Ligated Boryl Radicals. Part 2.[1] Electron Spin Resonance Studies of Trialkylamine–Boryl Radicals

Jehan A. Baban, Vernon P. J. Marti, and Brian P. Roberts *
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

Transient amine–boryl radicals $R_3N\rightarrow\dot{B}H_2$ (**1**) have been generated in solution by hydrogen-atom abstraction from a variety of amine–borane complexes $R_3N\rightarrow BH_3$, and studied by e.s.r. spectroscopy. The e.s.r. spectrum of (**1**; R = Me), and not of $[Me_3N\rightarrow BH_3]^{-\cdot}$ as previously proposed, is also detected after γ-irradiation of polycrystalline $Me_3N\rightarrow BH_3$ at 77 K. The hyperfine splitting constants for (**1**) indicate a pyramidal arrangement of ligands about the boron centre, in contrast to the effectively planar geometry at the radical centre in isoelectronic primary alkyl radicals. In solution, (**1**; R = Et) rapidly abstracts halogen from alkyl bromides and less readily from alkyl chlorides; at 246 K Bu^tBr is only 1.2 times more reactive than Pr^nBr. The radical (**1**; R = Et) adds to MeCN to give an iminyl radical and displaces a methyl radical from MeNC; it fails to add to ethylene, but adds readily to the more electron-deficient double bond in trimethyl(vinyl)silane. Amine–boryls undergo β-scission much more readily than their isoelectronic alkyl radical counterparts; this difference is attributable to the greater exothermicity of the former cleavage. The aziridine– and azetidine–boryl radicals undergo rapid ring opening; C–N cleavage in the *cis*-isomer of the 2-methylaziridine–boryl radical gives mainly the secondary alkyl radical, while the *trans*-isomer gives mainly the less stable primary alkyl radical. Substituted but-3-enylamine–boryl radicals, analogues of the hex-5-enyl radical, undergo regioselective 1,5-*exo*-cyclisation to give analogues of cyclopentylmethyl. Relative rates of β-scission and cyclisation of amine–boryl radicals have been determined in competition with their abstraction of bromine from ethyl bromide.

Ever since Gomberg's discovery of triphenylmethyl,[2] the formation, structures, and reactions of carbon-centred free radicals have been studied extensively, and a very large body of data has accumulated in the literature. In contrast, very little is known about boron-centred radicals, even those which are isoelectronic with well known carbon-centred species, although it is expected that both families of radical will possess a similarly rich chemistry.

We have begun a programme designed to explore the chemistry of boron-centred radicals in solution, emphasising the comparison with isoelectronic carbon counterparts. The ligated boryl radicals, $L\rightarrow\dot{B}X_2$ constitute an important class of boron-centred radicals, and Part 1[1] of this series was concerned with the phosphine–boryls, $X_3P\rightarrow\dot{B}H_2$, which are isoelectronic with silylmethyl radicals, $X_3Si\text{–}\dot{C}H_2$. In this paper we describe e.s.r. studies of amine–boryl radicals $R_3N\rightarrow\dot{B}H_2$ (isoelectronic with $R_3C\text{–}\dot{C}H_2$) derived by hydrogen abstraction from the borane complexes of tertiary aliphatic amines. Results obtained with borane complexes of the secondary amines aziridine and azetidine are also included in this report; some of the work on amine–boryl radicals has been published in the form of preliminary communications.[3,4]

Results

E.s.r. spectra were recorded during continuous u.v. irradiation of liquid samples in the spectrometer cavity, as described previously.[5] Amine–boranes are relatively polar compounds (the dipole moment[6] of $Me_3N\rightarrow BH_3$ is 4.59 D) and they are often only sparingly soluble in hydrocarbons at low temperatures. When possible, mixtures of cyclopropane with oxirane, tetrahydrofuran (THF), dimethyl ether, t-butyl alcohol, or t-pentyl alcohol were used as solvents, although for some compounds one of the more polar solvents or a mixture of these was necessary.

t-Butoxyl radicals, produced by photolytic cleavage of di-t-butyl peroxide (DTBP), readily abstract hydrogen from the BH_3 group of an amine–borane to give the corresponding amine–boryl radical (**1**). An e.s.r. spectrum, part of which is shown in Figure 1, assigned to the trimethylamine–boryl radical (**1**; R = Me) was obtained during photolysis of a $Bu^tOH\text{–}Me_2O$ solution containing DTBP (*ca.* 15% v/v) and $Me_3N\rightarrow BH_3$ (*ca.* 1M). Under similar conditions, spectra of amine–boryl radicals produced by hydrogen (or deuterium) abstraction from $Me_3N\rightarrow BD_3$, $(CD_3)_3N\rightarrow BH_3$, $Et_3N\rightarrow BH_3$, $Et_3N\rightarrow BD_3$, and *N*-methylpyrrolidine–borane were observed; the e.s.r. parameters are collected in Table 1. In general, the spectra were not strong because of the large number of lines present. The best quality spectrum of $Me_3N\rightarrow\dot{B}H_2$ was obtained at relatively high temperatures (*ca.* 280 K) whilst that of $Et_3N\rightarrow\dot{B}H_2$ was best at lower temperatures (*ca.* 190 K), when the fortuitous equality of a(N) and $a(6H_\gamma)$ leads to more intense signals.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\cdot \qquad (1)$$

$$Bu^tO^\cdot + R_3N\rightarrow BH_3 \longrightarrow Bu^tOH + \underset{(\mathbf{1})}{R_3N\rightarrow\dot{B}H_2} \qquad (2)$$

The natural abundances of ^{11}B (I = 3/2) and ^{10}B (I = 3) are 80.2 and 19.8%, respectively, but in some experiments amine–boranes containing 97.5 atom % ^{11}B and 2.5 atom % ^{10}B were used in order to simplify the e.s.r. spectra and increase their intensities.

Self-reaction of Amine–Boryl Radicals.—At 190 K the concentration of (**1**; R = Et) was proportional to the square root of the incident light intensity, implying second-order decay by radical–radical reaction, presumably combination to give the bis(triethylamine) complex of diborane(4). The rate coefficient for combination was measured by the 'kinetic e.s.r.' technique,[7] using a rotating sectored disc to provide intermittent sample irradiation, and at 190 K the value of $2k_t$ was $(8 \pm 2) \times 10^8$ dm^3 mol^{-1} s^{-1} for an initial radical concentration of *ca.* 5×10^{-7}M.

$$2Et_3N\rightarrow\dot{B}H_2 \xrightarrow{2k_t} Et_3N\rightarrow BH_2\text{–}BH_2\leftarrow NEt_3 \qquad (3)$$

Table 1. E.s.r. parameters for amine–boryl radicals $R_3N\rightarrow\dot{B}H_2$

				Hyperfine splittings (G)[b]			
Radical	Solvent[a]	T/K	g-Factor[b]	$a(^{11}B)$	$a(2H_\alpha)$	a(N)	Others
$Me_3N\rightarrow\dot{B}H_2$	A	280	2.0022	51.3	9.6	1.4	1.4 ($9H_\gamma$)
	B	260	2.002	57.4	9.5		
$Me_3N\rightarrow\dot{B}D_2$	A	280	2.0022	51.2	1.5[c]	1.4	1.4 ($9H_\gamma$)
	B	260	2.002	57.6			
$(CD_3)_3N\rightarrow\dot{B}H_2$	A	265	2.0022	51.3	9.6	*d*	*d*
$Et_3N\rightarrow\dot{B}H_2$	C	193	2.0023	47.5	12.9	2.2	2.2 ($6H_\gamma$)
	C	226	2.0022	47.5	13.0	2.2	2.2 ($6H_\gamma$)
	A	251	2.0022	47.1	12.5	*e*	*e*
$Et_3N\rightarrow\dot{B}D_2$	C	193	2.0023	48.2	2.0[c]	2.2	2.2 ($6H_\gamma$)
$\overline{CH_2[CH_2]_3N}(Me)\rightarrow\dot{B}H_2$	D	206	2.0023	50.7	11.3	1.6	1.6 ($4H_\gamma$)

[a] A = t-butyl alcohol–dimethyl ether (4:1 v/v); B = polycrystalline parent amine–borane, radical generated by γ-irradiation at 77 K; C = cyclopropane–THF (3:1 v/v); D = cyclopropane–THF (4:1 v/v). [b] Corrected for second-order effects. [c] Calculated [a(D) = a(H)/6.514] splitting from two deuterons; experimentally the difference between a(D) and a(N) or $a(H_\gamma)$ was not resolvable. [d] Not resolved. The shape and width (ΔB_{p-p} 3.9 G) of each line of the α-proton triplet was consistent with a(N) = 1.4 and a(9D) = 0.21 G, and not with a(N) = 2.8 and a(9D) = 0.21 G. This result rules out the possibility, which could not be entirely excluded by computer simulation because of the poor signal:noise ratio (see Figure 1), that a(N) = 2.8 and a(9H) = 1.4 G for $(CH_3)_3N\rightarrow\dot{B}H_2$. [e] Further fine structure was present, but the spectrum was not strong enough to permit analysis.

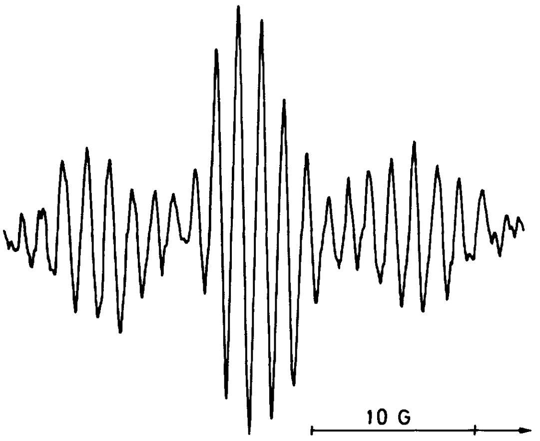

Figure 1. Lowest-field [$I(^{11}B)$ + 3/2] multiplet from the e.s.r. spectrum of the trimethylamine–boryl radical (**1**; R = Me) in $Bu^tOH–Me_2O$ (4:1 v/v) at 280 K

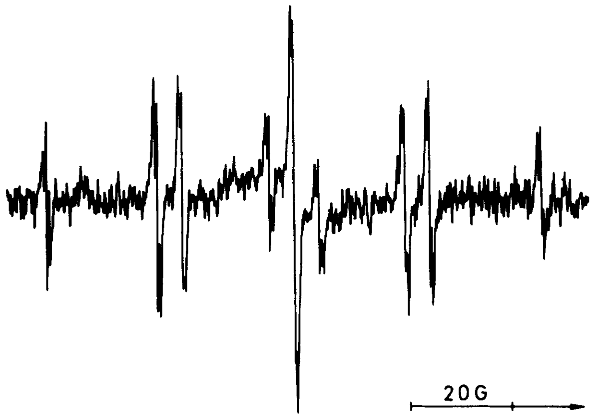

Figure 2. E.s.r. spectrum of (**3**; R = H, n = 2) produced by ring opening of the azetidine–boryl radical in cyclopropane–oxirane (1:1 v/v) at 285 K

Radical–Molecule Reactions of Amine–Boryls.—These were investigated by including the relevant reactant (1—2M) in the sample along with the amine–borane and DTBP.

In the presence of ethyl or n-propyl bromide in the temperature range 200—270 K, the spectrum of each amine–boryl radical was completely replaced by that of the appropriate alkyl radical, presumably formed by abstraction of bromine [equation (4)]. Halogen abstraction from alkyl chlorides is less

$$R_3N\rightarrow\dot{B}H_2 + R'Br \longrightarrow R_3N\rightarrow BH_2Br + R'^{\bullet} \quad (4)$$

rapid and both (**1**; R = Et) and $Pr^{n\bullet}$ were detected during photolysis of a cyclopropane–THF (3:1 v/v) solution containing $Et_3N\rightarrow BH_3$, DTBP, and Pr^nCl (1.5M) at 200 K. However, in similar experiments with Bu^tCl (1.2M) the spectrum of $Bu^{t\bullet}$ was strong, whilst that of (**1**; R = Et) was barely detectable at 200 K.

Competition experiments were carried out to determine the relative reactivities of t-butyl and n-propyl bromides towards (**1**; R = Et) by measuring the relative concentrations of $Bu^{t\bullet}$ and $Pr^{n\bullet}$ during generation of the amine–boryl radical in the presence of a mixture of these halides ([Pr^nBr]/[Bu^tBr] = 1—2.5).[1] Assuming that the rate coefficients for removal of $Bu^{t\bullet}$ and $Pr^{n\bullet}$ by self- and cross-reactions are all equal,[8] the value of (k_{Bu^tBr}/k_{Pr^nBr}) was 1.2 ± 0.1 at 246 K in cyclopropane–THF (3:1 v/v).

Methyl radicals only were detected during generation of (**1**; R = Et) in the presence of methyl isocyanide (*ca.* 1.5M) and no spectrum which might be ascribed to an imidoyl adduct $Et_3N\rightarrow BH_2\dot{C}{=}NMe$ could be detected down to 200 K. However, with methyl cyanide the spectrum of an iminyl adduct [$a(^{11}B)$ 21.3, a(N) 9.4, a(3H) 2.8 G, g 2.0029 at 257 K] was obtained [equation (5)].

$$Et_3N\rightarrow\dot{B}H_2 + CH_3C{\equiv}N \longrightarrow Et_3N\rightarrow BH_2(CH_3)C{=}N^{\bullet} \quad (5)$$

Addition to ethylene (*ca.* 5M) was not detectable between 173 and 223 K, but a poor quality spectrum of the adduct $Et_3N\rightarrow BH_2CH_2\dot{C}HSiMe_3$ [$a(1H_\alpha)$ *ca.* 18, $a(2H_\beta)$ *ca.* 17, $a(^{11}B)$ *ca.* 25 G in cyclopropane–THF (4:1 v/v)] was observed when

Table 2. Radicals formed by β-scission of amine–boryl radicals

Amine–boryl radical	Solvent[a]	T/K	Radicals detected[b]
$Pr^i_2NEt\rightarrow\dot{B}H_2$	A	190—270	$Pr^{i\cdot}$
$Bu^tNMe_2\rightarrow\dot{B}H_2$	A	195—280	$Bu^{t\cdot}$
$PhCH_2NMe_2\rightarrow\dot{B}H_2$	B	295[c]	$Ph\dot{C}H_2$
$Me_2N\text{-}NMe_2\rightarrow\dot{B}H_2$	C,D	183—258	$Me_2N^{\cdot}$
$\overline{CH_2CH_2N}H\rightarrow\dot{B}H_2$	A	226—290	$^{\cdot}CH_2CH_2\overset{+}{N}H{=}\overset{-}{B}H_2$
$\overline{CH_2CH_2N}Me\rightarrow\dot{B}H_2$	E	245—260	$^{\cdot}CH_2CH_2\overset{+}{N}Me{=}\overset{-}{B}H_2$
cis-$Me\overline{CHCH_2N}H\rightarrow\dot{B}H_2$	C	151	(**6**) (4%) + (**7**) (96%)
	C	196	(**6**) (*ca.* 3%) + (**7**) (*ca.* 97%)
	D	235	(**6**) (5%) + (**7**) (95%)
trans-$Me\overline{CHCH_2N}H\rightarrow\dot{B}H_2$	C	151	(**6**) (66%) + (**7**) (34%)
	C	196	(**6**) (69%) + (**7**) (31%)
	D	235	(**6**) (69%) + (**7**) (31%)
$\overline{CH_2[CH_2]_2N}H\rightarrow\dot{B}H_2$	A	179—275	$^{\cdot}CH_2[CH_2]_2\overset{+}{N}H{=}\overset{-}{B}H_2$

[a] A = cyclopropane–oxirane (1:1 v/v); B = cyclopropane–dimethyl ether (3:1 v/v); C = cyclopropane–oxirane (2:1 v/v); D = cyclopropane–t-pentyl alcohol (3:1 v/v); E = dimethyl ether–t-pentyl alcohol (1:1.2 v/v). [b] When two radicals are detected the relative concentrations are given in parentheses. [c] Temperature range restricted by low solubility of the amine–borane.

(**1**; R = Et) was generated in the presence of trimethyl(vinyl)silane (*ca.* 1M) at 210 K. The central line of each triplet resulting from coupling with the β-protons was relatively broad, suggesting restriction of rotation about C_α–C_β and a preferred conformation in which the B–C_β bond eclipses the singly occupied C_α $2p_\pi$ orbital. This conformational preference is also in accord with the magnitudes of $a(H_\beta)$ and $a(^{11}B)$.

β-Scission of Amine–Boryl Radicals.—Although the e.s.r. spectrum of (**1**; R = Et) could be observed up to 260 K, photolysis of DTBP in the presence of $Pr^i_2EtN\rightarrow BH_3$ afforded a strong spectrum of the isopropyl radical even at 200 K, and $Pr^i_2EtN\rightarrow\dot{B}H_2$ was not detected. The latter amine–boryl radical thus undergoes cleavage of the weaker N–C bond [equation (6)] and this β-scission is fast compared with amine–boryl dimerisation at 200 K.†

$$Pr^i_2EtN\rightarrow\dot{B}H_2 \longrightarrow Pr^{i\cdot} + Pr^i(Et)\overset{+}{N}{=}\overset{-}{B}H_2 \longleftrightarrow Pr^i(Et)\ddot{N}{-}BH_2 \quad (6)$$

Similarly, only t-butyl or benzyl radicals were detected in analogous experiments with $Bu^tNMe_2\rightarrow BH_3$ or $PhCH_2NMe_2\rightarrow BH_3$, respectively, and spectra of the corresponding amine–boryl radicals were not observed. At 270 K and above, irradiation of a solution of $Et_3N\rightarrow BH_3$ in neat DTBP afforded a weak e.s.r. spectrum of the ethyl radical, showing that rupture of a primary C–N bond occurs under forcing conditions. The results are summarised in Table 2.

Relief of angle strain present in the aziridine– and azetidine–boryl radicals leads to rapid ring-opening β-scission of these species to give primary alkyl radicals [equation (7; R = H, n = 1 or 2)] and at the lowest accessible temperatures the spectra of the amine–boryl radicals were undetectable. The spectrum of (**3**; R = H, n = 2) derived from azetidine–borane is shown in Figure 2. The N-methylaziridine–boryl radical (**2**; R = Me, n = 1) also undergoes ring opening, although at very low temperatures (*ca.* 176 K) the spectrum of (**3**) was weak, suggesting that cleavage of (**2**) is relatively slow although the spectrum of the latter radical could not be identified with certainty. The N-methylpyrrolidine–boryl radical (**2**; R = Me, n = 3) did not undergo ring opening at a detectable rate up to 295 K.

Ring opening of the *cis*- and *trans*-isomers of the 2-methylaziridine–boryl radical (**4**) was investigated to compare with the regioselective ring cleavage undergone by the isoelectronic 2-methylcyclopropylmethyl radicals.[12] The *cis*- and *trans*-(**4**) were generated by hydrogen abstraction from the corresponding isomerically pure *cis*- and *trans*-amine–boranes (**5**), which were separated by h.p.l.c. from the isomeric mixture obtained from the reaction of 2-methylaziridine with borane in THF. Only carbon-centred radicals resulting from ring opening were detected from either isomer; *cis*-(**4**) gave almost exclusively the secondary radical (**7**), whilst *trans*-(**4**) gave mainly the less stable primary radical (**6**). The relative concentrations of (**6**) and (**7**), which were determined by double integration of the spectra and confirmed by computer simulation, did not vary significantly between 151 and 235 K (see Table 2). The relative concentrations of (**6**) and (**7**) did not depend on the extent of sample photolysis, implying that *cis*- and *trans*-(**5**) do not interconvert under the experimental conditions. If we make the usual assumption[8] that the rate coefficients for removal of small, uncharged carbon-centred radicals will be effectively the same, since such processes are diffusion-controlled, the value of [(**7**)]/[(**6**)] will be equal to the ratio of rate coefficients for ring opening to form the secondary and primary radicals, respectively. The e.s.r. parameters for all the radicals produced by ring opening of cyclic amine–boryls are given in Table 3.

Competition experiments were carried out to compare the rates at which amine–boryls undergo β-scission with those for abstraction of halogen from ethyl bromide. If possible, the concentration of the alkyl halide was adjusted so that the intensity of the spectrum of ethyl was similar to that of the radical formed by β-scission. Appropriate, sometimes overlapping, peaks in the spectra of both radicals were recorded as a function of total irradiation time and peak heights were extrapolated to zero time. The 'zero time' spectrum was then computer-simulated to obtain the corresponding radical

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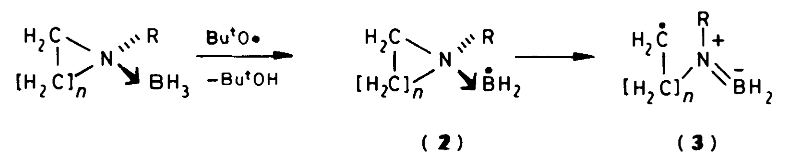
† Dialkylaminoboranes will be represented by charge-separated structures of the type $R_2\overset{+}{N}{=}\overset{-}{B}H_2$ to emphasise the analogy with alkenes. However, although the NB bond order appears to be close to two, the net polarisation of electrons is away from boron and the nitrogen carries a partial negative charge, because σ electron donation by the electropositive boron outweighs π electron donation from N to B.[9,10] N,N-Dimethylaminoborane, $Me_2\overset{+}{N}{=}\overset{-}{B}H_2$, is dimeric under ambient conditions but dissociates to the monomer when heated *in vacuo*.[11]

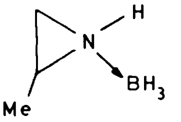
Table 3. E.s.r. parameters for radicals formed by ring opening of cyclic amine–boryl radicals

Radical	Solvent[a]	T/K	g-Factor	Hyperfine splittings (G)[b]
$^{\bullet}CH_2CH_2\overset{+}{N}H{=}\overset{-}{B}H_2$	A	226	2.0027	22.3 ($2H_\alpha$), 31.4 ($2H_\beta$), 3.1 (1N)
$^{\bullet}CH_2CH_2\overset{+}{N}Me{=}\overset{-}{B}H_2$	E	245	2.0028	22.2 ($2H_\alpha$), 30.4 ($2H_\beta$), 3.1 (1N)
$^{\bullet}CH_2CHMe\overset{+}{N}H{=}\overset{-}{B}H_2$ (**6**)	C	151	2.0029	22.1 ($2H_\alpha$), 34.0 ($1H_\beta$), 3.4 (1N)
	C	196		22.1 ($2H_\alpha$), 32.4 ($1H_\beta$), 3.7 (1N)
	D	235		22.1 ($2H_\alpha$), 31.4 ($1H_\beta$), 3.9 (1N)
$Me\dot{C}HCH_2\overset{+}{N}H{=}\overset{-}{B}H_2$ (**7**)	C	151	2.0029	21.6 ($1H_\alpha$), 28.0 ($2H_\beta$), 24.9 ($3H_\beta$), 3.2 (1N)
	C	196		21.6 ($1H_\alpha$), 26.1 ($2H_\beta$), 25.0 ($3H_\beta$), 3.5 (1N)
	D	235		21.6 ($1H_\alpha$), 25.7 ($2H_\beta$), 25.0 ($3H_\beta$), 3.7 (1N)
$^{\bullet}CH_2[CH_2]_2\overset{+}{N}H{=}\overset{-}{B}H_2$	A	179		22.2 ($2H_\alpha$), 28.6 ($2H_\beta$)
	A	255	2.0029	22.2 ($2H_\alpha$), 27.6 ($2H_\beta$), 0.6 ($2H_\gamma$)

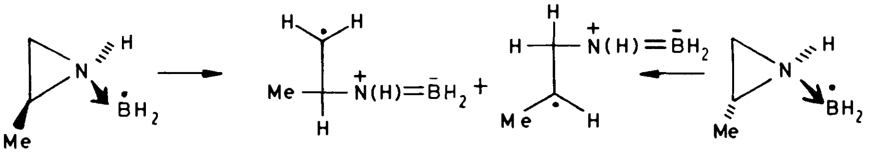
[a] See footnote *a* to Table 2. [b] Numbers of equivalent nuclei shown in parentheses.



(**2**) (**3**) (7)



(**5**)



cis-(**4**) (**6**) (**7**) *trans*-(**4**) (8)

concentration ratio; this procedure was essential to achieve reliable results, since in many experiments the concentration of ethyl bromide was relatively small. With the assumption of equal rate coefficients for the radical–radical reactions of R$^\bullet$ and Et$^\bullet$,[8] equation (11) may be derived; the values of (k_9/k_{10}) given in Table 4 were obtained from measurements at 255 K.

$$R_3N{\rightarrow}\dot{B}H_2 \xrightarrow{k_9} R^\bullet + R_2\overset{+}{N}{=}\overset{-}{B}H_2 \quad (9)$$

$$R_3N{\rightarrow}\dot{B}H_2 + EtBr \xrightarrow{k_{10}} R_3N{\rightarrow}BH_2Br + Et^\bullet \quad (10)$$

$$(k_9/k_{10}) = [R^\bullet][EtBr]/[Et^\bullet] \quad (11)$$

The e.s.r. spectrum of the dimethylaminyl radical [a(N) 15.2, a(6H) 27.9 G] was observed during photolysis of a cyclopropane–oxirane (2:1 v/v) solution containing DTBP and the borane complex of tetramethylhydrazine; no other radical was detected even at 183 K. Although other interpretations are possible, the most reasonable explanation of this result is that the hydrazine–boryl radical is formed initially, but undergoes very rapid β-scission to give $Me_2N^\bullet$ [equation (12)]. When the

$$Me_2N\text{-}NMe_2{\rightarrow}\dot{B}H_2 \longrightarrow Me_2N^\bullet + Me_2\overset{+}{N}{=}\overset{-}{B}H_2 \quad (12)$$

hydrazine–borane was replaced by the free hydrazine, the dimethylaminyl radical was still detectable, but only above *ca.* 250 K. At lower temperatures, a much more complex (and as yet uninterpreted) spectrum was observed which might be due to $Me_2N\text{-}N(Me)\dot{C}H_2$. β-Scission of this hydrazinomethyl radical is the most likely source of the dimethylaminyl radical [equation (13)].

$$Me_2N\text{-}N(Me)\dot{C}H_2 \longrightarrow Me_2N^\bullet + MeN{=}CH_2 \quad (13)$$

Cyclisation of But-3-enylamine–Boryl Radicals.—To explore further the analogy with carbon-centred radicals, we have investigated the behaviour of the amine–boryls derived from the unsaturated amine–boranes (**8**; R = H or Me). Even at temperatures as low as 161 K, no spectra which might be assigned to (**9**) were detected from either precursor; *exo*-cyclisation to give the five-membered ring system (**10**) appears to occur rapidly and with high regioselectivity for both amine–boryls. The e.s.r. spectrum of (**10**; R = H) is shown in Figure 3; the spectroscopic parameters [$a(2H_\alpha)$ 19.9, $a(1H_\beta)$ 19.9, $a(^{11}B)$ 26.3 G, g 2.0027 at 161 K in cyclopropane–oxirane (1:1 v/v)] are in accord with the structure assigned and are not as expected for (**11**), the product of *endo*-cyclisation. Similarly, the e.s.r. parameters [$a(6H_\beta)$ 20, $a(1H_\beta)$ 10, a (^{11}B) 20 G at 161 K] for (**10**; R = Me) are not unreasonable for the proposed structure, although the linewidth was large (*ca.* 5 G) and the quality of the spectrum was poor such that its analysis should be considered tentative.

By competition experiments similar to those described above, it was shown that the rate coefficient for abstraction of bromine

Table 4. Relative rate coefficients for β-scission of and bromine abstraction from ethyl bromide by amine–boryl radicals in cyclopropane–oxirane (1 : 1 v/v) at 255 K

Amine–Boryl radical	[EtBr] M	k_9/k_{10} M	k_9 (rel)[a]
$Pr^i_2NEt\to\dot{B}H_2$	0.18	0.03 ± 0.01	1
$Bu^tNMe_2\to\dot{B}H_2$	0.25	0.05 ± 0.01	1.7
$\overline{CH_2[CH_2]_2NH}\to\dot{B}H_2$	1.12	0.75 ± 0.05	25
$\overline{CH_2CH_2NH}\to\dot{B}H_2$	1.12	4.5 ± 0.4	150

[a] Calculated by assuming that k_{10} is independent of the structure of the amine–boryl radical.

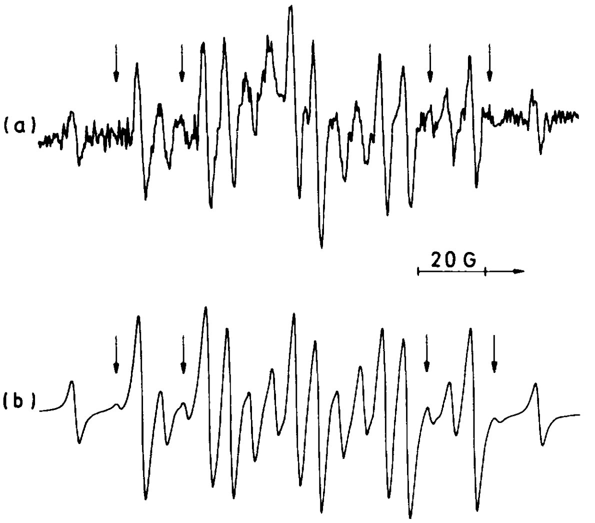


Figure 3. (*a*) E.s.r. spectrum of the radical (**10**; R = H) produced by cyclisation of the *N*,*N*-dimethylbut-3-enylamine–boryl radical in cyclopropane–oxirane (1:1 v/v) at 163 K. The parent amine–borane contained the natural abundance of ^{10}B and ^{11}B. (*b*) Computer simulation of the spectrum of (**10**; R = H), obtained using the parameters given in the text, as a mixture of radicals containing ^{10}B and ^{11}B in natural abundance. The arrows indicate visible lines due to the ^{10}B-containing species

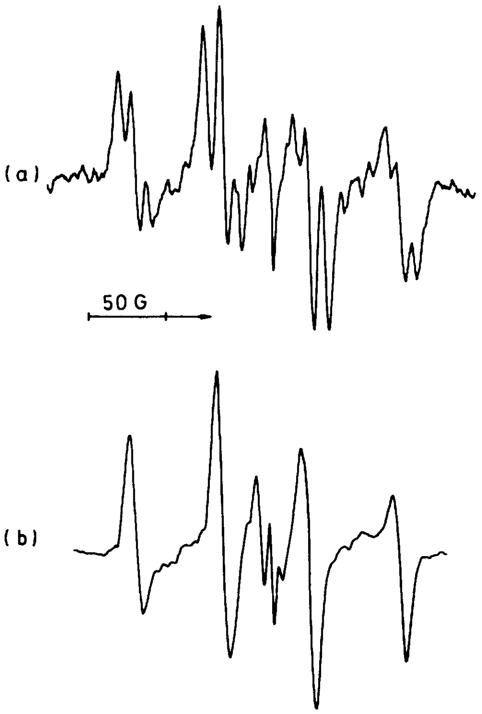
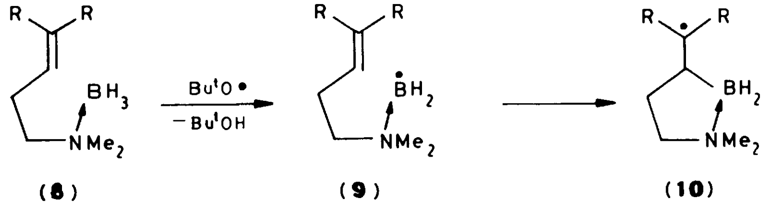


Figure 4. E.s.r. spectra at 255 K of (a) $Me_3N\to\dot{B}H_2$ (80.2 atom % ^{11}B) and (b) $Me_3N\to\dot{B}D_2$ (97.5 atom % ^{11}B) obtained from the γ-irradiated polycrystalline amine–boranes. The central peaks are not part of the spectra of the amine–boryl radicals



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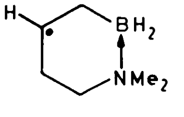


(**11**)

from ethyl bromide by (**9**; R = H) is approximately 1.3 times that for *exo*-cyclisation in cyclopropane–oxirane at 254 K.

γ-Irradiation of Polycrystalline Trimethylamine–Borane.—An e.s.r. study of γ-irradiated $Me_3N\to BH_3$ has been reported previously by Claxton *et al.*[13] At 77 K, following γ-irradiation at the same temperature, a spectrum comprising four broad lines [a(^{11}B) 58 G] was observed and no additional hyperfine splitting could be resolved. This spectrum, which was ascribed to the amine–borane radical anion $[Me_3N\to BH_3]^{-\bullet}$, was replaced by a more intense and complex spectrum [analysed in terms of a(3H) 43, a(6H) 24, a(1N) 18, a(^{11}B) 12 G at 77 K] during annealing to 150 K. The second radical was thought to be $Me_2\dot{N}\to BH_3$ and this assignment was supported by deuterium-labelling studies.

Although the interpretation offered by Claxton *et al.* might have seemed reasonable at the time, it clearly needed to be reassessed in the light of our results obtained in solution and we have consequently reinvestigated the radicals produced by γ-irradiation of $Me_3N\to BH_3$. With commercially obtained (Aldrich) amine–borane our experimental results agreed well with those reported by Claxton *et al.* However, with $Me_3N\to BH_3$ prepared by reaction of diborane with Me_3N in THF or with commercial material which had been purified by h.p.l.c., strikingly different results were obtained. Thus, at 77 K after γ-irradiation of chemically pure $Me_3N\to BH_3$ the quartet of broad lines was detected as before, but the spectrum could now be recorded up to much higher temperatures and the second spectrum observed with the impure material did not appear. At 255 K the spectrum afforded by the pure material showed further fine structure due to coupling with two equivalent protons and this splitting was absent in the spectrum derived from $Me_3N \rightarrow {}^{11}BD_3$ (see Figure 4). We are therefore forced to reassign this spectrum to the trimethylamine–boryl radical (**1**; R = Me).

Commercial samples of $Me_3N \rightarrow BH_3$ were shown by ^{11}B n.m.r. and h.p.l.c. analysis to contain up to 3 mol % of $Me_2NH \rightarrow BH_3$; evidently* this compound may be formed as a side product in the synthesis[14] of $Me_3N \rightarrow BH_3$ from commercial quality sodium borohydride and trimethylamine hydrochloride. The radical detected by Claxton *et al.* at higher temperatures thus appears to originate from $Me_2NH \rightarrow BH_3$; we obtained support for this proposal in experiments with pure $Me_3N \rightarrow BH_3$ which had been doped with *ca.* 3% $Me_2NH \rightarrow BH_3$ by co-sublimation of the two solids, since the sublimate gave results indistinguishable from those obtained using the impure commercial material. The spectrum of the second radical could also be detected after γ-irradiation of $Me_2NH \rightarrow BH_3$ alone, but resolution was much poorer than that obtained from doped $Me_3N \rightarrow BH_3$. The spherical shape of the host cavities in $Me_3N \rightarrow BH_3$ (isoelectronic with neopentane) could well facilitate motional averaging of anisotropic hyperfine interactions.

It seems likely that the original identification[13] of the 'second radical' as $Me_2\dot{N} \rightarrow BH_3$ (**12**) is probably correct, although the mechanistic details of its formation remain to be elucidated. The radical (**12**) does not appear to be a primary product of radiation damage and possible precursors are $[Me_2NH \rightarrow BH_3]^{+\bullet}$ or $Me_2NH \rightarrow \dot{B}H_2$ (**13**) [which is probably less stable than the isomer (**12**)]. It is also possible that hydrogen atoms, produced initially, could move through the matrix during annealing and abstract hydrogen from the N–H group of $Me_2NH \rightarrow BH_3$. Since it is conceivable that a very small amount of the aminoborane $Me_2\overset{+}{N}{=}\overset{-}{B}H_2$ could accompany the $Me_2NH \rightarrow BH_3$ in all the above experiments or that $Me_2\overset{+}{N}{=}\overset{-}{B}H_2$ could be formed from dimethylamine–borane under the influence of γ-irradiation, we cannot entirely rule out the aminoborane as a precursor of (**12**).

$Me_2\dot{N} \rightarrow BH_3$
(**12**)

$Me_2NH \rightarrow \dot{B}H_2$
(**13**)

The spectrum of (**12**) was also observed down to 175 K during photolysis of DTBP in the presence of $Me_2NH \rightarrow BH_3$ in oxirane–cyclopropane; this radical could now be formed directly by hydrogen abstraction from nitrogen or by intra- or inter-molecular rearrangement of (**13**) following hydrogen abstraction from boron. It is unlikely that an intramolecular 1,2-hydrogen atom shift could take place sufficiently rapidly at such low temperatures and thus we favour an intermolecular pathway. Work is in progress to elucidate the mechanism of formation of (**12**); we note that (**12**) and (**13**) are isoelectronic with the t-butyl and isobutyl radicals, respectively.

Discussion

Ryschkewitsch and his co-workers[15–17] have proposed that certain reactions of amine–boranes proceed by homolytic chain mechanisms which involve intermediate amine–boryl radicals. The reactions of trimethylamine- and 4-methylpyridine–borane with carbon tetrachloride at about 353 K to give the corresponding amine–chloroboranes are markedly accelerated by addition of small quantities of dibenzoyl peroxide and a chain pathway with propagation steps as shown in equations (15) and (16) was suggested.[15] Similar, but more rapid, reactions take

$$Cl_3C^{\bullet} + R_3N \rightarrow BH_3 \longrightarrow Cl_3CH + R_3N \rightarrow \dot{B}H_2 \qquad (15)$$

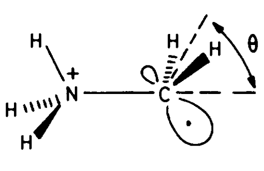
$$R_3N \rightarrow \dot{B}H_2 + Cl_4C \longrightarrow R_3N \rightarrow BH_2Cl + Cl_3C^{\bullet} \qquad (16)$$

place with Cl_3CBr to give exclusively the bromoborane adduct from 4-methylpyridine-borane, but a 2:3 mixture of $Me_3N \rightarrow BH_2Cl$ and $Me_3N \rightarrow BH_2Br$ results from trimethylamine–borane. Analogous mechanisms were proposed for the *B*-chlorination of amine–boranes by chlorodimethylamine,[17] antimony pentachloride,[16] and sulphuryl chloride.[16]

Our results show that t-butoxyl radicals abstract hydrogen very rapidly from amine–boranes, since with $Et_3N \rightarrow BH_3$ in the presence of a molar excess of THF co-solvent there was no evidence for competing hydrogen abstraction from this reactive[18] ether.† Although there is a clear need for reliable kinetic and thermodynamic data in this field, it seems likely that the B–H bonds in $R_3N \rightarrow BH_3$ are somewhat weaker than the corresponding C–H bonds in $R_3C–CH_3$.[19] Furthermore, polar effects will be important since the *B*-hydrogen atoms are more electron rich than those in an analogous CH_3 group and thus charge transfer to the electrophilic t-butoxyl radical, as illustrated by structures (**14a** and **b**), should impart greater stability to the transition state for hydrogen abstraction from $R_3N \rightarrow BH_3$.

$$\underset{\textbf{(14a)}}{R_3\overset{+}{N}{-}\overset{-}{B}H_2{-}H\ {}^{\bullet}OBu^t} \longleftrightarrow \underset{\textbf{(14b)}}{R_3\overset{+}{N}{-}BH_2\ H^{\bullet}\ \overset{-}{O}Bu^t}$$

The magnitude and temperature dependence of the e.s.r. parameters for the borane radical anion $H_3B^{-\bullet}$ indicate a planar equilibrium geometry,[20–22] although out-of-plane bending probably requires less input of energy than does the corresponding deformation of the isoelectronic $H_3C^{\bullet}$.[23] The extent of any deviation from planarity at the radical centre induced by replacement of H with a different substituent is likely to be greater for $H_3B^{-\bullet}$ than for $H_3C^{\bullet}$. Significantly different coupling constants have been reported for the methyleneammonium radical cation $H_3\overset{+}{N}{-}\dot{C}H_2$ in aqueous solution[24] or trapped in a single crystal of α-glycine[25] and it has been concluded[25,26] that the isolated radical is pyramidal at carbon, as shown in (**15**), but that the planar structure is very close in



(15)

energy and this could result in the observed matrix dependence of the e.s.r. spectrum. The value of θ obtained from recent *ab initio* molecular orbital (MO) calculations[27] was 21.7°.

Comparison of the splitting constants for $H_3B^{-\bullet}$ [a(3H) 15.2, $a(^{11}B)$ 19.9 G at 253 K][22] with those for (**1**) demonstrates clearly that the boron centre is non-planar in the amine–boryl radicals. The B 2*s* contribution[28] to the SOMO is 2.8% for $H_3B^{-\bullet}$ but *ca.* 7% for (**1**). The magnitude of the α-proton splitting for the latter is smaller than for $H_3B^{-\bullet}$, implying the presence of an appreciable positive contribution to $a(H_\alpha)$ for (**1**) which acts to offset the negative contribution arising from spin

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* Claxton *et al.* apparently obtained $Me_3N \rightarrow BD_3$ contaminated with $Me_2NH \rightarrow BD_3$ or $Me_2ND \rightarrow BD_3$ from the reaction of trimethylamine hydrochloride with sodium borodeuteride.[13] In our hands, $Me_3N \rightarrow BH_3$ prepared in this way from $NaBH_4$ did not contain $Me_2NH \rightarrow BH_3$ and gave only (**1**; R = Me) after γ-irradiation.

† Deuterium abstraction from $Et_3N \rightarrow BD_3$ does, however, compete with hydrogen abstraction from THF co-solvent.

polarisation. Because of the 'excess charge effect',[29,30] the (negative) α-proton splitting for a *planar* $R_3N\rightarrow\dot{B}H_2$ could well be *larger* than that for the negatively charged $H_3B^{-\bullet}$. The α-proton splitting for the neopentyl radical $Me_3C{-}\dot{C}H_2$ is 21.4 G,[31] which is in accord with an effectively planar geometry at C_α.

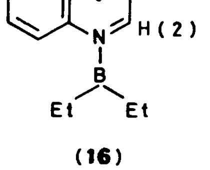
The splittings for (**1**; R = Me) are similar for the radical trapped in polycrystalline $Me_3N\rightarrow BH_3$ or in polar solvents, suggesting that the radical centre is less easily deformed than that in $R_3\overset{+}{N}{-}\dot{C}H_2$.

The coupling constants for (**1**) vary only slightly with temperature or as a result of replacement of H with D at the radical centre. Changes of opposite sign in the splittings would be predicted for planar and strongly pyramidal geometries [32,33] and possibly our measurements were made in the temperature region where little net effect would be noticed [*cf.*[34] the small temperature dependence of $a(^{13}C_\alpha)$ for t-butyl between 160 and 300 K].

The pyramidal equilibrium geometry of (**1**) probably results from a number of inter-related causes; attempts to account for the geometries of carbon-centred radicals have not always been particularly convincing. On the basis of the simple ideas put forward by Pauling[35] replacement of H in $H_3B^{-\bullet}$ by the much more electronegative $R_3\overset{+}{N}$ group should result in a significantly more pyramidal radical centre, because of hybridisation changes in the bond to boron and in the SOMO. In addition to this σ-inductive effect, Dewar[36] has recently drawn attention to the part played by σ-conjugative interactions in determining radical geometry and, on the basis of such effects, replacement of H by $R_3\overset{+}{N}$ should also result in pyramidalisation. In addition, torsional and steric effects may also be important in determining the structure of (**1**), as they appear to be for t-butyl.[37]

In marked contrast, the radical centre in a phosphine–boryl radical $R_3P\rightarrow\dot{B}H_2$ appears to be effectively planar[1] and we have proposed that a stabilising interaction between the B $2p_\pi$ orbital is maximised in the planar structure.[1] For $R_3N\rightarrow\dot{B}H_2$, the R_3N group π* orbital will be higher in energy and such a stabilising interaction should be much smaller than for $R_3P\rightarrow\dot{B}H_2$. Furthermore, interaction between the doubly occupied R_3N group π orbital and the unpaired electron could be *destabilising*[3,38] and, as such, would be relieved by pyramidalisation at boron. A related explanation has been given for the difference in geometry (pyramidal and planar, respectively) of the ylides $R_3\overset{+}{N}{-}\overset{-}{C}H_2$ and $R_3\overset{+}{P} = \overset{-}{C}H_2$.[39]

Köster *et al.*[40–42] have reported a number of e.s.r. spectra, showing splittings from more than one boron nucleus, which they attribute to pyridine or quinoline complexes of di-organoboryl radicals associated to various extents in solution. However, we do not consider that the structures of these persistent radicals can be regarded as established unequivocally. According to Köster *et al.* the radical (**16**)* appears to be monomeric in benzene solution and it was claimed[41] that a remarkably large 1:1 doublet splitting of 14 G from a single proton identified[42] as H(2) was discernible in the e.s.r. spectrum.



(**16**)

(**17**)

More recently, Schlüter and Berndt[43] have reported that reduction of $Bu^t_2BB(CH_2Bu^t)Bu^t$ or $Bu^t(Bu^tCH_2)BB(CH_2Bu^t)Bu^t$ in the presence of 4-t-butylpyridine gives a persistent radical identified as (**17**). The e.s.r. parameters reported for (**17**) are more reasonable and further investigation of such species, which are isoelectronic with benzylic radicals, would be worthwhile.

Self-reaction of Amine–Boryls.—Like the isoelectronic carbon-centred radicals,[8] the amine–boryls undergo self-reaction at close to the diffusion-controlled rate in solution. For the tertiary amine–boryls (**1**), disproportionation is not possible and presumably decay occurs by B–B coupling to give a bis(amine) complex of diborane(4).

Reactions with Alkyl Halides.—The amine–boryl (**1**; R = Et) abstracts halogen rapidly from alkyl bromides and less readily from alkyl chlorides. In this sense, its reactivity is much greater than that of an alkyl radical and comparable with that of a trialkylsilyl radical.[44] The amine–boryls thus exhibit 'metalloidal' properties and are rather more reactive than the phosphine–boryls which do not abstract chlorine from simple alkyl chlorides, as judged by e.s.r. spectroscopy.[1]

Probably both thermodynamic and polar factors are responsible for the higher reactivity of $R_3N\rightarrow\dot{B}H_2$ compared with $R_3C{-}\dot{C}H_2$. The bond to halogen is likely to be stronger in $R_3N\rightarrow BH_2Hal$ than in $R_3C{-}CH_2Hal$ and charge transfer to halogen [see (**18a** and **b**)] in the transition state may be substantial (especially for bromides) and will also favour abstraction by the boron-centred radical. The amine–boryl (**1**; R = Et) abstracts bromine from Bu^tBr 1.2 times more rapidly than from Pr^nBr at 246 K; the corresponding relative reactivities towards $H_3B^{-\bullet}$, $B_2H_6^{-\bullet}$, $H_2\dot{B}CN^-$, and $Bu^n_3P\rightarrow\dot{B}H_2$ are 1.2 (203 and 244 K),[22,45] 1.7 (244 K),[45] 5.1 (203 K),[22] and 5.6 (240 K),[1] respectively. The selectivities of (**1**; R = Et) and $H_3B^{-\bullet}$ are both very low and suggest high absolute reactivities, similar to those reported for trialkylsilyl radicals.[44]

$$\underset{\textbf{(18a)}}{R_3\overset{+}{N}{-}\overset{-}{B}H_2{}^{\bullet}\ Hal{-}R} \longleftrightarrow \underset{\textbf{(18b)}}{R_3\overset{+}{N}{-}BH_2\ Hal^-\ R^{\bullet}}$$

Other Radical–Molecule Reactions of (**1**).—Although addition of (**1**; R = Et) to ethylene could not be detected by e.s.r. spectroscopy, addition to the more electron-deficient double bond in trimethyl(vinyl)silane could be. Both $H_3B^{-\bullet}$ and $H_2\dot{B}CN^-$ also add readily to trimethyl(vinyl)silane and the conformation in which the $B{-}C_\beta$ bond eclipses the C_α $2p_\pi$ orbital of the unpaired electron is preferred for all three adducts.[22]

Unlike alkyl radicals, the nucleophilic amine–boryl radicals add readily to MeCN and the splitting constants for the iminyl adduct derived from (**1**; R = Et) are similar to those reported[22] for the corresponding adduct of $H_3B^{-\bullet}$. Silyl,[46] but not alkyl, radicals add readily to alkyl isocyanides under e.s.r. conditions to form imidoyl adducts (**19**) which break down at higher temperatures to give alkyl radicals. Addition also appears to take place with (**1**; R = Et), but the adduct must be very short-lived and only the methyl radical resulting from its fragmentation is detected. Similar behaviour is shown by $H_3B^{-\bullet}$.[22]

$$R_3Si^{\bullet} + R'NC \longrightarrow \underset{\textbf{(19)}}{R'N{=}\dot{C}SiR_3} \longrightarrow R'^{\bullet} + R_3SiCN \qquad (17)$$

β-*Scission of Amine–Boryls.*—Acyclic amine–boryl radicals undergo β-scission much more readily than the isoelectronic alkyl radicals. Whilst only $Bu^{t\bullet}$ is detectable by e.s.r. spectroscopy when $Bu^tNMe_2\rightarrow\dot{B}H_2$ is generated at 200 K, no evidence for β-scission of its organic counterpart $Bu^tCMe_2{-}\dot{C}H_2$ was

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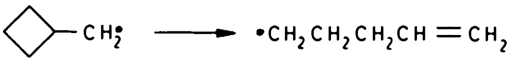
* The structure shown is as drawn by Köster *et al.*[41]

found at *ca.* 298 K.[47] The amine–boryls $PhCH_2NMe_2\rightarrow\dot{B}H_2$ and $Pr^i{}_2EtN\rightarrow\dot{B}H_2$ undergo similarly rapid cleavage of the weaker N–C bond in each. Even the relatively strong primary C–N bond in $Et_3N\rightarrow\dot{B}H_2$ undergoes cleavage at a detectable rate (*k ca.* 10^2—10^3 s^{-1}) at about 270 K. If it is assumed that the rate coefficient for abstraction of bromine from ethyl bromide is independent of the nature of the amine–boryl radical, the relative rates of β-scission (Table 4) increase as the strength of the rupturing C–N bond decreases.

The aziridine- and azetidine–boryl radicals undergo extremely rapid β-scission, presumably because of the angle strain relieved by ring opening. Insufficient strain is present in the five-membered ring system of *N*-methylpyrrolidine–boryl to induce its β-scission at a detectable rate. The more rapid β-scission of amine–boryls, compared with the isoelectronic alkyls, can be clearly seen for azetidine–boryl, which undergoes ring opening much more readily than cyclobutylmethyl. The activation energy for ring opening of the latter radical [equation (18)] is 50 kJ mol^{-1} and the pentenyl radical is only detectable under e.s.r. conditions above *ca.* 250 K.[48]


(18)

We propose that β-scission of an amine–boryl is much more favourable thermodynamically than β-scission of a comparable alkyl radical, and that this is reflected in a lower activation energy for cleavage of the former. The enthalpies of atomisation of (**20**) and (**21**) may be expressed as sums of bond energy terms[49] (*E*) and, assuming that the same values of *E*(C–H), *E*(C–X), and *E*(Y–H) apply to both (**20**) and (**21**), equations (20) and (21) may be derived.* Taking $\Delta H^{\circ}_{at}(Me^{\bullet})$ to be 1 223 kJ mol^{-1},[51] we calculate ΔH°_{19} and $[E(X{=}Y) - E(X{-}Y)]$ to be +111 and +256 kJ mol^{-1}, respectively, when X = Y = C; the former value is to be compared with +112 kJ mol^{-1} calculated directly from the enthalpies of formation[51] of reactants and products.

$$\underset{(\mathbf{20})}{Me_3X\text{–}\dot{Y}H_2} \longrightarrow Me^{\bullet} + \underset{(\mathbf{21})}{Me_2X{=}YH_2} \qquad (19)$$

$$\Delta H^{\circ}_{19} = [\Delta H^{\circ}_{at}(\mathbf{20}) - \Delta H^{\circ}_{at}(\mathbf{21})] - \Delta H^{\circ}_{at}(Me^{\bullet}) \qquad (20)$$

$$[\Delta H^{\circ}_{at}(\mathbf{20}) - \Delta H^{\circ}_{at}(\mathbf{21})] = 3E(C\text{–}H) + E(C\text{–}X) - [E(X{=}Y) - E(X\text{–}Y)] \qquad (21)$$

Ab initio MO calculations[9] yield an enthalpy of hydrogenation for $H_2\overset{+}{N}{=}\overset{-}{B}H_2$ [equation (22)] of +18.5 kJ mol^{-1}, in remarkable agreement with the value (+18.7 kJ mol^{-1}) obtained by semi-empirical (MNDO) calculations.[10] Using this calculated value in conjunction with equation (23) we estimate ΔH°_{19} and $[E(X{=}Y) - E(X{-}Y)]$ to be −41 and +363 kJ mol^{-1}, respectively, when X = N and Y = B.

$$H_2\overset{+}{N}{=}\overset{-}{B}H_2 + H_2 \longrightarrow H_3N\rightarrow BH_3 \qquad (22)$$

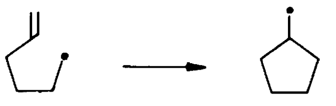
$$[E(\overset{+}{N}{=}\overset{-}{B}) - E(N\rightarrow B)] = \Delta H^{\circ}_{22} - \Delta H^{\circ}_{at}(H_2) + E(N\text{–}H) + E(B\text{–}H) \qquad (23)$$

Hence, β-scission of the neopentyl radical (**20**; X = Y = C) is *endothermic* by 111 kJ mol^{-1}, while loss of methyl from trimethylamine-boryl (**20**; X = N, Y = B) is *exothermic* by 41 kJ mol^{-1}. The large difference of 152 kJ mol^{-1} is due mainly to the much larger value of $[E(X{=}Y) - E(X{-}Y)]$ when X = N and Y = B and partly to the smaller value of *E*(C–N) compared with *E*(C–C).

We have also carried out semi-empirical MO calculations at the MNDO level[52] to obtain estimates of ΔH°_{19}; β-scission of (**20**; X = N, Y = B) was found to be more favourable than that of (**20**; X = Y = C) by 268 kJ mol^{-1}.† This result is unrealistically large, but the calculations do serve to confirm the foregoing conclusions.

The regioselective ring opening of the *cis*- and *trans*-isomers of 2-methylaziridine–boryl parallels closely the result obtained with the isoelectronic 2-methylcyclopropylmethyl radicals;[12] in particular, the *trans*-isomers of both radicals undergo ring opening to give predominantly the thermodynamically less stable primary carbon-centred radical. Our rationalisation[4] of the kinetically controlled product distribution obtained from the amine–boryls follows closely that proposed to account for the regioselective ring cleavage of the carbon analogues[12,53,54] and therefore need only be summarised here. For the *trans*-isomer, the optimum transition state geometry for ring opening should be achieved when the axis of the SOMO eclipses the bond undergoing rupture. In the absence of steric constraints, the unsubstituted C–N bond should be cleaved preferentially leading to the primary radical, since the antibonding σ orbital associated with this bond will be lower in energy, and thus more closely matched with the energy of the SOMO, than the other σ* C–N orbital. However, in the *cis*-isomer steric interference between the methyl and $\dot{B}H_2$ substituents hinders adoption of the transition state leading to the primary radical, but not that which leads to the secondary radical, and the latter is now the major product. These arguments can also be framed in terms of 'polar effects' which operate in the transition states.[55]

Cyclisation of But-3-enylamine-Boryls.—Cyclisation of the hex-5-enyl radical to cyclopentylmethyl [equation (24)] is one of the best known homolytic rearrangements[56] and one for which reliable activation parameters are available[57] [$\log_{10}(A/s^{-1})$ = 10.37 ± 0.32, E_a = 28.7 ± 1.8 kJ mol^{-1}]. The rate coefficient for 1,5-*exo*-cyclisation is *ca.* 15 s^{-1} at 163 K and 2.2 × 10^5 s^{-1} at 298 K, when *endo*-cyclisation to give the more stable cyclohexyl radical is about 72 times slower.[58] The 2,2-dimethylhex-5-enyl radical (**22**) undergoes 1,5-*exo*-cyclisation about 10 times more rapidly than its unsubstituted parent at 353 K[59] and with a higher regioselectivity (k_{exo}/k_{endo} > 100). The increased rate of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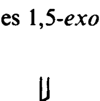
(**22**)

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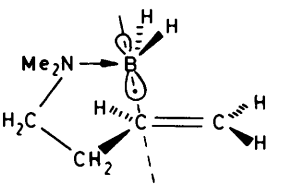
* Bond energy terms taken from the literature are *E*(C–H) 414, *E*(B–H) 389, *E*(N–H) 391, *E*(C–C) 348, *E*(C–N) 303, and *E*(C=C) 604 kJ mol^{-1}.[49,50]

† Unrestricted[52a] and restricted[52] Hartree–Fock calculations were carried out for radicals and closed-shell molecules, respectively. Geometries were optimised for the 'all staggered' (C_s) conformations of (**20**) and for the planar (C_{2v}) structures[52b] of (**21**). The geometry at the radical centre in (**20**; X = Y = C) was close to planar whilst that in (**20**; X = N, Y = B) was strongly pyramidal; the calculated out-of-plane angles corresponding to θ in (**15**) were 2° for (**20**; X = Y = C) and 47° for (**20**; X = N, Y = B). The enthalpies of formation (kJ mol^{-1}) obtained were (**20**; X = Y = C) +19.8; (**20**; X = N, Y = B) +213, (**21**; X = Y = C) −8.6,[52b] (**21**; X = N, Y = B) −82.9, and $Me^{\bullet}$ +103.[52a]

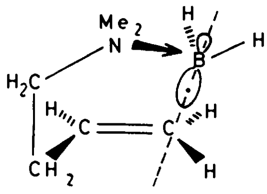
cyclisation may be attributed to the Thorpe–Ingold or '*gem*-dialkyl' effect.[59,60]

As judged by e.s.r. spectroscopy, the but-3-enylamine–boryl (**9**; R = H) also undergoes regioselective 1,5-*exo*-cyclisation to give (**10**) with a rate coefficient which must be at least as great as that for cyclisation of its isoelectronic analogue (**22**) under the same conditions. Since the sizes of boron, carbon, and nitrogen atoms are similar, it seems likely that (**10**; R = H) will be *less stable* than the six-membered ring isomer (**11**). The 1,5-*exo*-cyclisation mode would be expected to be even more favoured for (**9**; R = Me), and the six-membered cyclic species is now probably the less stable isomer.

The kinetic preference for 1,5-*exo*-cyclisation of the but-3-enylamine–boryl (**9**; R = H) may be understood in terms of stereoelectronic effects, by making use of arguments similar to those put forward previously to account for 1,5-*exo*-cyclisation of the hex-5-enyl radical. The preferred direction of approach of the radical centre to the double bond is thought to be perpendicular to the plane of this bond and in the plane containing the olefinic carbon atoms, such that the axis of the SOMO is directed along the line of the new bond being formed.[56] Of the two transition states (**23**) and (**24**) the former will be less strained and lower in energy than the latter which would lead to the six-membered ring system.

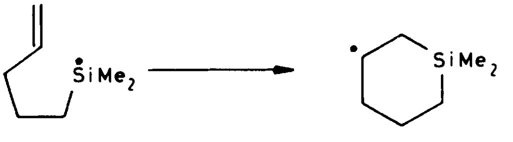


(**23**)



(**24**)

As already noted, amine–boryls resemble silyl radicals in some respects, but this similarity does not extend to cyclisation of hex-5-enyl analogues. Thus, *endo*-cyclisation of (**25**) is the favoured mode of ring closure, probably because the longer C–Si bonds make the transition state for *exo*-cyclisation more difficult to achieve.[58,61] It was also suggested that the pyramidal radical centre in (**25**) further militates against the *exo*-transition state and leads to reduced strain in that for *endo*-cyclisation.[58] We note that the radical centre in amine–boryls is also non-planar, as indicated in (**23**) and (**24**), although it is probably less pyramidal and more flexible than that in a silyl radical.



(**25**)

(**25**)

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, for the detection of transient photochemically generated free radicals, and for determination of their decay kinetics have been described previously.[1,5,7b,22] The light source was an Osram HBO-500 W/2 mercury discharge lamp; after focussing with two 10 cm focal length quartz lenses and passage through an aqueous $NiSO_4$–$CoSO_4$ filter solution, the light incident on the sample was mainly in the wavelength range 240—340 nm.

g-Factors and hyperfine splitting constants were computed from the measured microwave frequency and line positions, the latter determined using an n.m.r. gaussmeter and corrected for the field difference between the sample and the n.m.r. probe using the pyrene radical anion (*g* 2.002 71) as standard.[62] Usually, best-fit spectroscopic parameters were obtained using Preston's program ESRLSQ which employs an exact solution of the isotropic Hamiltonian and an iterative least-squares fitting procedure.[63]

γ-Irradiation.—Polycrystalline samples of the amine–boranes were sealed in evacuated Suprasil quartz tubes (3 mm o.d., 2 mm i.d.). The samples were immersed in liquid nitrogen and positioned *ca.* 50 cm from a 3 000 Ci ^{60}Co source for 2—4 h.

Materials.—N.m.r. spectra (C_6D_6 solvent) were obtained with a Varian XL-200 instrument, with tetramethylsilane internal standard (^{1}H, ^{13}C) or $BF_3{\cdot}Et_2O$ external standard (^{11}B). Where stated, purification by high-performance liquid chromatography (h.p.l.c.) was carried out on Partisil 5 silica gel using light petroleum (b.p. 40—60 °C)–ethyl acetate (55:45 v/v) as eluant. Preparation and handling of amine–boranes were conducted under dry nitrogen or argon.

N-Methylaziridine was prepared as described by Bergmann and Kaluszyner.[64] Perdeuteriotrimethylamine was prepared by pyrolysis of ethyltris(trideuteriomethyl)ammonium deuterioxide according to the method of Tanaka *et al.*[65] and was converted into the deuteriochloride by passage into an excess of DCl in D_2O followed by removal of the excess and drying by pumping under reduced pressure.

N,N-*Dimethylbut-*3-*enylamine* was prepared by a modification of the published method.[66] 4-Bromobut-2-ene (20 g) was added dropwise with stirring to an excess of anhydrous dimethylamine (170 g) maintained at 0 °C. After stirring for a further 2 h at 0 °C, pentane (30 ml) was added and the mixture was left to warm to room temperature overnight, during which time the excess of dimethylamine evaporated. The residual slurry was filtered, the solid washed on the sinter with pentane (10 ml), and the combined filtrate subjected to fractional distillation. The fraction boiling between 87 and 94 °C at atmospheric pressure was redistilled to yield the pure *amine* (7.0 g; b.p. 87—89 °C at 756 Torr).

N,N-*Dimethyl-*4-*methylpent-*3-*enylamine* (6.4 g; b.p. 32—33 °C at 6 Torr) was prepared in a similar way from 2-methyl-5-bromopent-2-ene (20 g) and dimethylamine (170 g). The ^{13}C n.m.r. spectrum showed δ 17.8 (q, CH_3C), 25.9 (q, CH_3C), 27.2 (t, $CH_2C{=}C$), 45.5 (q, Me_2N), 60.0 (t, CH_2N), 123.1 (d, $CH{=}CMe_2$), and 131.7 p.p.m. (s, $Me_2C{=}CH$).

Triethylamine–borane and di-isopropylethylamine–borane were commercial products (Aldrich) and were redistilled before use. Commercial trimethylamine–borane (Aldrich or Pfaltz and Bauer) was purified by h.p.l.c. (see Results section).

Amine–boranes containing the normal isotopic distribution of boron were prepared by passing a small excess of diborane, generated from $NaBH_4$ and $BF_3{\cdot}Me_2O$ in bis-(2-methoxyethyl) ether,[67] into a stirred solution of the amine in THF at 0 °C. After removal of the solvent, the complex was isolated by distillation or recrystallisation and some were further purified by h.p.l.c. Known amine–boranes derived from Me_3N,[14] $PhCH_2NMe_2$,[68] Bu^tNMe_2,[69] *N*-methylaziridine,[70] *N*-methylpyrrolidine,[71] azetidine,[72] and tetramethylhydrazine[73] were prepared in this way. Amine–boranes containing 97.5 atom % ^{11}B were prepared by a similar method, except that the diborane was generated by addition of isotopically enriched $BF_3{\cdot}Me_2O$ (Centronic Ltd.) to a stirred slurry of lithium aluminium hydride in 1,2-dimethoxyethane (DME).[74] Amine complexes of trideuterioborane were prepared from B_2D_6 obtained from the reaction of $LiAlD_4$ with $BF_3{\cdot}Me_2O$ in DME.

Aziridine–borane was prepared by the method of Akerfeldt *et* *al.*[75] Perdeuteriotrimethylamine–borane was prepared from $(CD_3)_3N{\cdot}DCl$ as described for the unlabelled compound;[14] its ^1H n.m.r. spectrum showed only the absorption from the BH_3 group.

The new amine–boranes used in this work and those which have not been adequately characterised previously are described below.

Dimethyl-t-butylamine–borane[69] was recrystallised from hexane (m.p. 169—170 °C) (Found: C, 62.7; H, 15.8; N, 12.2. $C_6H_{18}BN$ requires C, 62.7; H, 15.8; N, 12.2%). The ^{11}B n.m.r. spectrum showed δ −11.1 p.p.m. (q, $^1J_{BH}$ 99 Hz).

N-*Methylpyrrolidine–borane*[71] was purified by distillation, b.p. 57—59 °C at 1.4 Torr (Found: C, 60.4; H, 14.2; N, 14.1. $C_5H_{14}BN$ requires C, 60.7; H, 14.3; N, 14.2%). The ^{11}B n.m.r. spectrum showed δ −9.6 p.p.m. (q, $^1J_{BH}$ 98 Hz).

Azetidine–borane[72] was a crystalline solid which was purified by h.p.l.c. (m.p. 53—55 °C) (Found: C, 50.8; H, 14.3; N, 19.9. $C_3H_{10}BN$ requires C, 50.8; H, 14.2; N, 19.8%). The n.m.r. spectrum showed: ^{11}B, δ −15.8 p.p.m. (q, $^1J_{BH}$ 94 Hz); ^{13}C, δ 16.8 (t, C-3), 53.5 p.p.m. (t, C-2).

cis- *and* trans-2-*Methylaziridine–boranes* (**5**) were prepared as an isomeric mixture by the reaction of 2-methylaziridine with $BH_3{\cdot}THF$ at 0 °C. The ^{11}B n.m.r. spectrum of the mixture showed two binomial quartets at δ −15.5 ($^1J_{BH}$ 97 Hz) and −19.9 p.p.m. ($^1J_{BH}$ 96 Hz) and integration of the proton-decoupled spectra gave the relative intensities as 1.4:1, respectively. When a benzene solution of this mixture (with or without an added molar equivalent of 2-methylaziridine) was heated for 3 h at 100 °C in a sealed tube, the intensity of the lower-field resonance increased at the expense of the other peak such that the final relative integrals were 4.5:1 at 20 °C. We attribute these changes to equilibration of *cis*-(**5**) with the more stable *trans*-(**5**), since it is very likely that the relative stabilities of the *cis*- and *trans*-isomers of (**5**) are similar to those of the isoelectronic 1,2-dimethylcyclopropane.[76] The ^{13}C chemical shifts for *trans*-1,2-dimethylcyclopropane are all greater than those of the corresponding carbons in the *cis*-isomer.[77] The ^{13}C [15.8 (q), 34.9 (t), and 37.4 (d)] and ^{11}B (−15.5) chemical shifts for the isomer of (**5**) assigned the *trans*-structure are all greater (less negative for ^{11}B) than those [^{13}C; 11.2 (q), 33.8 (t), 32.5 (d); ^{11}B, −19.9] assigned to corresponding nuclei in the *cis*-isomer. These differences between *cis*- and *trans*-isomers are similar in magnitude for the cyclopropane and amine–borane, thus providing further support for our structural assignment.

The ^1H n.m.r. spectra of (**5**) were complex and did not provide further evidence to aid the assignment of configuration. At 400 MHz (Bruker) the *trans*-isomer showed δ 0.77 (d, *J* 6.0 Hz, CH_3), 1.40 (t, *J* 6.5 Hz, C*H*H), 1.68 (t, *J* 5.9 Hz, CH*H*), 1.95 (septet, *J ca.* 5.8 Hz, C*H*Me), 2.28 (q, *J* 97 Hz, BH_3), and 2.54 (br s, NH), and the *cis*-isomer showed δ 1.12 (d, *J* 6.0 Hz, CH_3), 1.22 (t, *J* 5.7 Hz, C*H*H), 1.72 (t, *J* 7.6 Hz, CH*H*), 1.82 (septet, *J ca.* 6.5 Hz, C*H*Me), 1.98 (q, *J* 93 Hz, BH_3), and 2.89 (br s, NH).

The geometrical isomers of (**5**) could be separated completely by h.p.l.c., although subsequent distillation of the *trans*-isomer (b.p. 64—65 °C at 0.05 Torr) was accompanied by *ca.* 6% conversion into the *cis*-isomer. The distillate was analytically pure (Found: C, 51.0; H, 14.1; N, 19.9. $C_3H_{10}BN$ requires C, 50.8; H, 14.2; N, 19.8%).

N,N-*Dimethylbut*-3-*enylamine–Borane* (**8**; R = H). Diborane, generated by addition of $BF_3{\cdot}Me_2O$ (4.6 g, 0.040 mol) in bis-(2-methoxyethyl) ether (15 ml) to a stirred solution of sodium borohydride (1.25 g, 0.033 mol) in the same solvent (15 ml), was carried in a slow stream of dry argon into a stirred solution of the amine (4.0 g, 0.040 mol) in THF (70 ml) maintained at −78 °C. After addition of the $BF_3{\cdot}Me_2O$ during 30 min, the diborane generator was heated at 60—70 °C for 1 h to complete reaction. The THF was removed under reduced pressure and the residual *amine–borane** was purified by distillation; b.p. 58—60 °C at 2 Torr (Found: C, 63.9; H, 14.3; N, 12.4. $C_6H_{16}BN$ requires C, 63.8; H, 14.3; N, 12.4%). The n.m.r. spectrum showed: ^{11}B, δ −8.9 (q, $^1J_{BH}$ 98 Hz); ^1H, δ 2.08 (s, Me_2N), 2.11 (q, $^1J_{BH}$ 97 Hz, BH_3), 2.20 (t, *J* 8.4 Hz, CH_2N), 2.42 (m, CH_2C), 4.9 (m, $C{=}CH_2$), and 5.44 (m, $C{=}CHCH_2$).

N,N-*Dimethyl*-4-*methylpent*-3-*enylamine–borane* (**8**; R = Me), b.p. 59—61 °C at 0.05 Torr, was prepared in a similar way from the appropriate amine (Found: C, 68.1; H, 14.2; N, 10.2. $C_8H_{20}BN$ requires C, 68.1; H, 14.3; N, 9.9%). The n.m.r. spectrum showed: ^{11}B, δ −9.0 (q, $^1J_{BH}$ 97 Hz); ^1H, δ 1.48 (s, MeC), 1.59 (s, MeC), 2.13 (q, $^1J_{BH}$ 97 Hz, BH_3), 2.23 (t, *J* 8.0 Hz, CH_2N), 2.38 (m, $CH_2C{=}C$), and 4.84 (t, *J* 6.7 Hz, $C{=}CH$).

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