) and (**23**) and their various *N*-methylated derivatives; the results are summarised in Table 4. Again, (**21**) was predicted to be highly pyramidal at boron (ø 47.4°), whilst (**23**) was near planar at nitrogen (ø 2.7°) and similar geometries at B and N were found for the *N*-methylated radicals. The isomer (**23**) was calculated to be more stable than (**21**) by 48 kJ mol^{-1} and the aminyl–borane became progressively more stable than the isomeric amine–boryl radical as the number of *N*-methyl groups increased. The MNDO energy differences must be considered less trustworthy than the *ab initio* values, but the trend shown by the former should be more reliable and would indeed be predicted by analogy with related systems. Thus, *N*-alkylation of $H_3N\rightarrow BH_3$ is expected to have little effect on the strength of the B–H bond, but should lead to a reduction in DH^0(N–H), which is known[32] to decrease rapidly along the series H_4N^+ (515 kJ mol^{-1}), $MeNH_3^+$ (441), $Me_2NH_2^+$ (395), Me_3NH^+ (376). A similar decrease in DH^0(C–H) is observed with increasing methylation at carbon in methane.

In conclusion, it appears that both in the gas and in condensed phases $H_3N\rightarrow\dot{B}H_2$ is somewhat more stable than

Table 4. Enthalpies of formation, ionisation potentials, and dipole moments of amine–boryl and aminyl–borane radicals calculated by the MNDO-UHF method

Radical[a]	ΔH_f^0/kJ mol^{-1}	$\Delta\Delta H_f^0$/kJ mol^{-1}	Ionisation potential (eV)	Dipole moment[b] (D)
$H_3N\rightarrow\dot{B}H_2$ (**21**)	+100.0	+48.4	7.27	5.68
$H_2\dot{N}\rightarrow BH_3$ (**23**)	+51.6	0	11.03	4.64
$MeNH_2\rightarrow\dot{B}H_2$	+122.5	+77.7	7.17	5.71
$Me\dot{N}H\rightarrow BH_3$	+44.5	0	10.88	5.23
$Me_2NH\rightarrow\dot{B}H_2$	+161.2	+104.6	7.14	5.69
$Me_2\dot{N}\rightarrow BH_3$	+56.6	0	10.79	5.55

[a] Geometries of radicals from $H_3N\rightarrow BH_3$ and $Me_2NH\rightarrow BH_3$ were fully optimised within C_s symmetry; the radicals from $MeNH_2\rightarrow BH_3$ had no symmetry. No substantial conformational preference about the N→B bond was found for any radical. [b] In each radical the boron carried a partial negative charge (−0.24 to −0.29), whilst the nitrogen was slightly positively charged (+0.01 to +0.07) in the radicals derived from $H_3N\rightarrow BH_3$ and $MeNH_2\rightarrow BH_3$ and slightly negative (−0.01 to −0.04) in those derived from $Me_2NH\rightarrow BH_3$. The hydrogens attached to boron were negatively charged whilst those attached to nitrogen carried partial positive charges.

$H_2\dot{N}\rightarrow BH_3$, but that mono- or di-alkylation at nitrogen brings about an inversion of isomer stabilities such that the aminyl–boranes are now more stable than their amine–boryl counterparts.

The isotropic proton hyperfine splittings calculated (by MNDO) for $Me_2\dot{N}\rightarrow BH_3$ (6; R = Me) (averaged assuming freely rotating BH_3 and CH_3 groups) after annihilation of quartet state contamination were 49.7 G (3B*H*) and 19.5 G (6C*H*), in reasonable agreement with experiment. However, the computed nitrogen and boron splittings were in less good agreement and, taken overall, the splittings obtained from an INDO calculation[33] at the MNDO-optimised geometry [a(^{14}N) 15.8, a(^{11}B) 11.0, a(3B*H*) 31.6, a(6C*H*) 17.9 G] were in better accord with experiment.

Experimental

E.s.r. Spectroscopy.—Spectra were recorded with a Varian E-109 instrument operating at *ca.* 9.2 GHz. The techniques used for sample preparation and for the detection of transient photochemically generated free radicals have been described previously.[6] Samples were sealed in Suprasil quartz tubes having either 2 or 3 mm internal diameter depending on the dielectric constant of the contents. To circumvent problems arising from hydrogen evolution during photolysis, some sample tubes had relatively large spaces above the liquid and were filled with 100—200 Torr of nitrogen before closure. With solvent mixtures which are liquid at room temperature, sample tubes were usually closed with greaseless stopcocks rather than being flame sealed.

Materials.—N.m.r. spectra (C_6D_6 solvent) were obtained with a Varian XL-200 instrument, using tetramethylsilane internal standard (^{1}H, ^{13}C) or $BF_3{\cdot}Et_2O$ or 85% aqueous H_3PO_4 external standards (^{11}B or ^{31}P, respectively). Preparation and handling of amine–boranes were conducted under dry nitrogen or argon.

Dimethylamine–borane containing the normal isotopic distribution of boron was obtained commercially (Aldrich). Other amine–boranes were prepared by reaction of the dialkylamine with either $BH_3{\cdot}Me_2S$ (Aldrich) or BH_3·tetrahydrofuran (THF). The latter route involved passage of a small excess of diborane, generated by addition of $BF_3{\cdot}Me_2O$ to a stirred slurry of lithium aluminium hydride in 1,2-dimethoxyethane, into THF cooled to −78 °C followed by addition of the appropriate amine.[1] After removal of the solvent, the complex was isolated by distillation or recrystallisation or was purified by h.p.l.c. on Partisil 5 silica gel using light petroleum (b.p. 40—60 °C)—ethyl acetate (55:45 v/v) as eluant. Amine–boranes containing 97.5 atom % ^{11}B or 97.0 atom % ^{10}B were prepared using the $BH_3{\cdot}$THF route starting from isotopically enriched $BF_3{\cdot}Me_2O$ (Centronic Ltd.). The known borane complexes of Me_2NH,[34] Et_2NH,[34] Pr^i_2NH,[34] and azetidine[1] were prepared by these methods. New compounds are described below.

Pyrrolidine–borane has been reported previously[35] but was not characterised. It was obtained from the reaction of pyrrolidine with $BH_3{\cdot}$THF or $BH_3{\cdot}Me_2S$ as a crystalline solid (m.p. 28—29 °C) after recrystallisation from hexane–cyclohexane. Further purification by h.p.l.c. raised the m.p. to 30—32 °C (Found: C, 56.3; H, 14.1; N, 16.5. $C_4H_{12}BN$ requires C, 56.6; H, 14.2; N, 16.5%). The ^{11}B n.m.r. spectrum showed δ −15.8 p.p.m. (q, $^1J_{BH}$ 94 Hz).

2,2,6,6-*Tetramethylpiperidine–borane* was prepared from the amine and $BH_3{\cdot}$THF (m.p. 144—146 °C after purification by h.p.l.c.) (Found: C, 69.6; H, 14.5; N, 9.0. $C_9H_{22}BN$ requires C, 69.7; H, 14.3; N, 9.0%); δ(^{11}B) −20.9 p.p.m. (q, $^1J_{BH}$ 97 Hz).

t-Butyl(methyl)amine–borane. t-Butyl(methyl)amine (1.52 g, 17.5 mmol) was added dropwise with stirring to $BH_3{\cdot}Me_2S$ (1.74 ml of a 10M solution in dimethyl sulphide) maintaining the temperature at *ca.* 0 °C. After the addition, the mixture was stirred for a further 15 min before dimethyl sulphide was removed under reduced pressure. The residual solid was recrystallised from hexane–CH_2Cl_2 (10:1 v/v) (m.p. 82—83 °C) (Found: C, 59.2; H, 16.0; N, 13.9. $C_5H_{16}BN$ requires C, 59.5; H, 16.0; N, 13.9%); δ(^{11}B) −16.4 p.p.m. (q, $^1J_{BH}$ 97 Hz).

t-Butyl(isopropyl)amine–borane was prepared by the method used for $Bu^tMeNH\rightarrow BH_3$ (m.p. 83—84 °C) (Found: C, 64.9; H, 15.5; N, 11.1. $C_7H_{20}BN$ requires C, 65.2; H, 15.6; N, 10.9%); δ(^{11}B) −22.1 p.p.m. (q, $^1J_{BH}$ 98 Hz).

Bisperdeuterioisopropylamine–borane was prepared from the deuteriated amine[36] and $BH_3{\cdot}Me_2S$ in hexane solvent. The ^{1}H n.m.r. spectrum of the product showed only absorptions due to NH and BH_3 protons.

N-*Deuteriopyrrolidine–borane* was prepared by exchange of the protio compound with D_2O, as described by Myers and Ryschkewitsch[37] for $Me_2ND\rightarrow BH_3$. Pyrrolidine–borane (0.4 g) was stirred in D_2O (10 ml) at room temperature for 2 h. The product was extracted into dichloromethane (2 × 10 ml) which was dried overnight (K_2CO_3). Removal of the solvent under reduced pressure gave the amine–borane which was shown by mass spectroscopy to be ⩾95% deuteriated at nitrogen. No N*H* absorption was detectable in the ^{1}H n.m.r. spectrum.

Di-t-butyl hyponitrite was prepared as described by Kiefer and Traylor.[14] Diheptanoyl peroxide[38] and bis(cyclopropylformyl) peroxide[15] were prepared from the corresponding acids and hydrogen peroxide using the method of Staab.[39] Bis(cyclopropylformyl) peroxide was obtained as plates after recrystallisation from pentane. Its ^{13}C n.m.r. spectrum (in $CDCl_3$) showed δ 9.39 (tt, $^1J_{C-H}$ 168.5, $^2J_{C-H}$ 3.8 Hz, *C*H_2), 9.39 (d, $^1J_{C-H}$ 171.0 Hz, *C*H), and 171.0 p.p.m. (*C*O_2).

The possibility that diacyl peroxides might react with secondary amine–boranes in the absence of u.v. irradiation was investigated using n.m.r. spectroscopy. Under conditions comparable with those of the e.s.r. experiments, no reaction between pyrrolidine–borane (0.5M) and bis(cyclopropylformyl) peroxide (0.3M) in benzene–Pe^tOH (5:1 v/v) was detectable by ^{13}C or ^{11}B n.m.r. spectroscopy during 3 h at 268 K.

3-Bromo-3-methylpentane was prepared from 3-methylpentan-3-ol using the published route to t-butyl bromide,[40] b.p. 39—40 °C at 20 Torr (lit.,[41] 76 °C at 100 Torr); δ_H($CDCl_3$) 0.87 (t, 6 H), 1.44 (s, 3 H), and 1.4—1.8 (m, 4 H).

Diethyl 2,3,4-*trimethylpent*-3-*yl phosphite.* Methyl-lithium (37 ml of a 2.7M solution in diethyl ether) was added dropwise during 15 min to a stirred solution of 2,4-dimethylpentan-3-one (11.6 g, 0.10 mol) in dry ether (80 ml) cooled in an ice–water bath. After stirring for a further 30 min at room temperature, diethyl chlorophosphite (15.7 g, 0.10 mol) in ether (20 ml) was added dropwise with cooling (ice-bath). After the addition, the mixture was stirred for 30 min at room temperature and precipitated lithium chloride was removed by filtration. Evaporation of the solvent from the filtrate and distillation of the residual oil gave the *phosphite* (11.1 g, 44%), b.p. 49—50 °C at 0.03 Torr (Found: C, 57.7; H, 10.6; P, 12.4. $C_{12}H_{27}O_3P$ requires C, 57.6; H, 10.9; P, 12.4%); δ_P 134.0 p.p.m.; δ_H 0.90 (d, 6 H), 1.05 (d, 6 H), 1.15 (t, 6 H), 1.26 (d, 3 H, $^4J_{P-H}$ 2.1 Hz), 1.89 (septet, 2 H), and 3.75—4.00 (m, 4 H).

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