Homolytic Reactions of Ligated Boranes. Part 11.[1] Electron Spin Resonance Studies of Radicals Derived from Primary Amine–Boranes

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Photochemically generated t-butoxyl radicals react with the primary amine–boranes $RNH_2{\rightarrow}BH_3$ (R = Me or Bu^t) to form, initially, the nucleophilic amine–boryl radical $RNH_2{\rightarrow}\dot{B}H_2$, which subsequently abstracts hydrogen from the parent amine–borane to give the more stable isomeric aminyl–borane radical $R\dot{N}H{\rightarrow}BH_3$. The amine–boryl radicals can be intercepted by alkyl bromides or chlorides or by nitriles, with which they react by halogen-atom abstraction or by addition to the CN group to give iminyl radicals, respectively. The e.s.r. spectra of the aminyl–borane radicals show the presence of extensive hyperconjugative delocalisation of the unpaired electron onto the BH_3 group [*a*(3BH) 64–66 G]. Monoalkylaminyl–borane radicals react readily with alkenes, with arenes, and with conjugated or cumulated dienes to transfer a β-hydrogen atom from boron to give alkyl, cyclohexadienyl, or allyl radicals, respectively. Hydrogen atom transfer to alkenes from the electrophilic $Me\dot{N}H{\rightarrow}BH_3$ takes place with high regioselectivity to give the more stable alkyl radical when two adducts are possible; the rate of transfer increases as the ionisation potential of the alkene decreases along the series $CH_2{=}CH_2 < MeCH{=}CH_2 < Me_2C{=}CH_2 \approx Me_2C{=}CHMe < Me_2C{=}CMe_2$. The absolute rate coefficient for reduction of propene by $Me\dot{N}H{\rightarrow}BH_3$ to give the isopropyl radical was determined to be *ca.* 2×10^3 dm^3 mol^{-1} s^{-1} at 282 K. Competition experiments have been carried out to determine the relative rates of the various reactions undergone by $RNH_2{\rightarrow}\dot{B}H_2$ and $R\dot{N}H{\rightarrow}BH_3$. The results are interpreted with the aid of *ab initio* molecular-orbital calculations at the 6-31G** level for $RNH_2{\rightarrow}\dot{B}H_2$, $R\dot{N}H{\rightarrow}BH_3$, $RNH_2{\rightarrow}BH_3$, and $RNH{\rightrightarrows}BH_2$ (R = H or Me), together with similar calculations for the isoelectronic organic counterparts in which the NB moiety is replaced by a CC grouping.

The amine–boranes $R_nNH_{3-n}{\rightarrow}BH_3$ (n = 0–3) are isoelectronic analogues of the alkanes $R_nCH_{3-n}CH_3$. Electrophilic t-butoxyl radicals rapidly abstract electron-rich hydrogen atoms from the BH_3 group of a tertiary amine–borane to form the corresponding amine-boryl radical $R_3N{\rightarrow}\dot{B}H_2$.[2] Secondary amine–boranes react in a similar fashion to give initially $R_2NH{\rightarrow}\dot{B}H_2$ as the kinetically-controlled product, but this nucleophilic radical then rapidly abstracts the electron-deficient hydrogen atom from nitrogen in the parent amine–borane to yield the aminyl–borane radical $R_2\dot{N}{\rightarrow}BH_3$, which is calculated to be the more stable isomer.[3]

We have now extended these studies to include the primary amine–boranes $RNH_2{\rightarrow}BH_3$, the simplest example of which is methylamine–borane (1) an isoelectronic analogue of propane. Propane itself reacts with t-butoxyl radicals[4] to give mainly

$$\underset{(1)}{MeNH_2{\rightarrow}BH_3} \qquad \underset{(2)}{Bu^tNH_2{\rightarrow}BH_3}$$

the isopropyl radical (3) in preference to the n-propyl radical (4), which is less stable than (3) by 7–15 kJ mol^{-1} according to recent estimates.[5]

$$Bu^tO^\bullet + MeCH_2Me \begin{cases} \rightarrow \underset{(3)}{Me\dot{C}HMe} + Bu^tOH & \text{(1a)} \\ \rightarrow \underset{(4)}{MeCH_2\dot{C}H_2} + Bu^tOH & \text{(1b)} \end{cases}$$

In the present paper we describe e.s.r. spectroscopic studies of the structures and reactions of the radicals derived from (1) and from t-butylamine–borane (2) by hydrogen atom abstraction. A preliminary report of part of this work has appeared already.[6]

Results and Discussion

E.s.r. spectra were recorded during continuous u.v. irradiation of static liquid samples positioned in the microwave cavity of the spectrometer.[7] The usual primary source of radicals was di-t-butyl peroxide [DTBP, equation (2)]. The natural abundances of ^{11}B (I = 3/2) and ^{10}B (I = 3) are 80.2 and 19.8%,

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

respectively, and in order to facilitate interpretation of complex e.s.r. spectra, samples of (1) and (2) containing 97.5 atom% ^{11}B were often used ($\gamma^{10}B/\gamma^{11}B$ = 0.335).

The spectrum shown in Figure 1(*a*) and (*c*) was obtained during u.v. irradiation of DTBP (15% v/v) and (1) (1.7 mol dm^{-3}) in t-butyl alcohol–t-pentyl alcohol (3:1 v/v) solvent at 283 K (t-pentyl = Pe^t). This spectrum can be computer simulated [Figure 1(*b*) and (*d*)] on the basis of *a*(3 H) 63.9, *a*(3 H′) 24.1, *a*(1 H) 19.4, *a*(1 ^{14}N) 15.4, and *a*(1 ^{11}B) 13.3 G and is not in accord with expectation[2,8] for the methylamine-boryl radical (5). However, these splitting constants are very

$$\underset{(5)}{MeNH_2{\rightarrow}\dot{B}H_2} \qquad \underset{(6)}{Me\dot{N}H{\rightarrow}BH_3}$$

reasonable[3] for the methylaminyl-borane radical (6), an isoelectronic counterpart of the isopropyl radical (3). The larger three-proton splitting is assigned[3] to the BH_3 group and its magnitude shows that hyperconjugative delocalisation of the unpaired electron from nitrogen is much more efficient than similar delocalisation onto the *N*-methyl group. This is presumably a consequence of the lower electronegativity of boron

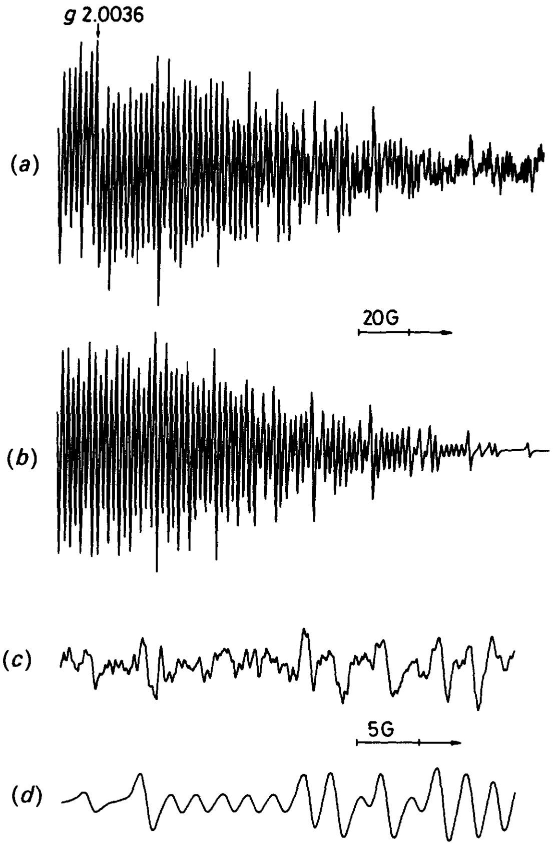

Figure 1. (*a*) High-field half of the e.s.r. spectrum of the methylaminyl–borane radical (**6**) (97.5 atom% ^{11}B) in Bu^{t}OH–Pe^{t}OH (3:1 v/v) at 283 K. (*b*) Computer simulation of (*a*) using the following splitting constants: 63.87 (3 H), 24.05 (3 H), 19.44 (1 H), 13.28 (1 ^{11}B), and 15.36 G (1 ^{14}N). The linewidth ($\Delta B_{\mathrm{p-p}}$) is 1.0 G and the lineshape is 80% Lorentzian (20% Gaussian). (*c*) Low-field region of the spectrum of (**6**) beginning with line 4 at 282 K. (*d*) Computer simulation of (*c*) using the same data as for (*b*).

compared with carbon, which leads to a closer energetic match between the N-2p$_{\pi}$ orbital and the filled π group orbital of an attached MH$_3$ substituent when M = B than when M = C. Assuming free rotation about the N→B bond in (**6**) and the usual 'cos^2 θ' dependence of β-proton coupling upon dihedral angle,[9] the proton of an 'eclipsed' B–H bond would give rise to a splitting of *ca.* 128 G, corresponding to 25% H-1s contribution to the SOMO.[10] In fact, aminyl–borane radicals may legitimately be regarded as derivatives of the perboryl radical[11] H$_4$B$^{\bullet}$ [*a*(2 H) 107 and *a*(2 H′) 7 G], in which one of the two strongly coupled protons has been replaced by an amino group, accompanied by distortion of the remaining BH$_3$ moiety.

When n-propyl bromide (1.0 mol dm^{-3}) was present along with methylamine–borane (1.1 mol dm^{-3}) and DTBP, only the spectrum of Pr$^{n\bullet}$ was observed at 282 K and that of (**6**) was not detected. Since dialkylaminyl–borane radicals do not appear to react with alkyl bromides to give alkyl radicals at significant rates under similar conditions,[3] it is the methylamine–boryl radical (**5**) which must be intercepted by propyl bromide [equation (3)]. This interpretation was supported by

$$\mathrm{MeNH_2{\rightarrow}\dot{B}H_2 + Pr^nBr \xrightarrow{k_3} Pr^{n\bullet} + MeNH_2{\rightarrow}BH_2Br} \quad (3)$$

$$\mathrm{MeNH_2{\rightarrow}\dot{B}H_2 + Bu^tBr \xrightarrow{k_4} Bu^{t\bullet} + MeNH_2{\rightarrow}BH_2Br} \quad (4)$$

competition experiments using mixtures of n-propyl and t-butyl bromides, which showed that the relative rates of generation of Pr$^{n\bullet}$ and Bu$^{t\bullet}$ were typical of their formation *via* halogen abstraction by an amine–boryl radical.[3] Making the usual assumptions,[12] the value of (k_4/k_3) was found to be 2.0 at 282 K in Bu^{t}OH–Pe^{t}OH (3:1 v/v) as the solvent. When oxirane was the solvent the value of (k_4/k_3) was similar at 282 K (2.2), but it decreased with decreasing temperature to 0.77 at 188 K. Methylamine–borane is known[13] to associate in solution, but the similar values of (k_4/k_3) obtained in protic and aprotic solvents suggest that any association of (**5**) with its parent amine–borane does not influence its selectivity appreciably. The inversion of the relative reactivities of Bu^{t}Br and Pr^{n}Br which takes place at low temperature was unexpected; it is probably related to the very rapid nature of the bromine abstraction, to the different steric requirements of tertiary and primary halides, and to the large degree of electron transfer from the ligated boryl moiety to the alkyl halide in the transition state.

These observations leave little doubt that, as for the secondary amine–boranes,[3] methylamine–borane (**1**) reacts with t-butoxyl radicals to give initially an amine–boryl radical, and that this subsequently abstracts hydrogen from (**1**) to give the thermodynamically more stable aminyl–borane radical (**6**), which is the isomer detected by e.s.r. spectroscopy in the absence of alkyl bromide [equations (5) and (6)].

$$\mathrm{Bu^tO^{\bullet} + MeNH_2{\rightarrow}BH_3 \longrightarrow \underset{\textbf{(5)}}{MeNH_2{\rightarrow}\dot{B}H_2} + Bu^tOH} \quad (5)$$

$$\mathrm{MeNH_2{\rightarrow}\dot{B}H_2 + MeNH_2{\rightarrow}BH_3 \xrightarrow{k_6} \underset{\textbf{(6)}}{Me\dot{N}H{\rightarrow}BH_3} + MeNH_2{\rightarrow}BH_3} \quad (6)$$

$$\mathrm{MeNH_2{\rightarrow}\dot{B}H_2 + Pr^nCl \xrightarrow{k_7} Pr^{n\bullet} + MeNH_2{\rightarrow}BH_2Cl} \quad (7)$$

n-Propyl chloride is less reactive towards halogen abstraction by ligated boryl radicals than is the bromide[2,3,7,14,15] and it proved possible to determine the value of (k_6/k_7) by competition experiments.[3] Thus, in Bu^{t}OH–Pe^{t}OH (1:1 v/v) solvent at 282 K with [Pr^{n}Cl] fixed at 0.96 mol dm^{-3}, the value of [(**6**)]/[Pr$^{n\bullet}$] (obtained by computer simulation of spectra and extrapolated to zero irradiation time) was measured as a function of [(**1**)] (0.47–1.57 mol dm^{-3}). If equal rate coefficients are assumed for the radical–radical reactions removing Pr$^{n\bullet}$ and (**6**),[12] it can be shown that equation (8) should hold and, indeed, all values of (k_6/k_7) thus obtained fell in the range 1.7 ± 0.3.

$$(k_6/k_7) = [(\mathbf{6})][\mathrm{Pr^nCl}]/[\mathrm{Pr^{n\bullet}}][(\mathbf{1})] \quad (8)$$

This result provides strong support for the proposal that (**6**) is formed indirectly by reaction (6) when t-butoxyl radicals are generated in the presence of methylamine–borane. It also indicates that the aminyl–borane (**6**) does not react with n-propyl chloride to produce propyl radicals under the experimental conditions.

Photolysis of dibutanoyl peroxide (0.8 mol dm^{-3}) [equation (9)] in the presence of methylamine–borane (1.57 mol dm^{-3}) in Bu^{t}OH–Pe^{t}OH (1:1 v/v) at 282 K afforded only a strong spectrum of the n-propyl radical and (**6**) was not detected {[(**6**)]/[Pr$^{n\bullet}$] < 0.1}, showing that the alkyl radical does not

$$\mathrm{Pr^nC(O)OOC(O)Pr^n \xrightarrow{h\nu} 2Pr^{n\bullet} + 2CO_2} \quad (9)$$

react with the amine–borane to generate either (**5**) or (**6**) under these experimental conditions.

In previous work[3] with dimethylamine–borane it was shown that reaction (10) is extremely rapid at low temperatures and n-propyl bromide was needed to intercept the amine–boryl radical [equation (11)]. At 173 K in oxirane–cyclopropane (2.5:1 v/v)

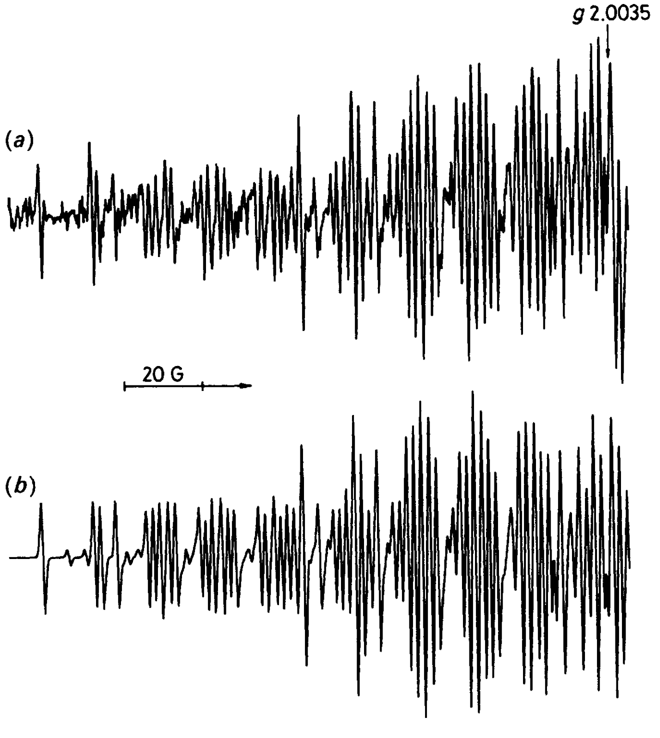

Figure 2. (*a*) Low-field half of the e.s.r. spectrum of the [$^2H_9$]-t-butylaminyl–borane radical (**8**) containing ^{11}B and ^{10}B in natural abundance in cyclopropane–oxirane (1:1 v/v) at 225 K. (*b*) Computer simulation of (*a*) using the following splitting constants: 65.90 (3 H), 19.10 (1 H), 15.10 ($1^{14}N$), 13.48 ($1^{11}B$) [4.52 ($1^{10}B$)]. The linewidth is 1.0 G and the lineshape is Gaussian.

$$Me_2NH{\rightarrow}\dot{B}H_2 + Me_2NH{\rightarrow}BH_3 \xrightarrow{k_{10}} Me_2\dot{N}{\rightarrow}BH_3 + Me_2NH{\rightarrow}BH_3 \quad (10)$$

$$Me_2NH{\rightarrow}\dot{B}H_2 + Pr^nBr \xrightarrow{k_{11}} Pr^{n\cdot} + Me_2NH{\rightarrow}BH_2Br \quad (11)$$

the value of (k_{10}/k_{11}) is 0.7 ± 0.1.[3] It is reasonable that the rate of halogen atom abstraction from a given alkyl halide should be similar for primary and secondary amine–boryl radicals and, if we assume that the value of (k_{10}/k_{11}) will be little different at 282 K, it follows that reaction (10) is much faster than reaction (6) under the same conditions. This would be expected since progressive methylation at nitrogen will lead to a weakening of the N–H bond in the $Me_nNH_{3-n}{\rightarrow}BH_3$ along the series $n = 0 < 1 < 2$, while having little effect on the strength of the B–H bond[3] (see later for relevant MO calculations).*

It was not possible to observe the e.s.r. spectrum of the amine–boryl radical (**5**) at low temperatures in oxirane solvent, even when relatively small concentrations of (**1**) (*ca.* 0.5 mol dm^{-3}) were present. However, the spectrum of (**5**) could be difficult to detect because of the high multiplicity and relatively broad lines which would be expected.[2,8]

t-Butylamine–Borane (**2**).—This compound is commercially available for use as a versatile reducing agent,[16] although the mechanisms by which it reacts have usually not been explored.

When a Bu^tOH–Pe^tOH (3:1 v/v) solution containing (**2**) (1.3 mol dm^{-3}) and DTBP (20% v/v) was irradiated with u.v. light at 282 K only the e.s.r. spectrum of the t-butyl radical was detected. Our previous work[2,17] has shown that secondary and tertiary amine–boryl radicals with an *N*-t-alkyl substituent undergo rapid β-scission at this temperature and the t-butyl radical is presumably formed by similar cleavage of the t-butylamine-boryl radical (**7**) [equation (13)]. When this experiment was repeated in oxirane–cyclopropane (1:1 v/v), the spectrum of $Bu^{t\cdot}$ became progressively weaker as the temperature was lowered and was replaced by a poorly defined spectrum which we were later able to assign to the t-butylaminyl–borane radical (**8**). At lower temperatures when [(**2**)] is ⩾*ca.* 0.5 mol dm^{-3}, the bimolecular isomerisation reaction (14) is evidently able to compete effectively with the unimolecular β-scission, reaction (13). The poor quality of the spectrum of (**8**) is a consequence of its high multiplicity, which in turn arises because of the significant splitting from the γ-protons of the *N*-t-butyl group. This problem was overcome by using [$^2H_9$]-t-butylamine-borane (containing ^{11}B and ^{10}B in natural abundance) and, at 225 K, the e.s.r. spectrum shown in Figure 2(*a*) was obtained. This spectrum can be computer simulated using a(3 H) 65.9, a(1 H) 19.1, $a(1^{14}N)$ 15.1, and $a(1^{11}B)$ 13.5 G, and undoubtedly arises from $C_4D_9\dot{N}H{\rightarrow}BH_3$; the contribution from the ^{10}B-containing radical [$a(^{10}B)$ 4.5 G] is clearly evident. The spectroscopic parameters for the aminyl–boranes (**6**) and (**8**) are compared with those of the isoelectronic alkyl radicals and of other related species in Table 1.

$$\underset{(\mathbf{2})}{Bu^tO^{\cdot} + Bu^tNH_2{\rightarrow}BH_3} \longrightarrow \underset{(\mathbf{7})}{Bu^tNH_2{\rightarrow}\dot{B}H_2} + Bu^tOH \quad (12)$$

$$Bu^tNH_2{\rightarrow}\dot{B}H_2 \longrightarrow Bu^{t\cdot} + H_2N{\rightleftharpoons}BH_2 \quad (13)$$

$$\underset{(\mathbf{7})}{Bu^tNH_2{\rightarrow}\dot{B}H_2} + Bu^tNH_2{\rightarrow}BH_3 \longrightarrow \underset{(\mathbf{8})}{Bu^t\dot{N}H{\rightarrow}BH_3} + Bu^tNH_2{\rightarrow}BH_3 \quad (14)$$

As with methylamine–borane, the e.s.r. spectrum of the appropriate alkyl radical was observed in the presence of an alkyl bromide, indicating that the amine–boryl radical (**7**) was abstracting a halogen atom. Competition experiments showed that Bu^tBr was 0.70 times as reactive as Pr^nBr towards (**7**) at 186 K in oxirane. The selectivity of (**7**) is thus very similar to that of (**5**) under the same conditions.

Reactions of Primary Amine–Boryl Radicals with Nitriles.—We have reported previously[2,7] that tertiary amine–boryl radicals add readily to nitriles to give iminyl radicals of the type

$$R_3N{\rightarrow}\dot{B}H_2 + R'CN \longrightarrow \underset{(\mathbf{9})}{R_3N{\rightarrow}BH_2C(R'){=}N^{\cdot}} \quad (15)$$

(**9**). The ammonia–boryl radical ($H_3N{\rightarrow}\dot{B}H_2$) undergoes similar addition to nitriles,[18] but under comparable conditions secondary amine–boryl radicals could not be trapped before they underwent isomerisation to dialkylaminyl–borane radicals by abstracting hydrogen from the parent amine–borane.[3] Analogous isomerisation [equations (6) and (14)] is slower for primary amine–boryl radicals, and these species could be intercepted by a variety of nitriles present in moderate concentrations.

The e.s.r. spectrum of the iminyl adduct (**10**; R = 1-Ad) was observed during u.v. irradiation at 282 K of a Bu^tOH–Pe^tOH

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* Analogous trends are, of course, shown by the isoelectronic hydrocarbons $Me_nCH_{3-n}CH_3$.[5]

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

Radical	Solvent[a]	T/K	g Factor[b]	Hyperfine splittings (G) $a(^{14}N)$	$a(^{11}B)$	Others
$Me\dot{N}(H)\rightarrow BH_3$ (**6**)	A	283	2.0036	15.4	13.3	63.9 (3 B*H*), 24.1 (3 C*H*), 19.4 (N*H*)
$Bu^t\dot{N}(H)\rightarrow BH_3$ (**8**)[c]	B	225	2.0035	15.1	13.5	65.9 (3 B*H*), 19.1 (N*H*)
$Me_2N\rightarrow\dot{B}H_3$[d]	C	175	2.0039	17.4	11.6	46.4 (3 B*H*) 23.2 (6 C*H*)
$Me_3N\rightarrow\dot{B}H_2$[e]	D	280	2.0022	1.4	51.3	9.6 (2 B*H*), 1.4 (9 C*H*)
$Me\dot{C}(H)Me$[f]	E	273	2.0027	41.5[g]	—	24.7 (6 C*H*), 21.9 (1 C*H*)
$Bu^t\dot{C}(H)Me$[h]	E	236	2.0027	—	—	25.1 (3 C*H*), 21.8 (1 C*H*), 0.56 (9 C*H*)
$Me\dot{N}(H)\rightarrow O$[i,j]	F	298	—	13.8	—	13.8 (3 C*H*), 13.8 (1 N*H*)
$Bu^t\dot{N}(H)\rightarrow O$[j,k]	G	298	2.0060	13.0	—	10.6 (N*H*)

[a] A = Bu^{t}OH–Pe^{t}OH (3:1 v/v), B = cyclopropane–oxirane (1:1 v/v), C = cyclopropane–oxirane (1:2.5 v/v), D = Bu^{t}OH–Me_2O (4:1 v/v), E = cyclopropane, F = MeOH, G = toluene. [b] Corrected for second-order effects. [c] Data for the [$^2H_9$]Bu^t-containing radical. [d] Data from ref. 3. [e] Data from ref. 2. [f] Data from D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975. [g] ^{13}C-Splitting. [h] This work; generated by u.v. irradiation of DTBP (20% v/v) and Bu^tCH_2Me (20% v/v) in cyclopropane. [i] Data from J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654. [j] The radicals are nitroxides; the BH_3 group is isoelectronic with an oxygen atom. [k] Data from Th. A. J. W. Wajer, A. Mackor, and Th. J. DeBoer, *Tetrahedron*, 1969, **25**, 175.

Table 2. Iminyl radicals $L\rightarrow BH_2C(R){=}N^\bullet$ derived from addition of $L\rightarrow\dot{B}H_2$ to nitriles.

L	R	Solvent[a]	T/K	g Factor	Hyperfine splittings (G) $a(^{14}N)$	$a(^{11}B)$	Others
$MeNH_2$	Me	A	282	2.0025	9.5	22.5	2.7 (3 H)[b]
	CD_3	A	281	2.0025	9.5	22.6	—
	1-Ad	A	283	2.0027	9.4	22.2	—
Bu^tNH_2	CD_3	A	282	2.0025	9.4	22.5	—
	Me	B	234	2.0025	9.3	22.4	2.8 (3 H)
	Et	B	236	2.0027	9.5	22.4	3.0 (2 H)
	Pr^i	B	234	2.0027	9.3	22.5	3.1 (1 H)
	Bu^t	B	223	2.0026	9.3	20.9	—
	1-Ad	B	234	2.0027	9.3	21.6	13.7 (^{13}C)[c]

[a] A = Bu^{t}OH–Pe^{t}OH (3:1 v/v), B = cyclopropane–oxirane (1:1 v/v). [b] Poorly resolved triplet splitting of *ca.* 0.6 G from the BH_2 protons also present. [c] Data for the iminyl radical from 1-Ad^{13}CN.

(3:1 v/v) solution containing methylamine–borane (1.2 mol dm^{-3}), DTBP (20% v/v), and 1-cyanoadamantane (*ca.* 0.5 mol dm^{-3}) [equation (16)]. No spectrum of the aminyl–borane

$$MeNH_2\rightarrow\dot{B}H_2 + RCN \longrightarrow \underset{(\mathbf{10})}{MeNH_2\rightarrow BH_2C(R){=}N^\bullet} \quad (16)$$

radical (**6**) was detected and evidently reaction (16) is faster than the isomerisation reaction (6) under these conditions. With acetonitrile (*ca.* 1 mol dm^{-3}), the spectrum of the adduct (**10**; R = Me) was observed and again (**6**) was not detected; the spectroscopic parameters for all iminyl radicals are gathered in Table 2. In addition to a splitting of 2.7 G [absent for (**10**; R = CD_3)] from the *C*-methyl protons, (**10**; R = Me) showed a poorly resolved splitting of *ca.* 0.6 G from the protons attached to boron. This last splitting was absent (as were the lines due to the ^{10}B-containing radical) when $MeNH_2\rightarrow{}^{11}BD_3$ was used, resulting in a much more intense spectrum.

With t-butyl or isopropyl cyanide (1.5 mol dm^{-3}) in Bu^{t}OH–Pe^{t}OH solvent at 282 K no iminyl adducts were detected, but spectra of the alkyl radicals produced by their β-scission[18] were observed [equation (17; R = Pr^i or Bu^t)].

$$MeNH_2\rightarrow BH_2C(R){=}N^\bullet \longrightarrow R^\bullet + MeNH_2\rightarrow BH_2CN \quad (17)$$

In similar experiments with t-butylamine–borane (**2**) (1.2 mol dm^{-3}) at 282 K, the amine-boryl radical was trapped by CD_3CN (1.2 mol dm^{-3}) before it underwent β-scission and only (**11**; R = CD_3) was detected. Since (**2**) is more soluble than (**1**),

$$Bu^tNH_2\rightarrow\dot{B}H_2 + RCN \longrightarrow \underset{(\mathbf{11})}{Bu^tNH_2\rightarrow BH_2C(R){=}N^\bullet} \quad (18)$$

the former was used to investigate the addition of primary amine-boryl radicals to nitriles over a range of temperature in oxirane–cyclopropane (1:1 v/v). With methyl, ethyl, isopropyl, t-butyl, or 1-adamantyl cyanides at 234 K, only the iminyl adduct (**11**) was detected (see Table 2), but as the temperature was increased the spectrum of $R^\bullet$ produced by its β-scission also became evident for some of the nitriles [*cf.* equation (17)]. As judged from the relative intensities of the e.s.r. spectra of (**11**) and $R^\bullet$, the ease of β-scission increased along the series R = CH_3, 1-Ad $\ll$ Et < Pr^i < Bu^t, in parallel with the decreasing strength of the R–C bond. At *ca.* 245 K only (**11**; R = Pr^i) was detected, but the spectrum of $Bu^{t\bullet}$ was present alongside that of (**11**; R = Bu^t). At *ca.* 255 K the spectrum of $Pr^{i\bullet}$ became apparent and above *ca.* 275 K only this radical was detected. The spectrum of (**11**; R = 1-Ad) is shown in Figure 3; no β-scission of this radical or of (**11**; R = Me) was evident up to 306 K.

Molecular-orbital Calculations.—Because of the paucity of experimental thermodynamic data for amine–boranes, aminoboranes, and for the derived radicals within the framework of which to discuss their chemistry, we have carried out a number of *ab initio* molecular-orbital calculations for these species using the GAUSSIAN 82 series of programs.[19,20] In addition to the molecules containing nitrogen–boron bonds, the isoelectronic carbon–carbon bonded analogues were investigated for comparative purposes.

Equilibrium geometries were optimised, within any imposed symmetry constraints, at the Hartree–Fock level using the standard 6-31G** basis set; the spin-restricted (RHF) and spin-unrestricted (UHF) methods were used for closed-shell molecules and radicals, respectively. The nature of each stationary point was determined by computing the set of normal harmonic vibrational frequencies and zero-point vibrational energies (ZPVEs) were evaluated. Electron-correlation energies were calculated for the Hartree–Fock equilibrium geometries using Møller–Plesset perturbation theory taken to third-order (MP3); core electrons were included. Total energies (E_0) and reaction energies (ΔE_0) at 0 K were obtained using equation (19), in which the ZPVE is scaled by a factor of 0.9 to allow for the overestimation of vibrational frequencies at this level of theory.[20] The values of ΔE_0 will differ only slightly from the corresponding reaction enthalpies at 298 K.[21] Calculated energies, dipole moments, and ionisation potentials are given in Table 3 and the equilibrium geometries are shown in Figure 4. It should be emphasised that these energies and geometries refer to isolated molecules in the gas phase. Many of the boron-containing species investigated, particularly those incorporating a formal N→B dative single bond, possess substantial dipole moments and consequently molecular association and solvation effects should be taken into account when relating the calculations to experimental observations made in condensed phases. It is such charge separation together with differences in bond strengths which are basically responsible for the variety of structural and chemical differences observed when a CC linkage in an organic molecule is replaced by an NB moiety.

$$E_0 = E(\text{MP3/6-31G**//HF/6-31G**}) + 0.9\text{ZPVE} \quad (19)$$

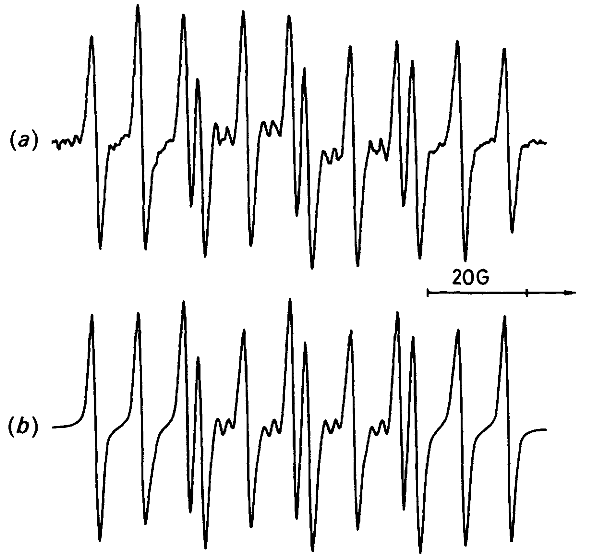

Figure 3. (*a*) E.s.r. spectrum of the iminyl radical (**11**; R = 1-Ad) containing ^{11}B and ^{10}B in natural abundance in cyclopropane–oxirane (1:1 v/v) at 237 K. (*b*) Computer simulation of (*a*) using the parameters given in Table 2; the linewidth is 1.6 G and the lineshape is 65% Lorentzian (35% Gaussian).

Table 3. Properties calculated using GAUSSIAN 82 in conjunction with the 6-13G** basis set.

Molecule	Imposed symmetry	Total energy/Hartree[a] U(R)HF	Total energy/Hartree[a] MP3(full)	ZPVE[b]/ (kJ mol^{-1})	E_0 Hartree[a]	$\mu_{calc.}(\mu_{expt.})$/D	$E_{i\,calc.}$[c]($E_{i\,expt.}$) eV
$H_3N{\rightarrow}\dot{B}H_2$[d]	C_s	−81.986 170	−82.290 719	162.9	−82.234 878	5.69	6.63
$H_2\dot{N}{\rightarrow}BH_3$[d]	C_s	−81.990 908	−82.289 623	148.0	−82.238 890	5.15	11.09
$H_2N{\rightleftarrows}BH_2$[e]	C_{2v}	−81.499 210	−81.794 793	133.4	−81.749 065	1.81(1.84)[f]	11.79(11.36)[g]
$H_3N{\rightarrow}BH_3$[h]	C_{3v}	−82.624 973	−82.959 423	194.0	−82.892 921	5.54(5.22)[i]	11.16(9.44)[j]
$MeNH_2{\rightarrow}\dot{B}H_2$ (**5**)	C_s	−121.017 405	−121.481 343	244.4	−121.397 565	5.65	6.50
$Me\dot{N}H{\rightarrow}BH_3$ (**6**)[k]	C_1	−121.031 500	−121.488 204	229.1	−121.409 670	5.52	10.81
$MeNH{\rightleftarrows}BH_2$	C_s	−120.527 022	−120.982 004	213.7	−120.908 749	1.83	10.85
$MeNH_2{\rightarrow}BH_3$ (**1**)[l]	C_s	−121.655 887	−122.149 583	275.2	−122.055 247	5.52(5.19)[m]	11.02(9.66)[j]
$H_3C{-}\dot{C}H_2$[n]	C_s	−78.605 526	−78.914 623	165.2	−78.857 994	0.21	9.55(8.51)[o]
$H_2C{=}CH_2$	D_{2h}	−78.038 841	−78.349 913	143.1	−78.300 859	0	10.16(10.51)[p]
$H_3C{-}CH_3$	D_{3d}	−79.238 235	−79.583 016	208.0	−79.511 715	0	13.24(12.1)[p]
$MeCH_2{-}\dot{C}H_2$ (**4**)[q]	C_s	−117.642 816	−118.111 411	246.5	−118.026 913	0.21	9.50(8.1)[r]
$Me\dot{C}H{-}Me$ (**3**)[s]	C_s	−117.646 908	−118.115 933	245.9	−118.031 640	0.17	8.85(7.69)[o]
$MeCH{=}CH_2$	C_s	−117.081 614	−117.551 847	223.1	−117.475 370	0.32(0.37)[t]	9.71(9.73)[p]
$MeCH_2Me$	C_{2v}	−118.276 159	−118.780 683	288.4	−118.681 822	0.06(0.08)[t]	12.91(11.5)[p]
Me•	D_{3h}	−39.564 457	−39.715 003	81.0	−39.687 237	0	10.43(9.84)[o]
H•		−0.498 233	−0.498 233	0	−0.498 233	0	13.56(13.60)[t]

[a] 1 Hartree = 2 625.5 kJ mol^{-1}. [b] Zero-point vibrational energy computed at the U(R)HF/6-31G** level; all vibrational frequencies were positive for every structure. [c] Calculated vertical ionisation potential is the negative of the HOMO energy for a closed-shell molecule or the negative of the energy of the most loosely bound α electron for a radical. [d] See also reference 3. [e] Compare J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 3402. [f] Gas phase; M. Sugie, M. Takeo, and C. Matsumura, *Chem. Phys. Lett.*, 1979, **64**, 573. [g] N. P. C. Westwood and N. H. Werstiuk, *J. Am. Chem. Soc.*, 1986, **108**, 891. [h] Compare J. S. Binkley and L. R. Thorne, *J. Chem. Phys.*, 1983, **79**, 2932. [i] Gas phase; R. D. Suenram and L. R. Thorne, *Chem. Phys. Lett.*, 1981, **78**, 157. [j] D. R. Lloyd and N. Lynaugh, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 947. [k] The BH_3 and CH_3 rotations appear to be essentially free. No significant gain in stability was achieved when the constraint on the dihedral angles H^{1}BN* and H^{4}CN* was removed and the optimisation begun from very different starting points. [l] Compare R. Bonaccorsi, P. Palla, R. Cimiraglia, and J. Tomasi, *Int. J. Quantum Chem.*, 1983, **24**, 307. [m] In benzene solution; H. Nöth and H. Beyer, *Chem. Ber.*, 1960, **93**, 939. [n] Compare J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1978, **68**, 4276. [o] F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 4067. [p] G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213. [q] Compare J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1979, **71**, 2095; T. A. Claxton and A. M. Graham, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 121. [r] F. A. Elder, C. Giese, B. Steiner, and M. Inghram, *J. Chem. Phys.*, 1962, **36**, 3292. [s] Compare J. Pacansky and M. Yoshimine, *J. Phys. Chem.*, 1987, **91**, 1024. [t] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 55th edn., CRC Press, Cleveland, 1974.

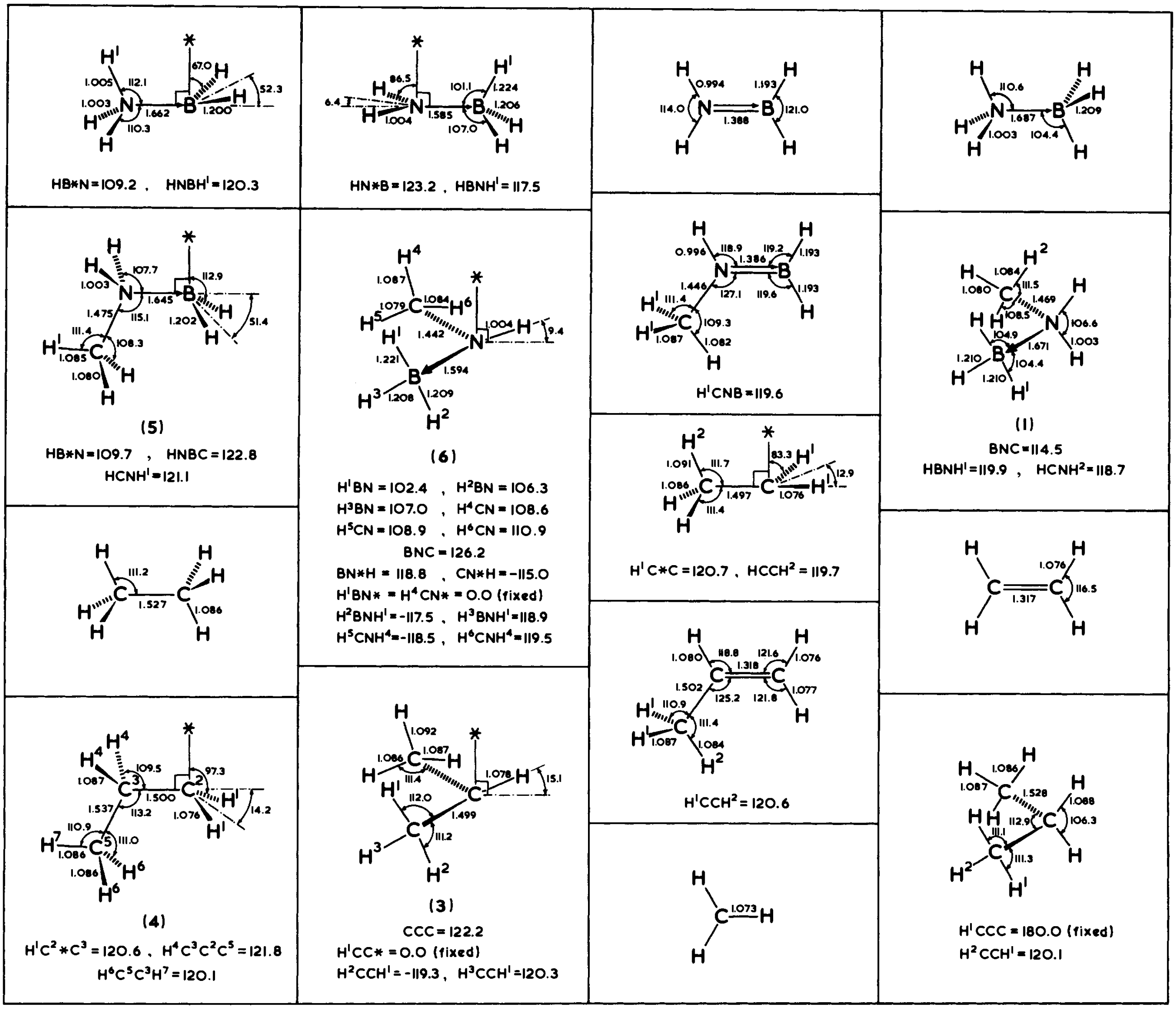

Figure 4. Optimised geometries for the molecules listed in Table 3. Bond lengths are given in Å and bond angles in degrees; ABCD is the dihedral angle between the planes ABC and BCD. The asterisk respresents a dummy atom used to help define molecular geometry. In structure (**6**) the dummy atom is positioned such that the N* vector is perpendicular to the CNB plane. In structure (**1**) the NH_2 plane is constrained to be perpendicular to the BNC plane and H^1 and H^2 are constrained to lie in the BNC plane.

As reported previously,[2,3] both e.s.r. experimental data and calculations show that amine-boryl radicals are pyramidal at the boron centre, although the vibrationally averaged structures observed in solution by e.s.r. spectroscopy are appreciably less pyramidal than the computed gas-phase minima. Experiment and theory concur that aminyl-boranes are much closer to planar at the nitrogen radical centre. The β-B–H bonds which eclipse the N-$2p_\pi$ orbital in the aminyl- and methylaminyl-borane radicals are appreciably longer than the other two B–H bonds, suggesting the existence of a significant hyperconjugative interaction between the eclipsing bond and the unpaired electron. For the methylaminyl-borane radical (**6**) in solution this hyperconjugative interaction is evidently stronger than for the computed structure in the gas phase, since the average values of $a(3BH)$ calculated for the equilibrium geometry by the *ab initio* (+29.6 G) and INDO[22] (+29.2 G) methods are much smaller than the observed value [(+)63.9 G]. The remaining calculated splittings [*ab initio*, INDO, and observed (in G)] are $a(^{14}N)$ +33.0, +16.9, (+)15.4, $a(^{11}B)$* −14.9, −10.9, (−)13.3, $a(NH)$ −43.9, −19.9, (−)19.4, and $a(3C\bar{H})$ +25.5, +21.7, (+)24.1. The INDO results are in generally good agreement with experiment; the *ab initio* results are, as expected,[23] less good.

The calculated ionisation potentials for the aminyl-boranes $H_2\dot{N}{\rightarrow}BH_3$ and $Me\dot{N}H{\rightarrow}BH_3$ are over 4 eV greater than for the respective isomeric amine-boryls. Amine-boryl radicals are strongly nucleophilic species, while aminyl-boranes must be regarded as much more electrophilic.

The isopropyl radical is calculated to be more stable than n-propyl by 12.4 kJ mol⁻¹, compared with the experimental difference in their standard enthalpies of formation[5] of 7–15 kJ mol⁻¹. The aminyl-borane radical is calculated to be more stable than ammonia-boryl by 10.5 kJ mol⁻¹ and methylation at nitrogen increases the relative stability of the nitrogen-centred isomer such that $Me\dot{N}H{\rightarrow}BH_3$ is now 31.8 kJ mol⁻¹ more stable than $MeNH_2{\rightarrow}\dot{B}H_2$. These results are consistent with the detection by e.s.r. spectroscopy of $H_3N{\rightarrow}\dot{B}H_2$ when $Bu^tO^\bullet$ is generated in the presence of $H_3N{\rightarrow}BH_3$,[8] but of $Me\dot{N}H{\rightarrow}BH_3$ when the alkoxyl radical is generated in the presence of $MeNH_2{\rightarrow}BH_3$.

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* A scaling factor of 720.8 G per ^{11}B-2s electron was used in the INDO calculations.[10]

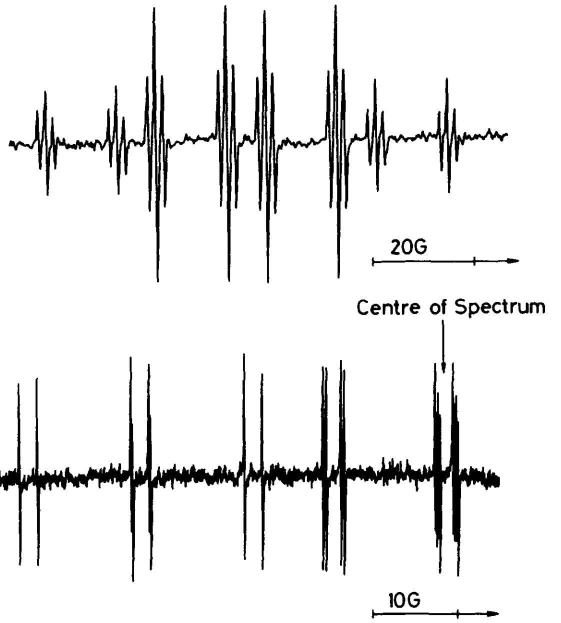

Figure 5. E.s.r. spectra at 282 K in Bu^tOH–Pe^tOH (3:1 v/v) of (*a*) the 1-ethoxyethyl radical (**12**) and (*b*) the oxacylopentenyl radical (**13**).

The strengths of the B–H and N–H bonds in $H_3N\rightarrow BH_3$ and $MeNH_2\rightarrow BH_3$ may be estimated by consideration of the isodesmic reactions (20) and (21). The computed values of

$$CH_3\dot{C}H_2 + H_3N\rightarrow BH_3 \longrightarrow CH_3CH_3 + H_3N\rightarrow\dot{B}H_2 \quad (20)$$

$$CH_3CH_2\dot{C}H_2 + MeNH_2\rightarrow BH_3 \longrightarrow CH_3CH_2CH_3 + MeNH_2\rightarrow\dot{B}H_2 \quad (21)$$

$\Delta E_0(20)$ and $\Delta E_0(21)$ are +11.3 and +7.3 kJ mol^{-1}, respectively, which when combined with $DH^{\circ}(RCH_2\text{–}H)$ for ethane and propane (419.7 and 417.1 kJ mol^{-1}, respectively[5b]) lead to values of $DH^{\circ}(B\text{–}H)$ for $H_3N\rightarrow BH_3$ and $MeNH_2\rightarrow BH_3$ of 431 and 424 kJ mol^{-1}, respectively.* When the relative stabilities of aminyl-borane and amine-boryl radicals are taken into account, the computed values of $DH^{\circ}(N\text{–}H)$ for $H_3N\rightarrow BH_3$ and $MeNH_2\rightarrow BH_3$ are 421 and 392 kJ mol^{-1}, respectively.

Both $H_3N\rightarrow\dot{B}H_2$ and $H_2\dot{N}\rightarrow BH_3$ are calculated to be unstable with respect to $H^{\bullet} + H_2N\overset{\rightharpoonup}{-}BH_2$, by 32.6 and 22.1 kJ mol^{-1}, respectively. The transition states for these β-scissions have been located previously[3] and, at the present level of theory including ZPVEs, the activation energies for unimolecular loss of $H^{\bullet}$ are 73.8 kJ mol^{-1} for $H_3N\rightarrow\dot{B}H_2$ and −4.8 kJ mol^{-1} for $H_2\dot{N}\rightarrow BH_3$. β-Scission of the ammonia-boryl radical, although more favourable thermodynamically, has a much higher activation energy. The activation energy for β-scission of $H_2\dot{N}\rightarrow BH_3$ becomes negative only after inclusion of the correlation corrections for the UHF-optimised structures; it is zero within the limitations of the computational method.

Unimolecular loss of a β-hydrogen atom from $MeNH_2\rightarrow\dot{B}H_2$ is calculated to be exothermic by 24.7 kJ mol^{-1}, while $Me\dot{N}H\rightarrow BH_3$ is slightly more stable (by 7.1 kJ mol^{-1}) than $H^{\bullet} + MeNH\overset{\rightharpoonup}{-}BH_2$. Although the transition states have not been investigated, it seems safe to assume that the activation energy for loss of a β-hydrogen atom from boron in $Me\dot{N}H\rightarrow BH_3$ will be much smaller than for β-cleavage of an N–H bond in $MeNH_2\rightarrow\dot{B}H_2$.

The methylamine-boryl radical (**5**) is calculated to be very unstable (by 101.7 kJ mol^{-1}) with respect to $Me^{\bullet}$ + $H_2N\overset{\rightharpoonup}{-}BH_2$, accounting for the facility with which alkylamine-boryl radicals (including $Bu^tNH_2\rightarrow\dot{B}H_2$) undergo β-scission with loss of an alkyl radical from nitrogen.[2,17]

Reactions of Aminyl-Borane Radicals with Alkenes and with Furan.—The thermodynamic instability of aminyl- borane and amine-boryl radicals with respect to loss of a β-H atom suggests that these species might function as efficient reducing agents by hydrogen-atom transfer to unsaturated substrates. The isoelectronic alkyl radicals are very much more stable with respect to the analogous β-scission and prefer to add to alkenes through C_{α} rather than undergo β-H atom transfer.[6,24]

The β-H atom transfer reactions (22) and (23) are calculated to be exothermic by 174.5 and 145.3 kJ mol^{-1}, respectively. These large exothermicities, coupled with the

$$H_2\dot{N}\rightarrow BH_3 + MeCH{=}CH_2 \longrightarrow Me_2\dot{C}H + H_2N\overset{\rightharpoonup}{-}BH_2 \quad (22)$$

$$Me\dot{N}H\rightarrow BH_3 + MeCH{=}CH_2 \xrightarrow{k_{23}} Me_2\dot{C}H + MeNH\overset{\rightharpoonup}{-}BH_2 \quad (23)$$

availability of a low-energy pathway for β-H atom tansfer as indicated by the effectively zero activation energy calculated for β-scission of $H_2\dot{N}\rightarrow BH_3$ and the very large magnitudes of *a*(3B*H*) for $Me\dot{N}H\rightarrow BH_3$ and $Bu^t\dot{N}H\rightarrow BH_3$, suggest that reactions (22) and (23) might proceed rapidly under mild conditions. Although β-H atom transfer from the isomeric amine-boryl radicals to alkenes is thermodynamically somewhat more favourable, the corresponding indicators point to a less easy pathway.†

When a Bu^tOH–Pe^tOH (3:1 v/v) solution containing methylamine-borane (1–1.5 mol dm^{-3}), DTBP (20% v/v), and propene (0.1–2.9 mol dm^{-3}) was irradiated with u.v. light at 282 K, the e.s.r. spectrum of the methylaminyl-borane radical (**6**) was replaced by that of the isopropyl radical to an extent which increased with the concentration of alkene. There was no evidence for addition of (**5**) or (**6**) to propene and, with alkene concentrations in excess of *ca.* 0.6 mol dm^{-3}, only the isopropyl radical could be detected (see Figure 1 in ref. 6). Even under very forcing instrumental conditions, it was not possible to detect with certainty the spectrum of the n-propyl radical and the value of $[Pr^{i}]/[Pr^{n}]$ must be >30.‡ A wide variety of other alkenes can be reduced to alkyl radicals under similar conditions, the more stable radical being formed with high regioselectivity when two isomers are possible. For example, $Me_2C{=}CH_2$, $Me_2C{=}CHMe$, and $Me_2C{=}CMe_2$ yield $Bu^{t\bullet}$, $Pe^{t\bullet}$, and $Me_2CH\dot{C}Me_2$, respectively; none of the less stable regioisomer was detected from the first two alkenes. β-H-Atom transfer to ethyl vinyl ether and to furan took place readily to give the corresponding α-oxyalkyl radicals (**12**)[26] and (**13**),[27] respectively (see Figure 5). The allylic radical (**13**) has also been generated previously by addition of hydrogen atoms, produced

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* The computed values of ΔE_0 for simple homolytic cleavage of R–H to give $R^{\bullet}$ and $H^{\bullet}$ are 408 (R = Et), 411 (R = Pr^n), and 399 (R = Pr^i) kJ mol^{-1}, in remarkably good agreement with the experimental bond-dissociation enthalpies.[5]

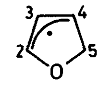
† In contrast with the efficient hyperconjugative spin transfer to the β-BH_3 group which takes place for $R\dot{N}H\rightarrow BH_3$, hyperconjugation is not very efficient for $H_3N\rightarrow\dot{B}H_2$ as evidenced by the small value of *a*(3N*H*) (11.0 G).[8]

‡ Addition of thermalised hydrogen atoms to propene at 77 K, studied by e.s.r. spectroscopy using the rotating cryostat technique, is reported to yield 98% isopropyl and 2% n-propyl radicals.[25]

by radiolysis of water, to furan.[28] When second-order effects[29,30] are taken into account, the spectrum of (**13**) can be satisfactorily analysed in terms of equal splitting of 36.12 G from the two protons attached to C-5. This contrasts with the analysis proposed by Ko *et al.*[27] in which the splitting of *ca.* 0.4 G evident on the central lines has been taken to indicate non-equivalence of the two C-5 protons. The remaining parameters obtained for (**13**) at 282 K are $a(1\ H^{2\ \mathrm{or}\ 4})$ 13.37, $a(1\ H^{4\ \mathrm{or}\ 2})$ 13.17, $a(1\ H^3)$ 2.14 G, and g 2.0032.

$Et O\dot{C}HMe$

(**12**)



(**13**)

In an attempt to investigate β-H-atom transfer to an electron-deficient alkene, we examined trimethyl(vinyl)silane. However, even when the concentration of the silane was low (*ca.* 0.2 mol dm^{-3}) and that of methylamine–borane was high (*ca.* 2.0 mol dm^{-3}), the major spectrum observed was that of the adduct (**14**) [$a(1\ H_\alpha)$ 18.6, $a(2\ H_\beta)$ 18.6, $a(^{11}B)$ 22.3 G, and g 2.0027 at 282 K]. Under these conditions some lines not due to (**14**) could be detected, but these did not appear to be attributable to either $Me_3Si\dot{C}HMe$ or to $Me_3SiCH_2\dot{C}H_2$; they were not present with higher silane and lower amine–borane concentrations. Evidently the nucleophilic amine–boryl radical (**5**) is trapped by the

$$MeNH_2\rightarrow\dot{B}H_2 + Me_3SiCH{=}CH_2 \longrightarrow \underset{(\mathbf{14})}{Me_3Si\dot{C}HCH_2BH_2\leftarrow NH_2Me} \quad (24)$$

electron-deficient alkene before isomerisation to (**6**) can take place; possibly hydrogen-atom transfer is not the major reaction between (**6**) and the vinyl silane. The triethylamine-boryl[2] and triethylsilyl[31] radicals also undergo addition to trimethyl(vinyl)silane.

U.v. irradiation at 282 K of samples containing $MeNH_2\rightarrow BD_3$ (0.5–1.7 mol dm^{-3}), DTBP 20% v/v, and $Me_2C{=}CMe_2$ (1.0–1.6 mol dm^{-3}) in Bu^{t}OH–Pe^{t}OH (3:1 v/v), 2,2,5,5-tetramethyltetrahydrofuran–oxirane (5:1 v/v), or dioxane afforded the e.s.r. spectrum of $Me_2CD\dot{C}Me_2$, although $Me_2CH\dot{C}Me_2$ was also detected. However, the relative concentration of the protiated radical increased, initially rapidly, with the duration of photolysis and extrapolation indicated that $Me_2CD\dot{C}Me_2$ was essentially the only product at zero irradiation time. This result demonstrates that it is the aminyl-borane (**6**) which is the active reducing agent and that the isomeric amine-boryl radical (**5**) is not involved, at least at *ca.* 282 K when the amine–borane concentration is >*ca.* 0.5 mol dm^{-3}. It is noteworthy that no radicals resulting from hydrogen abstraction from $Me_2C{=}CMe_2$ or from oxirane[32,33] were detected in these experiments, testifying to the high rate of H/D abstraction from boron in the amine–borane. A small amount of competitive hydrogen abstraction from dioxane solvent was evident.

An i.r. spectroscopic investigation* showed that protium exchange into $MeNH_2\rightarrow BD_3$ takes place rapidly during u.v. irradiation in the presence of DTBP with or without added alkene. In dioxane solution $MeNH_2\rightarrow BH_3$ gave rise to three resolved absorption bands in the 2 200–2 400 cm^{-1} region, at 2 271, 2 320, and 2 356 cm^{-1}. By analogy with previous assignments for similar compounds, the last peak is ascribed to the BH_3 antisymmetric stretching mode[34] and was used to monitor the concentration of amine–borane by assuming the Beer–Lambert law to hold. The corresponding antisymmetric BD_3 stretching vibration of $MeNH_2\rightarrow BD_3$ gave rise to a band at 1 766 cm^{-1} which was broader than the 2 356 cm^{-1} band for the protiated material. A single very weak absorption band at 2 330 cm^{-1} was also detected in the 2 200–2 400 cm^{-1} region for the deuteriated material and is attributed to the presence of a trace of $MeNH_2\rightarrow BD_2H$, which arises because the primary source of deuterium ($LiAlD_4$) contained only *ca.* 98 atom% D. A series of solutions containing known concentrations of $MeNH_2\rightarrow BD_3$ and 0–50 mol% $MeNH_2\rightarrow BH_3$ were examined and a plot of the optical density ratio (A_{2356}/A_{1766}) against $[MeNH_2\rightarrow BH_3]/[MeNH_2\rightarrow BD_3]$ gave a good straight line of slope 0.87.

Samples containing $MeNH_2\rightarrow BD_3$ were prepared and treated exactly as those used to obtain the e.s.r. spectra, except that their volumes were smaller to ensure that all the solution was positioned inside the microwave cavity and thus received the same dose of u.v. light. After photolysis at 282 K, all volatiles were removed under reduced pressure and the residue (mainly amine–borane) was dissolved in dioxane and examined by i.r. spectroscopy. The recovered amine–borane showed a single band at 2 330 cm^{-1} which was more intense the longer the duration of photolysis; as before, this band is assigned to the BH stretching vibration in $MeNH_2\rightarrow BD_2H$. The peak at 1 766 cm^{-1} was used to monitor the residual $MeNH_2\rightarrow BD_3$ and will also include a contribution from the BD stretch of $MeNH_2\rightarrow BD_2H$.

After 0, 3, 10, and 20 min u.v. irradiation of a Bu^{t}OH–Pe^{t}OH solution containing $MeNH_2\rightarrow BD_3$ (1.4 mol dm^{-3}) and DTBP (20% v/v), the recovered amine–borane showed (A_{2330}/A_{1766}) 0.07, 0.13, 0.29, and 0.60, respectively. Using the same factor (0.87) which relates (A_{2354}/A_{1766}) to $[MeNH_2\rightarrow BH_3]/[MeNH_2\rightarrow BD_3]$, these relative optical densities correspond to values of 0.06, 0.11, 0.25, and 0.52 for $[MeNH_2\rightarrow BD_2H]/[MeNH_2\rightarrow BD_3] + [MeNH_2\rightarrow BD_2H]$ ($\equiv P$). In the presence of $Me_2C{=}CMe_2$ (1.1 mol dm^{-3}), the corresponding values of P were 0.05, 0.06, 0.16, and 0.36 and, in the absence of DTBP, the value of P was unchanged at 0.05 after 0, 10, and 20 min u.v. irradiation, similar to the value (0.04) for untreated $MeNH_2\rightarrow BD_3$ as prepared from 98 atom% D $LiAlD_4$.

Accepting the uncertainties over the extinction coefficients for $MeNH_2\rightarrow BD_2H$ and the presence of reaction products in the recovered amine–borane, these results still show that substantial H/D exchange takes place rapidly under the conditions of the e.s.r. experiments. The smaller extent of isotopic exchange in the presence of alkene suggests that the isomerisation of (**5**) to (**6**) by reaction with amine–borane may be reversible to some extent [equation (25)] under the conditions of the experiment; when alkene is present (**6**) is efficiently trapped by β-H atom transfer.

$$\underset{(\mathbf{5})}{MeNH_2\rightarrow\dot{B}H_2} + MeNH_2\rightarrow BH_3 \rightleftharpoons \underset{(\mathbf{6})}{Me\dot{N}H\rightarrow BH_3} + MeNH_2\rightarrow BH_3 \quad (25)$$

The partial quenching of the spectrum of (**6**) which occurs with low concentrations of propene permits the rate coefficient for the β-H atom transfer reaction (23) to be estimated. If the isopropyl radical is removed only by self-reaction and by cross-reaction with (**6**) and if both these processes have the same (diffusion-controlled)[12] rate coefficient $2k_t$, then equation (26) should hold, in which $R = [Pr^{i\cdot}]/[(\mathbf{6})]$ measured during continuous u.v. irradiation.

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* All i.r. experiments were carried out using ^{11}B-enriched (97.5 atom%) material.

Table 4. Relative rates of hydrogen-atom transfer to alkenes from the methylaminyl–borane radical (**6**) at 282 ± 1 K.

Alkene[a]	Solvent	$k_{\text{rel.}}$	$k_{\text{rel.}}$ (H$^{\bullet}$)[b] at 298 K	Ionisation potential of alkene/eV
MeCH=CH_2	$\text{Bu}^t\text{OH–Pe}^t\text{OH}$ (3:1 v/v)	(1.0)	(1.0)	9.73
$\text{MeCH}_2\text{CH=CH}_2$		1.2	1.03	9.63
$\text{Bu}^t\text{CH}_2\text{CH=CH}_2$		1.0		
$\text{Me}_2\text{C=CH}_2$		3.4	2.52	9.24
cis-MeCH=CHMe		0.5	0.47	9.12
trans-MeCH=CHMe		0.7	0.59	9.12
$\text{Me}_2\text{C=CHMe}$		2.8	1.03	8.68
$\text{Me}_2\text{C=CMe}_2$		4.7	0.84	8.27
EtOCH=CH_2		2.4		9.15[d]
Furan		0.7		8.99[e]
MeCH=CH_2	Dioxane	(1.0)	(1.0)	9.73
$\text{Me}_2\text{C=CH}_2$		3.3	2.52	9.24
$\text{Me}_2\text{C=CHMe}$		2.8	1.03	8.68
$\text{Me}_2\text{C=CMe}_2$		5.5	0.84	8.27

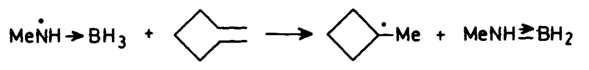
[a] Competition experiments were carried out between propene and every other alkene and between 2-methylpropene and most other alkenes; all results were internally consistent to within the experimental accuracy (±10%). [b] Data from ref. 39. [c] Data from G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213 unless otherwise noted. [d] Data from H. Friege and M. Klessinger, *J. Chem. Res.* (*S*), 1977, 208. [e] Data from P. Linda, G. Marino, and S. Pignataro, *J. Chem. Soc. B*, 1971, 1585.

$$k_{23} = 2k_t(R + 1)[\text{Pr}^i]/[\text{MeCH=CH}_2] \qquad (26)$$

At 282 K in $\text{Bu}^t\text{OH–Pe}^t\text{OH}$ (3:1 v/v), a constant value of $(R + 1)[\text{Pr}^i]/[\text{MeCH=CH}_2]$ $(1.1 \pm 0.05 \times 10^{-6})$ was obtained in three experiments in which $[\text{MeCH=CH}_2]$ was varied between* 0.15 and 0.38 mol dm^{-3}. Taking the value of $2k_t$ to be 2.1×10^9 dm^3 mol^{-1} s^{-1} (the rate coefficient for self-reaction of Pr^i in 3-methylpentan-3-ol at 282 K, extrapolated from the data reported by Lipscher and Fischer[35]), we obtain $k_{23} =$ *ca.* 2×10^3 dm^3 mol^{-1} s^{-1} at 282 K.

Relative rates of β-H atom transfer from (**6**) to a number of alkenes at 282 K were measured in competition experiments, with the usual assumptions[12] to relate stationary-state concentrations of radicals to their relative rates of formation. Selective removal of the product radicals by addition[36] to the pairs of alkenes was shown to be unimportant under the experimental conditions, since relative radical concentrations depended only on the *relative* amounts of alkenes and not on their *total* concentration. The results are summarised in Table 4.

Hydrogen-atom transfer to methylenecyclobutane (*ca.* 1 mol dm^{-3}) at 282 K in $\text{Bu}^t\text{OH–Pe}^t\text{OH}$ (3:1 v/v) afforded an e.s.r. spectrum which we ascribe to the 1-methylcyclobutyl radical (**15**) [$a(4\,\text{H}_\beta)$ 34.4, $a(3\,\text{H}_\beta)$ 23.2, $a(2\,\text{H}_\gamma)$ 1.13 G, and g 2.0027]. In contrast, a similar experiment with methylenecyclopropane afforded the spectrum of the but-3-enyl radical[37] (**16**), presumably formed by hydrogen-atom transfer to the substituted end of the double bond[38] followed by ring opening of the derived cyclopropylmethyl radical, along with lines from an unidentified radical.



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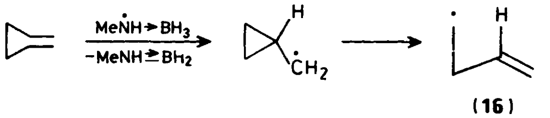

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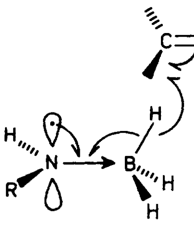
(16)

Ethene is also reduced by the aminyl–borane radical (**6**), although this alkene appears to be relatively unreactive. Thus, generation of (**6**) in the presence of ethane (1.0 mol dm^{-3}, provided all the alkene was in solution) at 282 K in $\text{Bu}^t\text{OH–Pe}^t\text{OH}$ (3:1 v/v), yielded overlapping spectra of the ethyl radical (**6**), and another radical which might possibly be the adduct $\text{MeNH}_2\text{→BH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$. The value of $[\text{Et}^{\bullet}]/[(\mathbf{6})]$ was only *ca.* 0.2, indicating that ethene is a less avid acceptor of hydrogen than propene.

The relative rates of β-H atom transfer to alkenes from (**6**) differ appreciably from the relative rates of free hydrogen-atom addition in the gas phase at 298 K (see Table 4).[39] Our initial attempts to compute meaningful transition-state structures for β-H atom transfer to alkenes, by examining the prototype reaction between $\text{H}_2\dot{\text{N}}\text{→BH}_3$ and $\text{CH}_2\text{=CH}_2$, have not proved successful, apparently because of the weakly bound nature of aminyl–borane radicals in the gas phase. However, a transition state closely resembling (**17**) (or, less likely, the *cisoid*-conformation) would appear to be most reasonable. Although aminyl–borane radicals have low SOMO energies (high i.p.s.), the hydrogen atoms attached to boron are relatively electron-rich and interactions between filled molecular orbitals of the aminyl–borane and the LUMO of the alkene might also be important along with the SOMO–HOMO interaction in a frontier-orbital analysis of β-H atom transfer.



(17)

Although the range of reactivities and alkene ionisation potentials is rather narrow, the two properties do appear to be correlated, providing support for the predominance of the

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* These propene concentrations have been calculated by assuming that 85% of the alkene is in solution (see the Experimental section).

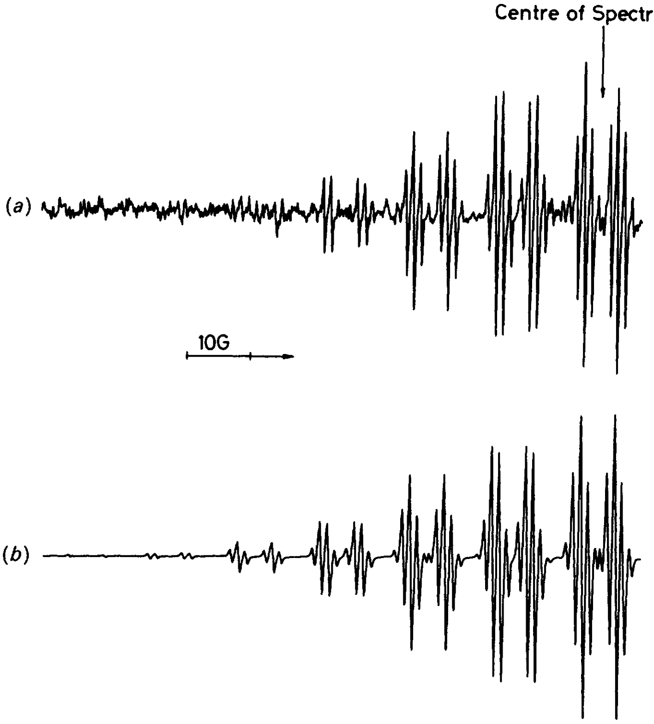


Figure 6. (*a*) Low-field half of the e.s.r. spectrum of the tetramethylallyl radical (**18**) derived from 2,4-dimethylpenta-2,3-diene in Bu^{t}OH–Pe^{t}OH (3:1 v/v) at 300 K. (*b*) Computer simulation of (*a*) using the following splitting constants: 14.16 (6 H), 12.98 (6 H), 5.40 G (1 H). The linewidth is 0.40 G and the lineshape is 60% Lorentzian (40% Gaussian).

SOMO–HOMO interaction or, in more classical terms, for the importance of charge transfer from the alkene to the aminyl–borane in the transition state. In particular, the more electron rich $Me_2C{=}CMe_2$ is more easily reduced than $Me_2C{=}CH_2$, although steric effects[40] should favour addition to the latter and a tertiary alkyl radical is produced from both alkenes.

The relatively low reactivity of furan, despite the allylic nature of the reduction product, is presumably a consequence of its aromaticity which is lost upon addition of a hydrogen atom. Changing the solvent from protic Bu^{t}OH–Pe^{t}OH to aprotic dioxane has little influence on the relative rates of β-H atom transfer from (**6**) and evidently any differences in the extent of solvation or association do not have large effects on the relative reactivities. In this context it is noteworthy that while the calculated dipole moment of (**6**) is 5.5 D, that of the aminoborane $MeNH\underline{\rightarrow}BH_2$ is only 1.8 D (see Table 3).

The *t*-butylaminyl–borane radical (**8**) donates a β-hydrogen atom to alkenes in a qualitatively similar way to (**6**), although the spectrum of the t-butyl radical [produced by β-scission of (**7**)] was often also observed. β-Hydrogen-atom transfer from the dimethylaminyl–borane radical[3] $Me_2\dot{N}\rightarrow BH_3$ to alkenes takes place less readily than from (**6**) or (**8**). For example, u.v. irradiation of Bu^{t}OH–Pe^{t}OH (3:1 v/v) solutions containing $Me_2NH\rightarrow BH_3$ (*ca.* 1 mol dm^{-3}), DTBP (*ca.* 20% v/v), and one of the alkenes $MeCH{=}CH_2$, $Me_2C{=}CH_2$, or $Me_2C{=}CMe_2$ (1–3 mol dm^{-3}) afforded only relatively weak spectra of Pr$^{i\cdot}$, Bu$^{t\cdot}$, and $Me_2CH\dot{C}Me_2$, respectively, and quenching of the spectrum of $Me_2\dot{N}\rightarrow BH_3$ was incomplete, even with 3 mol dm^{-3} $Me_2C{=}CMe_2$. Reduction of propene was especially slow, as expected by comparison with the results obtained for (**6**) (Table 4). The lower reactivity of the dialkylaminyl–borane parallels the smaller unpaired electron population on the β-BH$_3$ group, as evidenced by the appreciably smaller value of a(3B*H*) (46.4 G) shown[3] by $Me_2\dot{N}\rightarrow BH_3$. β-Hydrogen-atom transfer is probably also less favourable thermodynamically for $Me_2\dot{N}\rightarrow BH_3$ than for (**6**) or (**8**).

Finally, it is of interest to note that a gas, presumably dihydrogen,[3] is evolved during u.v. irradiation of samples when the stationary state concentrations of the aminyl–borane radicals (**6**) or (**8**) are large. However, when an alkene is present and the steady-state concentration of the aminyl–borane is very small, no gas evolution was evident. This observation provides support for the proposal[3] that self-reaction of aminyl–borane radicals can occur to form dihydrogen [*e.g.* equation (29)], perhaps in competition with the combination and disproportionation reactions shown by the isoelectronic alkyl radicals.

$$2Me\dot{N}H\rightarrow BH_3 \longrightarrow 2MeNH\underline{\rightarrow}BH_2 + H_2 \qquad (29)$$

Reactions of Aminyl–Borane Radicals with Other Compounds Containing Carbon–Carbon Multiple Bonds.—The 1,1,3,3-tetramethylallyl radical (**18**) was originally reported[41] to be formed by ring opening of the 2,2,3,3-tetramethylcyclopropyl radical, but this was later shown to be incorrect.[42] Although a number of 2-substituted derivatives, formed by radical addition to 2,4-dimethylpenta-2,3-diene (tetramethylallene), have been studied by e.s.r. spectroscopy,[43] the spectrum of the parent radical (**18**) has not yet been observed.

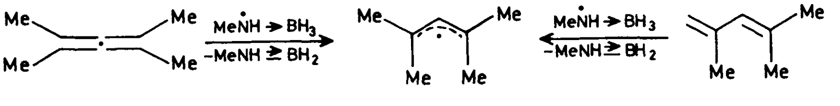
U.v. irradiation of a Bu^{t}OH–Pe^{t}OH solution containing methylamine–borane (1.1 mol dm^{-3}), DTBP (20% v/v), and tetramethylallene or its conjugated isomer 2,4-dimethylpenta-2,4-diene (1.0 mol dm^{-3}) afforded the same e.s.r. spectrum shown in Figure 6 and which we attribute to the tetramethylallyl radical (**18**). The spectroscopic parameters [a(6 H^1) 14.2, a(6 H^2) 13.0, a(1 H) 5.4 G, and g 2.0027 at 301 K] do not indicate significant sterically induced twisting of the allylic framework.[43]

Homolytic addition to 1,3,5-tri-t-butylbenzene has been investigated in the hope of producing persistent cyclohexadienyl radicals (**19**), but of the many addenda examined only pentafluorophenyl radicals gave an adduct detectable by e.s.r. spectroscopy.[44] However, when the diene in the previous experiments was replaced with 1,3,5-tri-t-butylbenzene (0.6 mol dm^{-3}), the e.s.r. spectrum of the cyclohexadienyl radical (**19**; X = H) was detected and that of (**6**) was not observed. The radical (**19**; X = H) was relatively long-lived ($t_{\frac{1}{2}}$ *ca.* 0.5 s at 304 K) and showed a(2 H) 41.6, a(2 H_{meta}) 2.65 G, and g 2.0027 at 304 K, in accord with expectation[44] for a cyclohexadienyl of this structure.

It has been shown previously that relatively persistent cyclohexadienyl radicals are also formed by homolytic addition to 1,3,5-tris(trimethylsiloxy)benzene,[45] and hydrogen-atom transfer from (**6**) to this arene also took place readily under e.s.r. conditions to yield the adduct (**20**) [a(2 H) 41.4, a(2 H_{meta}) 2.58 G, and g 2.0028 in 2,2,5,5-tetramethyltetrahydrofuran at 295 K]. We note that the e.s.r. spectrum of (**20**) exhibited pronounced emission-enhanced absorption polarisation.

Radicals Derived from Ammonia–Borane.—In agreement with previous work,[8] the e.s.r. spectrum of $H_3N\rightarrow\dot{B}H_2$ was observed during photolysis of DTBP in the presence of ammonia–borane (1.1 mol dm^{-3}) in Bu^{t}OH–Me$_2$O (4:1 v/v) at 282 K. No spectrum attributable to $H_2\dot{N}\rightarrow BH_3$ was detected and much dihydrogen gas was evolved under these conditions. However, in view of the detection of the corresponding alkylaminyl–boranes, rather than the isomeric amine–boryl radicals, with $RNH_2\rightarrow BH_3$ and $R_2NH\rightarrow BH_3$ under similar conditions, the question arises as to whether $H_2\dot{N}\rightarrow BH_3$ could also be present in low concentration with ammonia–borane.

The MO calculations indicate that $H_3N\rightarrow\dot{B}H_2$ and



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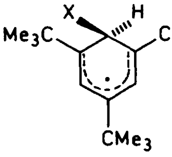

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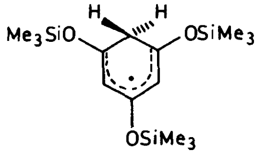

(20)

$H_2\dot{N}\rightarrow BH_3$ are very similar in energy (see Table 3), with the latter marginally more stable in the gas phase. However, the dipole moments of both radicals are large and solvation could be decisive in determining their relative stabilities in solution. In fact, it is possible that photolysis of DTBP in the presence of an amine–borane $R_nNH_{3-n}\rightarrow BH_3$ (n = 0–2), under the normal conditions of our e.s.r. experiments, could afford amine-boryl and aminyl-borane radicals in something approaching their equilibrium concentrations [equation (31)]. Such equilibration should be least rapid for ammonia–borane, since conversion of the initially-produced amine-boryl radical into the isomeric aminyl-borane would be relatively slow because the N–H bond in $H_3N\rightarrow BH_3$ is stronger than if the nitrogen is alkylated.

$$R_nNH_{3-n}\rightarrow \dot{B}H_2 + R_nNH_{3-n}\rightarrow BH_3 \rightleftharpoons R_n\dot{N}H_{2-n}\rightarrow BH_3 + R_nNH_{3-n}\rightarrow BH_3 \quad (31)$$

Since $a(3BH)$ increases significantly on going from $Me_2\dot{N}\rightarrow BH_3$ to $Me\dot{N}H\rightarrow BH_3$, it is likely that $H_2\dot{N}\rightarrow BH_3$ would show a still larger value of $a(3BH)$, probably paralleled by a greater thermodynamic instability towards β-scission. It is therefore possible that the lifetime of $H_2\dot{N}\rightarrow BH_3$ with respect to unimolecular loss of $H^\bullet$ or bimolecular β-H atom transfer to protic solvents or to parent ammonia–borane could be relatively short. To investigate the possibility that $H_2\dot{N}\rightarrow BH_3$ might be produced by the $H_3N\rightarrow BH_3$ + $Bu^tO^\bullet$ couple, we examined the effect of added $Me_2C=CMe_2$, since this alkene should readily accept a β-hydrogen-atom from $H_2\dot{N}\rightarrow BH_3$ while showing low reactivity towards addition of $H_3N\rightarrow \dot{B}H_2$.

When $Me_2C=CMe_2$ (1.5 mol dm^{-3}) was present along with DTBP and $H_3N\rightarrow BH_3$ (1.1 mol dm^{-3}) in Bu^tOH–Me_2O (4:1 v/v) at 281 K, the e.s.r. spectrum of $H_3N\rightarrow \dot{B}H_2$ was no longer observed but that of $Me_2CH\dot{C}Me_2$ was clearly evident. When $H_3N\rightarrow BD_3$ replaced the protiated material $Me_2CD\dot{C}Me_2$ was the main radical detected and the value of $[Me_2CD\dot{C}Me_2]/[Me_2CH\dot{C}Me_2]$ was *ca.* 4 shortly after beginning photolysis. The presence of $Me_2CH\dot{C}Me_2$ is probably mainly due to exchange of protium into the $H_3N\rightarrow BD_3$ as with $MeNH_2\rightarrow BD_3$, but we could not be sure that the protiated radical was absent at zero irradiation time. These results strongly indicate that $H_2\dot{N}\rightarrow BH_3$ is formed to some extent by the $H_3N\rightarrow BH_3$ + $Bu^tO^\bullet$ couple and that it readily reacts with $Me_2C=CMe_2$ by β-H atom transfer to give $Me_2CH\dot{C}Me_2$. It also seems likely that the exchange reaction (31; n = 0) proceeds on the millisecond timescale at 282 K when the concentration of ammonia–borane is *ca.* 1 mol dm^{-3}.

Experimental

E.s.r. spectra were recorded using a Varian E-109 instrument operating at *ca.* 9.1 GHz. Samples were contained in Suprasil quartz tubes (2 or 3 mm i.d., depending on the dielectric properties of the contents) which were either flame sealed or closed with greaseless stopcocks. Reaction mixtures were irradiated with u.v. light (λ *ca.* 240–340 nm) whilst in the microwave cavity of the spectrometer, as described previously.[7] Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and the results were confirmed by computer simulation using a modified[7] version of Krusic's program ESRSPEC2.[46] On the timescale of most measurements, extrapolation of radical concentration ratios to zero photolysis time gave negligible corrections.

Relative Reactivities of Alkenes Towards (**6**).—Mixtures containing pairs of alkenes were prepared using a standard calibrated vacuum line and sample tubes were back-filled with *ca.* 400 Torr of nitrogen before being flame sealed leaving the minimum dead space. Within experimental error (±5%) at the pressures employed (20–30 Torr), the alkenes behaved as ideal gases. This was shown by weighing the alkene condensed from the vacuum line into a glass bulb equipped with a greaseless stopcock and with a finger which could be cooled in liquid nitrogen. Because of the low boiling point of propene, it was considered possible that a proportion of this alkene might remain in the gas phase in the sealed tubes at the temperatures employed. To check for this, a Bu^tOH–Pe^tOH (3:1 v/v) solution containing propene and furan was prepared in an n.m.r. tube and sealed with a gas space of similar volume to that in the samples used for the e.s.r. experiments. The ^1H n.m.r. spectrum of this mixture was recorded at 282 K using a continuous wave spectrometer (100 MHz, Jeol PS-100) and the vinylic proton resonances were integrated to obtain the relative concentrations of propene and furan in solution. Assuming that all the furan originally condensed from the line was in solution, this showed that 85 ± 5% of the propene was also in solution under these conditions.

Materials.—N.m.r. spectra (C_6D_6 solvent) were obtained with a Varian XL-200 instrument (200 MHz for ^1H), using tetramethylsilane as an internal (^1H) or $Et_2O\rightarrow BF_3$ as an external standard (^{11}B). I.r spectra of methylamine–borane and the *B*-deuteriated complexes were recorded with a Perkin–Elmer PE983 instrument using *ca.* 0.1 mol dm^{-3} solutions in dioxane.

Preparations and manipulations of boron-containing compounds were carried out under an atmosphere of dry argon. Commercially available solvents and reagents which are liquids at room temperature were dried and distilled before use. Oxirane (Fluka), cyclopropane (Argo International), and dimethyl ether (Fluka) were used as received, as were the gaseous alkenes. Di-t-butyl peroxide (Aldrich) was purified as described previously[47] and dibutanoyl peroxide was prepared by a literature method.[47,48] 1,3,5-Tris(trimethylsiloxy)benzene (b.p. 102–104 °C at 0.05 Torr) was prepared from phloroglucinol and trimethylchlorosilane in the presence of pyridine.[49]

Dimethyl sulphide–borane containing ^{11}B and ^{10}B in natural abundance was obtained commercially (Aldrich); $Me_2S\rightarrow {}^{11}BH_3$ and $Me_2S\rightarrow {}^{11}BD_3$ (both 97.5 atom% ^{11}B) were prepared as described previously[50] starting from $Me_2O\rightarrow {}^{11}BF_3$ and $LiAlH_4$ or $LiAlD_4$, respectively.

Ammonia–borane (Aldrich) was either used as received or after vacuum sublimation, with indistinguishable results. Ammonia–borane, and the alkylamine–boranes,[13] along with the isotopically-enriched complexes were prepared by the reaction of the appropriate amine with dimethyl sulphide–borane or trideuterioborane as described below.

Methylamine (9.2 cm^3, *ca.* 0.2 mol) was condensed from a cylinder into a graduated trap cooled in solid CO$_2$–acetone slush and then allowed to evaporate into a stirred solution of dimethyl sulphide–borane (0.08 mol) in diethyl ether (10 cm^3) cooled to *ca.* −40 °C in a flask equipped with a condenser containing solid CO$_2$–acetone slush. When the addition was complete the mixture was allowed to attain room temperature and was then stirred for a further 2 h. The ether, sulphide, and excess amine were removed under reduced pressure and the residual methylamine–borane was dissolved in diethyl ether, the solution filtered, and the product precipitated with cyclohexane (yield 3.1 g, 86%), m.p. 56 °C (lit.,[13] m.p. 56 °C). (Found: C, 27.0; H, 17.8; N, 31.5. Calc. for CH_8BN: C, 26.8; H, 18.0; N, 31.2%); δ_H 1.67 (t, *J* 6.1, Hz, Me), 2.00 (q, J_{BH} 94 Hz, BH$_3$), and 2.54 (br s, NH$_2$); δ_B −17.6 (q, J_{BH} 97 Hz).

t-Butylamine (5.1 g, 0.070 mol) in hexane (10 cm^3) was added dropwise to a stirred solution of dimethyl sulphide–borane (0.065 mol) in hexane (10 cm^3) maintained at *ca.* 20 °C. After the addition was complete, the mixture was stirred for a further 2 h at room temperature before the precipitated t-butylamine–borane (5.1 g, 90%) was removed by filtration and dried under reduced pressure, m.p. 95–96 °C (lit.,[13] m.p. 96 °C), δ_H 0.83 (s, Bu^t), 2.02 (q, J_{BH} 94 Hz, BH$_3$), and 3.07 (br s, NH$_2$); δ_B −22.4 (q, $^1J_{B-H}$ 96 Hz). [$^2H_9$]-t-Butylamine–borane was prepared in the same way starting from [$^2H_9$]Bu^{t}NH$_2$, itself prepared from [$^2H_9$]Bu^{t}OD (Aldrich) using the method described by Charelli and Rassat.[51]

Acknowledgements

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