An Electron Spin Resonance Study of the Generation and Reactions of Borane Radical Anions in Solution

Jeremy R. M. Giles and Brian P. Roberts *
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

Photochemically or thermally generated t-butoxyl radicals rapidly abstract hydrogen from borohydride or cyanoborohydride anions to form $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$, respectively, which can be detected and their reactions studied in fluid solution using e.s.r. spectroscopy. The spectroscopic parameters confirm that the equilibrium geometry of $H_3B^{-\cdot}$ is planar, as is that of the isoelectronic $H_3C\cdot$, and the temperature dependences of $a(^{11}B)$ and $a(3H)$ result from Boltzmann population of out-of-plane vibrational states. The extent of conjugative delocalisation of the unpaired electron onto nitrogen is similar in $H_2\dot{B}CN^-$ and in the isoelectronic $H_2\dot{C}CN$. $H_3B^{-\cdot}$ adds to ethylene, trimethylvinylsilane, benzene, and pyridine, but $H_2\dot{B}CN^-$ is less reactive and addition to only $Me_3SiCH{=}CH_2$ was detected. The B–C bond eclipses the orbital of the unpaired electron in the preferred conformation of the ethylene adduct $H_3BCH_2\dot{C}H_2$, in contrast to the staggered conformation adopted by the isoelectronic propyl radical. Addition of $H_3B^{-\cdot}$ to electron deficient arenes is faster than to benzene, and the regioselectivities of these reactions also show that the borane radical anion is highly nucleophilic. Both $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ add to alkyl azides and cyanides to give triazenyl and iminyl radical adducts, respectively, and both borane radical anions displace alkyl radicals from alkyl isocyanides, perhaps through the intermediacy of a transient imidoyl radical adduct. $H_3B^{-\cdot}$ abstracts a halogen atom from alkyl chlorides, bromides, and iodides, while $H_2\dot{B}CN^-$ reacts rapidly with only bromides and iodides; neither reacts with alkyl fluorides. The reactivities of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ resemble those of $H_3Si\cdot$ and $R_3Si\cdot$ much more than those of $H_3C\cdot$ and $R_3C\cdot$.

Extensive investigations of the structures, stabilities, and reactivities of carbon-centred radicals have provided the foundation upon which the subject of free-radical chemistry has been built. In marked contrast, very little is known about the structures and chemical properties of boron-centred radicals. The borane radical anion ($H_3B^{-\cdot}$) is isoelectronic with the methyl radical and it might be expected that the diversity of structural and chemical properties exhibited by substituted methyl radicals of the type $XYZC\cdot$ will also be shown by the borane radical anions $XYZB^{-\cdot}$.

E.s.r. spectra of $H_3B^{-\cdot}$ [1,2] and $F_3B^{-\cdot}$,[3] produced by γ-irradiation of borohydrides and boron trifluoride, respectively, have been detected in rigid matrices. Long-lived borane radical anions have been generated by alkali-metal reduction of triarylboranes [4] or, very recently, of certain trialkylboranes [5] in ether solvents. It has also been proposed that the reductions of halogenobenzenes [6] and *gem*-dibromocyclopropanes [7] with sodium borohydride proceed by radical chain mechanisms, the propagation steps of which are illustrated in equations (i) and (ii).

$$H_3B^{-\cdot} + RBr \longrightarrow [H_3\bar{B}Br] + R\cdot \qquad \text{(i)}$$

$$R\cdot + H_4B^- \longrightarrow RH + H_3B^{-\cdot} \qquad \text{(ii)}$$

In a preliminary communication [8] we have reported that t-butoxyl radicals readily abstract hydrogen from borohydrides and cyanoborohydrides to give $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$, respectively, which may be detected in fluid solution by e.s.r. spectroscopy. E.s.r. studies of some reactions of $H_3B^{-\cdot}$ with alkyl halides, isocyanides and azides were also reported.

In the present paper, we present a full account of the preliminary work and describe further e.s.r. studies of the structures and reactions of transient borane radical anions.

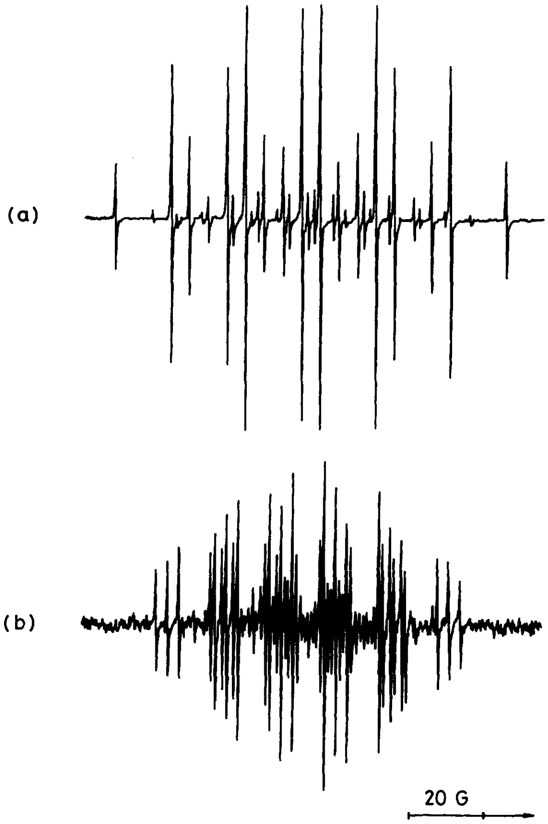


Figure 1. E.s.r. spectra of borane and cyanoborane radical anions in Me_2O–Bu^tOH (1.3 : 1 v/v): (a) $H_3B^{-\cdot}$ at 279 K; (b) $H_2\dot{B}CN^-$ at 289 K. Radicals containing ^{11}B and ^{10}B are present in the expected concentration ratio

Results

Generation of $H_3B^{-\cdot}$ *and* $H_2\dot{B}CN^-$.—U.v. photolysis of solutions containing di-t-butyl peroxide (*ca.* 15% v/v) and *ca.* 0.5M-tetra-n-butylammonium borohydride (TBAB) [9] or cyanoborohydride (TBAC) [10] in the cavity of an e.s.r. spectrometer [11] afforded spectra, shown in Figure 1, of the appropriate borane

Table 1. E.s.r. parameters for the borane and cyanoborane radical anions in Me_2O–Pe^tOH (1.3 : 1 v/v) and for the isoelectronic alkyl radicals

Radical	T/K	g Factor	Hyperfine splittings (G) [a]
$H_3B^{-\cdot}$ [b]	253	2.0023	15.2 (3 H), 19.9 (1 ^{11}B), 6.7 (1 ^{10}B)
$H_3B^{-\cdot}$ [c]	298	2.0023	15.1 (3 H), 20.7 (1 ^{11}B)
$D_3B^{-\cdot}$	253	2.0023	2.34 (3 D), 18.8 (1 ^{11}B)
$H_2\dot{B}CN^-$	252	2.0025	15.8 (2 H), 3.0 (1 N), 14.3 (1 ^{11}B), 4.8 (1 ^{10}B)
$H_3C\cdot$ [d]	96	2.0026	23.0 (3 H), 38.3 (1 ^{13}C)
$D_3C\cdot$ [d]	96		3.58 (3 D), 36.0 (1 ^{13}C)
$H_2\dot{C}CN$ [e]	306	2.0030	21.0 (2 H), 3.5 (1 N)

[a] Numbers of equivalent nuclei shown in parentheses. The natural abundances of ^{11}B (I 3/2) and ^{10}B (I 3) are 81.2 and 18.8%, respectively; $(\gamma_{10B}/\gamma_{11B}) = 0.335$. The temperature dependences of the splittings for $H_3{}^{11}B^{-\cdot}$ and $D_3{}^{11}B^{-\cdot}$ are shown in Figure 2. [b] $H_3B^{-\cdot}$ was also generated from $Oct^n{}_3NMeBH_4$ in Pe^tOH (2.8M)-Me_2O and at 293 K $a(^{11}B) = 20.29$ and $a(3\ H) = 15.04$ G, within experimental error in agreement with the values (20.28 and 15.06 G, respectively) for the radical generated from $Bu^n{}_4NBH_4$ at the same temperature. At 296 K in the aprotic solvent system Me_2O-$MeOCH_2CH_2OMe$ (1 : 1 v/v), $a(^{11}B) = 20.08$ and $a(3H) = 14.93$ G for $H_3B^{-\cdot}$ generated from $Oct^n{}_3NMeBH_4$. [c] Data from ref. 2 for the radical generated by γ-irradiation of Me_4NBH_4 in the solid state. [d] Data from ref. 32. [e] Data from R. Livingston and H. Zeldes, *J. Magn. Reson.*, 1969, **1**, 169.

radical anions.† Radicals containing ^{11}B (I 3/2, natural abundance 81.2%) and ^{10}B (I 3, natural abundance 18.8%) were detected. The trideuterioborane radical anion was generated in a similar way from $Bu^n{}_4NBD_4$.

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

$$Bu^tO\cdot + H_4B^- \longrightarrow Bu^tOH + H_3B^{-\cdot} \qquad \text{(iv)}$$

$$Bu^tO\cdot + H_3BCN^- \longrightarrow Bu^tOH + H_2\dot{B}CN^- \qquad \text{(v)}$$

$$Bu^tON{=}NOBu^t \xrightarrow{heat} 2Bu^tO\cdot + N_2 \qquad \text{(vi)}$$

Alcohols [ethyl, t-butyl, or t-pentyl (Pe^t)] or ethers (dimethyl ether, tetrahydrofuran, dioxan, or 1,2-dimethoxyethane) or binary mixtures of alcohol and ether were used as solvents. That most commonly employed for photochemical experiments was a mixture of Me_2O and Pe^tOH (1.3 : 1 v/v). When TBAB was replaced by lithium or sodium borohydride, the spectrum of $H_3B^{-\cdot}$ was also detected but because TBAB was much more soluble in organic solvents and in order to minimise possible counterion effects in the reactions of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$, the tetra-alkylammonium salts were used exclusively in this work.

The borane radical anions could also be detected during thermolysis at (333 K) of di-t-butyl hyponitrite [12] (*ca.* 0.5M) in the presence of TBAB or TBAC using neat Pe^tOH as solvent [equation (vi), followed by (iv) or (v)].

The e.s.r. parameters of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$, calculated from resonance fields and microwave frequencies using Preston's program ESRLSQ,[13] are given in Table 1. In photochemical experiments, the temperature dependence of the e.s.r. parameters for $H_3B^{-\cdot}$ and $D_3B^{-\cdot}$ were investigated in detail and these results are shown graphically in Figure 2.

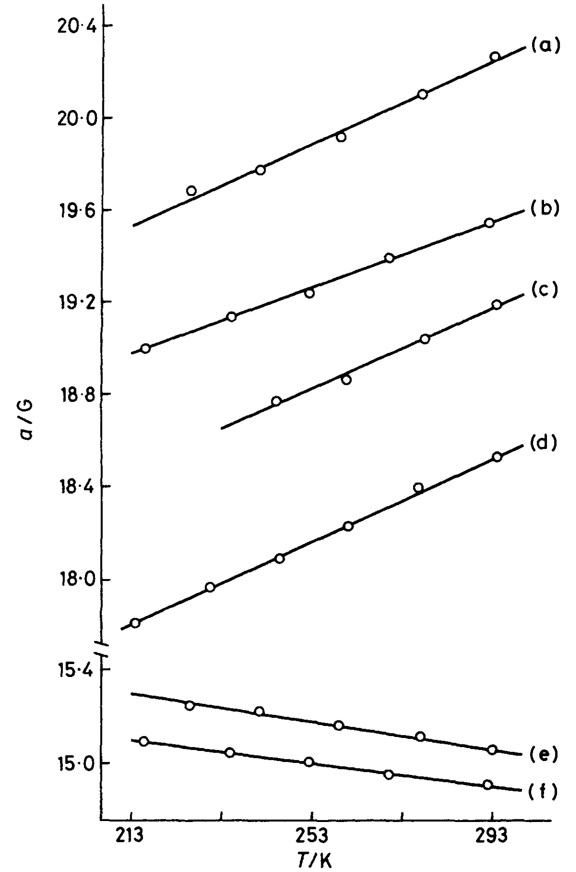


Figure 2. Temperature dependences of the boron-11 and proton hyperfine splittings for $H_3B^{-\cdot}$ and $D_3B^{-\cdot}$ in Me_2O–alcohol solvents. (a) $a(^{11}B)$ and (e) $a(3H)$ for $H_3B^{-\cdot}$ generated from $Bu^n{}_4NBH_4$ (0.5M) in Pe^tOH (2.8M)–Me_2O solvent; $d|a(^{11}B)|dT$ +9.1, $d|a(3H)|/dT$ −3.04 mG K^{-1}. (b) $a(^{11}B)$ and (f) $a(3H)$ for $H_3B^{-\cdot}$ generated from $Bu^n{}_4NBH_4$ (0.5M) in EtOH (2.8M)–Me_2O solvent; $d|a(^{11}B)|/dT$ +7.3, $d|a(3H)|dT$ −2.50 mG K^{-1}. (c) and (d) $a(^{11}B)$ for $D_3B^{-\cdot}$ generated from $Bu^n{}_4NBD_4$ in Pe^tOH (2.8M)–Me_2O [$d|a(^{11}B)|/dT$ +8.8 mG K^{-1}] and EtOH (2.8M)–Me_2O solvent [$d|a(^{11}B)|/dT$ +9.0 mG K^{-1}], respectively

Decay of $H_3B^{-\cdot}$.—At 275 K in Me_2O–Pe^tOH (1.3 : 1 v/v) the decay of $H_3B^{-\cdot}$ was followed by kinetic e.s.r. spectroscopy [14] and found to be approximately first-order ($t_{\frac{1}{2}}$ 14.5 ms for an initial concentration of 2.8×10^{-6}M). At lower temperatures, a significant second-order component was present.

At 275 K in Me_2O–THF (2.5 : 1 v/v) the steady-state radical concentration obtained during continuous photolysis was smaller than in Me_2O–Pe^tOH and, in a freshly prepared solution after a short total photolysis time, $H_3B^{-\cdot}$ decayed more rapidly by a first-order process in the aprotic solvent system (k 210 s^{-1}, $t_{\frac{1}{2}}$ 3.3 ms, initial [$H_3B^{-\cdot}$] 5.0×10^{-7}M). The rate of decay in Me_2O–THF decreased after prolonged photolysis of the sample, probably as a result of the build-up of hydroxylic reaction products and/or increased basicity of the sample. A more detailed investigation of the products and kinetics of decay of borane radical anions will be carried out.

Reactions of $H_3B^{-\cdot}$ *and* $H_2\dot{B}CN^-$.—A variety of reactions of these borane radical anions were studied using e.s.r. spectroscopy.

---

† TBAB or TBAC do not react thermally with Bu^tOOBu^t under the conditions employed. The results obtained in this work indicate that reactions of $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$ with Bu^tOOBu^t are also unimportant.

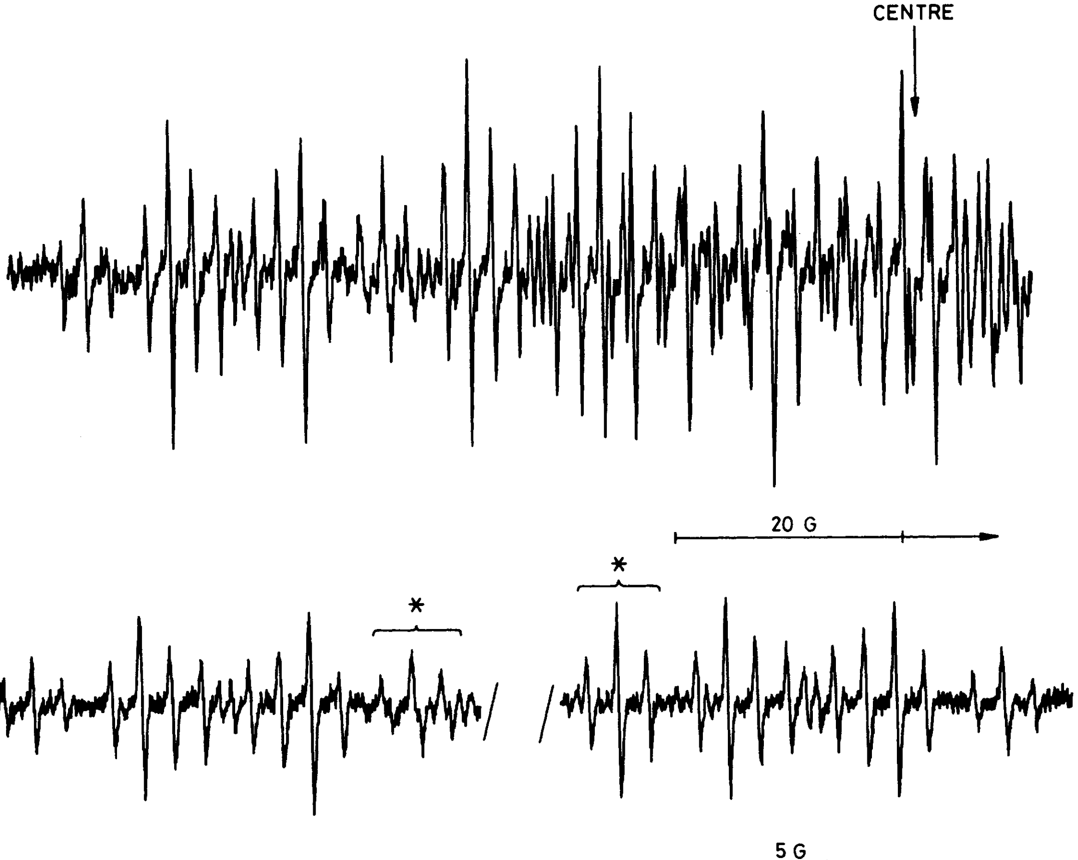
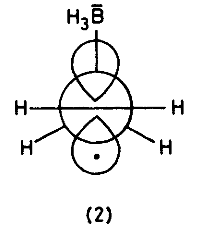


Figure 3. E.s.r. spectrum of the cyclohexadienyl radical (4) (partly deuteriated) formed by addition of $D_3B^{-\bullet}$ to benzene in Me_2O–Pe^{t}OH (1.3 : 1 v/v) at 295 K. The spectrum is asymmetric about the centre point because of second-order effects. For example, at low field the pair of triplets marked with an asterisk are separated by 0.4 G, whilst at high field the triplets are superimposed. Both ^{10}B- and ^{11}B-containing radicals are present

(i) *Addition to alkenes and arenes.* Photolysis of an Me_2O–Pe^{t}OH solution containing Bu^{t}OOBu^t, TBAB, and ethylene (*ca.* 4M) between 183 and 268 K afforded an e.s.r. spectrum which we assign to the β-substituted ethyl radical (1) [equation (vii)]. The spectrum of (1) was complicated by the presence of γ-proton splitting [1.5 G (3 H)] and the simplified spectrum obtained from the $D_3B^{-\bullet}$ adduct was investigated more thoroughly. The hyperfine splitting constants and their temperature dependences (see Table 2) indicate [15] that the most stable conformation of (1) is the ' eclipsed ' structure (2).

$$H_3B^{-\bullet} + CH_2{=}CH_2 \longrightarrow H_3\bar{B}CH_2\dot{C}H_2 \qquad \text{(vii)}$$

(1)



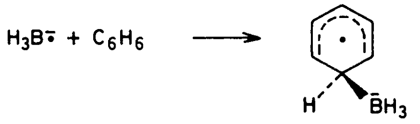
(2)

The cyanoborane radical anion failed to add to ethylene under similar conditions and only H_2BCN^- was detected between 198 and 248 K in experiments where TBAC replaced TBAB. However, both $H_3B^{-\bullet}$ and $H_2\dot{B}CN^-$ added readily to trimethylvinylsilane at low temperatures (188—248 K) as shown in equation (viii; X = H or CN), and the e.s.r. parameters of the adducts (3) are also given in Table 2.

$$H_2\dot{B}X^- + CH_2{=}CHSiMe_3 \longrightarrow H_2\bar{B}(X)CH_2\dot{C}HSiMe_3 \qquad \text{(viii)}$$

(3)

In similar experiments, $H_3B^{-\bullet}$ was shown to add to benzene (*ca.* 2M) and only the e.s.r. spectrum of the cyclohexadienyl adduct (4) (see Figure 3) could be detected above *ca.* 275 K.



(ix)

(4)

Between 275 and 240 K spectra of both $H_3B^{-\bullet}$ and (4) were apparent, while at lower temperatures only $H_3B^{-\bullet}$ was detected. The adduct (4) was short-lived and its spectrum decayed rapidly when photochemical generation was interrupted. At 293 K, decay followed second-order kinetics and $2k_t$ was *ca.* 4×10^7 l mol^{-1} s^{-1} for an initial concentration of *ca.* 8×10^{-7}M.

Addition of $H_2\dot{B}CN^-$ to benzene (or to the other arenes) was not detected in Me_2O–Pe^{t}OH up to 298 K and only the spectrum of the cyanoborane radical anion was observed. Addition to benzene was not detected up to 353 K in Pe^{t}OH solvent.*

Addition of the borane radical anion to monosubstituted benzenes ($PhCH_3$, $PhCF_3$, $PhCMe_3$, and $PhSiMe_3$) and to pyridine and some t-butyl-substituted pyridines was also investigated. Below *ca.* 240 K only $H_3B^{-\cdot}$ ($D_3B^{-\cdot}$) was detected in the presence of toluene (*ca.* 2M), but on raising the temperature a complex spectrum (total width *ca.* 150 G) was also observed and the latter eventually dominated at 295 K. However, because of the large number of lines and consequent poor signal to noise ratio, a full analysis of the spectrum was not possible, although the appearance was consistent with that expected for a cyclohexadienyl adduct (or mixture of adducts).

In the presence of $PhCF_3$ (*ca.* 2M) the spectrum of $D_3B^{-\cdot}$ was completely replaced by one which we assign to the *para*-cyclohexadienyl adduct (5) (see Table 2) and signals ascribable to the *ortho*- or *meta*-adducts were not detected.

Below 240 K addition of $D_3B^{-\cdot}$ to $PhCMe_3$ (*ca.* 2M) was not observed. At 253 K, $D_3B^{-\cdot}$ was still readily detectable but, in addition, a weak complex spectrum was observed to low and high field of that due to the former radical and at 293 K the intensities of the two spectra were similar. Analysis of the wider spectrum was possible using the wing lines, and it was assigned to the cyclohexadienyl radical (6) formed by addition to the *meta*-position. In contrast, addition of $D_3B^{-\cdot}$ to $PhSiMe_3$ was complete at 200 K and the resulting e.s.r. spectrum was most readily understood in terms of the presence of a mixture of *para*- and *ortho*-adducts (7) and (8). However, the *meta*-adduct might also have been present and, in view of the low intensity of the spectra, the interpretation should be regarded as preliminary.

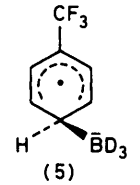
Similarly, the spectrum of $H_3B^{-\cdot}$ was completely quenched by pyridine (*ca.* 2M) at 240 K and replaced by that of the *para*-adduct (9). The assignment was confirmed by generating deuterium labelled analogues using $Bu^n_4NBD_4$ and [D_5]-pyridine (see Table 2). The radical (9) was also readily detected when $H_3B^{-\cdot}$ was generated thermally (333 K) in the presence of pyridine, showing that photoexcited pyridine [16] is not involved in its formation.

Blocking of the 4-position as in 4-t-butylpyridine caused $D_3B^{-\cdot}$ to add to the 2-position to give (10). Experiments between 228 and 268 K showed that $D_3B^{-\cdot}$ adds to 2,6-di-t-butylpyridine to give the relatively persistent ($t_{\frac{1}{2}}$ 8.7 s in Me_2O–Pe^{t}OH at 245 K) azacyclohexadienyl radical (11).

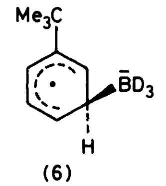
For comparison, the reactions of trimethylsilyl radicals with pyridines were investigated. In cyclopropane solution, photolysis of Bu^{t}OOBu^t and trimethylsilane (as a source of $Me_3Si\cdot$) [17] in the presence of pyridine afforded the spectrum of the *N*-silylpyridinyl radical (12), formed by addition to nitrogen. The hyperfine splittings (Table 2) for (12) agreed well with those reported previously [18] for the radical derived from another source, but the *g*-factor was lower than that given in the literature (2.0037). Similarly, $Me_3Si\cdot$ appears to add to the nitrogen of 4-t-butylpyridine to give (13),[19] but with 2,6-di-t-butylpyridine, addition takes place at the 4-position to give the azacyclohexadienyl radical (14) analogous to (11).[20]

The methyl radical adds to pyridine less rapidly than does the isoelectronic $H_3B^{-\cdot}$. Thus, photolysis of azomethane (MeN=NMe) in the presence of pyridine (2M) in cyclopropane between 153 and 283 K afforded only the spectrum of the methyl radical.

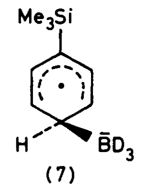
(ii) *Addition to alkyl azides.* Thermally or photochemically generated $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$ add to t-butyl or 1-adamantyl azide to afford strong spectra of relatively long-lived adduct radicals ($t_{\frac{1}{2}}$ *ca.* 26 s at 245 K for that derived from $H_3B^{-\cdot}$ and $1\text{-}AdN_3$ in Me_2O–Pe^{t}OH). The *g* factors (2.0014) are less than the free-spin value (2.0023) and the spectra show splitting



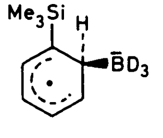
(5)



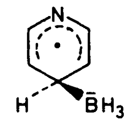
(6)



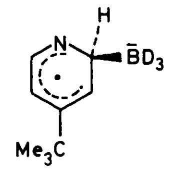
(7)



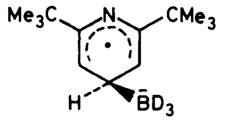
(8)



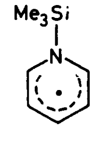
(9)



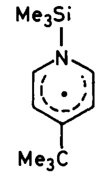
(10)



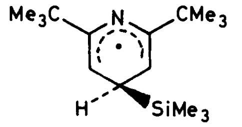
(11)



(12)

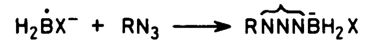


(13)



(14)

of 14—15 G from one ^{14}N nucleus. Trialkylsilyl radicals add to alkyl azides to give σ 1,3-triazenyl radicals $\overset{\cdot}{\widehat{\mathrm{RNNN}}}\mathrm{SiR_3}$ which show similar *g*-factors and coupling to the central nitrogen [21] and there is little doubt that the borane anions undergo a similar addition reaction to give 1,3-triazenyl radicals (15; X = H or CN).



$$H_2\dot{B}X^- + RN_3 \longrightarrow \overset{\cdot}{\widehat{\mathrm{RNNN}}}\bar{B}H_2X \qquad (x)$$

(15)

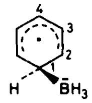
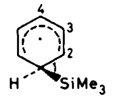
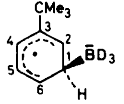
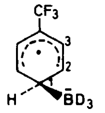
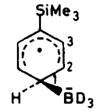
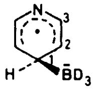
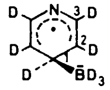
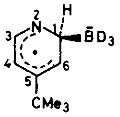
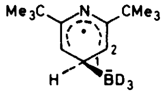
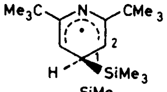
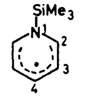
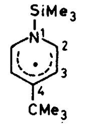
The spectroscopic parameters, along with those of dialkyl- and silyl(alkyl)-triazenyl radicals for comparison, are given in Table 3. That only two of the three nitrogens in (15) should give rise to resolvable splitting is reasonable in view of the small magnitude of the splitting from one nitrogen in $\overset{\cdot}{\widehat{\mathrm{RNNN}}}\mathrm{SiR_3}$.

The spectra resulting from similar reactions with methyl, n-hexyl, and isopropyl azides were weaker, since the adducts were shorter lived than those obtained from the tertiary alkyl azides, and complete analysis of their complex spectra was

---

* We cannot eliminate the possibility that addition of $H_2\dot{B}CN^-$ to arenes is also relatively rapid, but highly reversible.

Table 2. E.s.r. parameters for radicals formed by addition of borane or cyanoborane radical anions to alkenes or arenes in Me_2O–Pe^{t}OH (1.3 : 1 v/v)

Radical	*T*/K	*g* Factor	Hyperfine splittings (G) [a]
$H_3\bar{B}CH_2\dot{C}H_2$	225	2.0026	18.9 ($2H_\alpha$),[b] 17.5 ($2H_\beta$),[c] 1.5 ($3H_\gamma$),[d] 23.5 ($1^{11}B$) [e]
$H_3CCH_2\dot{C}H_2$ [f]	143	2.0027	22.1 ($2H_\alpha$), 31.1 ($2H_\beta$),[g] 0.3 ($3H_\gamma$)
$H_3SiCH_2\dot{C}H_2$ [h]	203		21.4 ($2H_\alpha$), 17.7 ($2H_\beta$), 2.8 ($3H_\gamma$)
$Me_3SiCH_2\dot{C}H_2$ [h]	161	2.0027	21.1 ($2H_\alpha$), 17.7 ($2H_\beta$),[i] 37.4 ($1^{29}Si$) [j]
$H_3\bar{B}CH_2\dot{C}(H)SiMe_3$ [k]	220	2.0027	17.8 ($1H_\alpha$), 15.5 ($2H_\beta$), 1.8 ($3H_\gamma$),[l] 23.5 ($1^{11}B$), 7.8 ($1^{10}B$)
$H_2\bar{B}(CN)CH_2\dot{C}(H)SiMe_3$	203	2.0027	18.2 ($1H_\alpha$), 15.9 ($2H_\beta$), 24.5 ($1^{11}B$)
	293	2.0027	41.0 ($1H^1$), 11.8 ($1H^4$), 7.5 ($2H^2$), 2.1 ($2H^3$), 0.2 (3H),[m] 26.7 ($1^{11}B$)
 [n]	213		37.8 ($1H^1$), 12.5 ($1H^4$), 8.3 ($2H^2$), 2.4 ($2H^3$)
	293	2.0027	41.4 ($1H^1$), 11.8 ($1H^4$), 7.7 ($1H^{2\text{ or }6}$), 7.2 ($1H^{2\text{ or }6}$), 2.1 ($1H^5$), 26.6 ($1^{11}B$)
	232	2.0024	35.4 ($1H^1$), 6.8 ($2H^2$), 1.4 ($2H^3$), 24.3 (3F), 24.9 ($1^{11}B$)
 [o]	298		40.3 ($1H^1$), 6.9 ($2H^2$), 1.7 ($2H^3$), 25.0 ($1^{11}B$)
	246	2.0032	38.0 ($1H^1$), 6.6 ($2H^2$), 0.50 ($2H^3$), 7.0 (1N), 27.0 ($1^{11}B$)
	248	2.0032	5.8 ($1D^1$), 1.0 ($2D^2$), 7.0 (1N), 27.0 ($1^{11}B$)
	246	2.0032	33.2 ($1H^1$), 10.7 ($1H^4$), 6.7 ($1H^6$), 1.6 ($1H^3$), 5.5 (1N), 24.8 ($1^{11}B$)
	246	2.0033	44.5 ($1H^1$), 6.8 ($2H^2$), 7.1 (1N), 28.9 ($1^{11}B$), 9.7 ($1^{10}B$)
 [p]	241	2.0032	39.3 ($1H^1$), 7.9 ($2H^2$), 6.9 (1N)
 [q]	235	2.0030	11.8 ($1H^4$), 6.3 ($2H^2$), 1.2 ($2H^3$), 4.1 (1N)
 [r]	363	2.0035	6.5 ($2H^2$), 1.5 ($2H^3$), 0.25 (9H), 4.1 (1N)

[a] Numbers of equivalent nuclei shown in parentheses. [b] d|a(2H)|/dT *ca.* 0 mGK^{-1}. [c] d|a(2H)|/dT +22 mG K^{-1}. [d] Splitting absent for $D_3\bar{B}CH_2\dot{C}H_2$. [e] d|$a(1^{11}B)$|/dT −17 mG K^{-1} for $D_3\bar{B}CH_2\dot{C}H_2$ between 173 and 228 K. [f] Data from D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, 1972, **94**, 6485. [g] d|a(2H)|/dT *ca.* −25 m G K^{-1}. [h] Data from ref. 15. [i] d|a(2H)|/dT +13 mG K^{-1}. [j] Value for $Et_3SiCH_2\dot{C}H_2$ at 125 K. [k] For $H_3\bar{B}CH_2\dot{C}(H)SiMe_3$ the central line of the triplet due to coupling with the β-protons broadens below 225 K and is undetectable at 195 K. A similar effect was apparent for $H_2\bar{B}(CN)CH_2\dot{C}(H)SiMe_3$. [l] Splitting absent for $D_3\bar{B}CH_2\dot{C}(H)SiMe_3$. [m] Splitting absent for the adduct derived from $D_3B^{-\cdot}$. [n] Data from ref. 39. [o] Other positional isomers were also present, see text. [p] First reported in ref. 20. [q] First reported in ref. 18; see text. [r] Data from ref. 19.

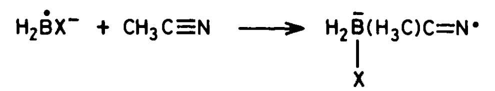
Table 3. E.s.r. parameters for the triazenyl radicals $R\overbrace{N^1N^2N^3}^{\cdot}\bar{B}H_2X$ ($X = H$ or CN) formed by addition of $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$ to alkyl azides in Pe^{t}OH

Radical	T/K	g Factor	Hyperfine splittings (G)				
			$a(N^1)$	$a(N^2)$	$a(N^3)$	$a(^{11}B)$	$a(H)$ [a]
$1\text{-Ad}\overbrace{NNN}^{\cdot}\bar{B}H_3$ [b]	323	2.0014	c	14.3	6.2	5.1 [d]	8.1 (3) [e]
$1\text{-Ad}\overbrace{NNN}^{\cdot}\bar{B}H_2CN$ [b]	321	2.0014	c	14.9	5.2	6.8	7.9 (2)
$Bu^t\overbrace{NNN}^{\cdot}\bar{B}H_3$ [b]	328	2.0014	c	14.0	6.3	4.8 [f]	8.3 (3)
$Bu^t\overbrace{NNN}^{\cdot}\bar{B}H_2CN$ [b]	328	2.0014	c	14.6	5.2	6.6	7.9 (2)
$H_3C\overbrace{NNN}^{\cdot}SiEt_3$ [g]	260	2.0009	1.8 [h]	17.1	3.6 [h]		c
$H_3C\overbrace{NNN}^{\cdot}CH_3$ [i]	226	2.0021	4.0	11.5	4.0		8.0 (6)
$Bu^t\overbrace{NNN}^{\cdot}Bu^t$ [i]	335	2.0019	3.3	12.4	3.3		

[a] Number of equivalent nuclei shown in parentheses. [b] $BH_3^{-\cdot}$ or H_3BCN^- generated thermally using Bu^{t}ON=NOBu^t. [c] Not resolved. [d] $a(^{10}B)$ 1.7 G. [e] $a(3D)$ 1.25 G for $1\text{-Ad}\overbrace{NNN}^{\cdot}\bar{B}D_3$. [f] $a(^{10}B)$ 1.6 G. [g] Data from ref. 21. [h] Assignment could be reversed. [i] Data from ref. 42.

not possible. However, we believe that 1,3-triazenyl adducts are also formed from the primary and secondary alkyl azides.

(iii) *Addition to alkyl cyanides.* Both $H_3B^{-\cdot}$ (or $D_3B^{-\cdot}$) and $H_2\dot{B}CN^-$ react readily with acetonitrile in Me_2O-Pe^{t}OH to afford spectra that we assign, on the basis of their hyperfine splittings, to iminyl radical adducts (16; X = H or CN). Addition of $D_3B^{-\cdot}$ to $^{13}CH_3CN$ and to $CH_3{}^{13}CN$ was also



$$H_2\dot{B}X^- + CH_3C{\equiv}N \longrightarrow H_2\underset{\displaystyle X}{\underset{|}{\bar{B}}}(H_3C)C{=}N\cdot \qquad \text{(xi)}$$

(16)

studied and the spectrum of unlabelled $D_3\bar{B}(H_3C)C{=}N\cdot$ is shown in Figure 4. Addition of borane radical anions to propiononitrile also gave iminyl radicals and the spectroscopic parameters of all the adducts are gathered in Table 4.

It appears that $H_3B^{-\cdot}$ is more reactive than $H_2\dot{B}CN^-$ towards acetonitrile. Thus, below *ca.* 220 K the spectrum of $H_2\dot{B}CN^-$ was observed in the presence of CH_3CN (*ca.* 2M) and the iminyl adduct was also detectable only above this temperature. With $H_3B^{-\cdot}$ under similar conditions only the adduct was observable down to 185 K.

The iminyl adducts were not detectable at high temperatures, probably because of their rapid fragmentation to give alkyl radicals and cyanoborohydride [equation (xii)]. Thus, in

$$H_3\bar{B}(R)C{=}N\cdot \longrightarrow R\cdot + H_3\bar{B}CN \qquad \text{(xii)}$$

$$MeN{=}NMe \xrightarrow{h\nu} 2Me\cdot + N_2 \qquad \text{(xiii)}$$

photochemical studies of the reaction of $H_3B^{-\cdot}$ with EtCN, only the spectrum of the ethyl radical was detected above 288 K. When $H_3B^{-\cdot}$ was generated in the presence of Bu^{t}CN * no iminyl adduct could be detected, even at 170 K, and only the spectrum of Bu$^t\cdot$ was observed between 170 and 295 K. Since it was considered feasible that some isomerisation of Bu^{t}CN to Bu^{t}NC might take place during photolysis, making interpretation of this result ambiguous (see below), $H_3B^{-\cdot}$ was generated thermally in the presence of Bu^{t}CN and, at 333 K, Bu$^t\cdot$ was again detected. In photochemical experiments after prolonged u.v. irradiation at 293 K the spectrum of Bu$^t\cdot$ was replaced by that of $H_2\dot{B}CN^-$, presumably formed by abstraction of hydrogen from $H_3\bar{B}CN$ [see equation (xii; R = Bu^t)].

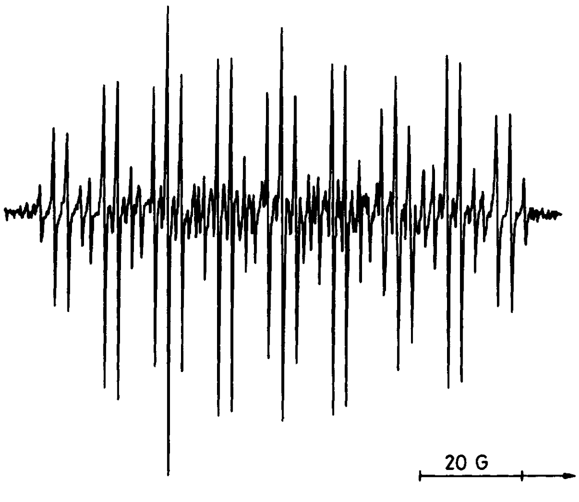


Figure 4. E.s.r. spectrum of the iminyl radical $D_3\bar{B}(H_3C)C{=}N\cdot$ produced by addition of $D_3B^{-\cdot}$ to methyl cyanide in Me_2O-Pe^{t}OH (1.3 : 1 v/v) at 250 K. Both ^{10}B- and ^{11}B-containing radicals are present. Some differential broadening, resulting from incomplete averaging of ^{11}B hyperfine anisotropy is evident

In an attempt to determine the importance of the reaction of methyl radicals with H_4B^- or $H_3\bar{B}CN$ under our e.s.r. conditions, azomethane was photolysed [equation (xiii)] in the presence of TBAB or TBAC, respectively, in Me_2O-Pe^{t}OH solution. Only Me· was detected between 180 and 260 K with either TBAB or TBAC and hydrogen abstraction from the borohydrides or addition to $H_3\bar{B}CN$ to give $H_3\bar{B}(H_3C)C{=}N\cdot$ must be slow under the conditions employed. Above 270 K, Me· was not detectable and weak, complex spectra which could be due to hydrazyl-type radicals were observed. This may indicate that hydrogen abstraction takes place at the

---

* It was shown by g.l.c. that the Bu^{t}CN contained no Bu^{t}NC.

Table 4. E.s.r. parameters for iminyl radicals formed by addition of $H_3B^{-\cdot}$ or H_2BCN^- to alkyl cyanides in Me_2O–Pe^tOH (1.3 : 1 v/v)

Radical	T/K	g Factor	Hyperfine splittings (G) [a]
$D_3\bar{B}(H_3C)C{=}N\cdot$ [b,c]	252	2.0026	9.9 (1N), 2.7 (3H), 22.6 ($1^{11}B$), 7.5 ($1^{10}B$)
$D_3\bar{B}(H_3C)^{13}C{=}N\cdot$	252	2.0026	13.7 ($1^{13}C$) [d]
$D_3\bar{B}(H_3{}^{13}C)C{=}N\cdot$	252	2.0026	49.3 ($1^{13}C$) [d]
$H_2(CN)\bar{B}(H_3C)C{=}N\cdot$	285	2.0027	9.7 (1N), 2.6 (3H), 0.7 (2H), 26.2 ($1^{11}B$)
$H_3\bar{B}(MeCH_2)C{=}N\cdot$	210	2.0027	9.9 (1N), 2.9 (2H), 0.3 (6H), 23.1 ($1^{11}B$)
$H_2(CN)\bar{B}(MeCH_2)C{=}N\cdot$	250	2.0028	9.8 (1N), 2.8 (2H), 0.5 (2H), 26.2 ($1^{11}B$)
$(H_3C)_2C{=}N\cdot$ [e]	220	2.0029	9.6 (1N), 1.4 (6H)
$H_3C(H)C{=}N\cdot$ [e]	220	2.0028	9.6 (1N), 77.1 (1H), 2.6 (3H)

[a] Numbers of equivalent nuclei shown in parentheses. [b] The γ-proton splitting was unresolved for $H_3\bar{B}(H_3C)C{=}N\cdot$, although the line-width (0.5 G) was greater than that (0.3 G) for the deuteriated analogue. [c] In Me_2O–$MeOCH_2CH_2OMe$ (1 : 1 v/v) at 252 K, a(1N) 9.7, a(3H) 2.7, $a(1^{11}B)$ 23.1 G. [d] Other splittings as for $D_3\bar{B}(H_3C)C{=}N\cdot$. [e] Data from ref. 21.

higher temperatures to give borane anions which subsequently add to the azomethane, but the result is ambiguous since the spectra could not be analysed and the extent of possible reaction between the azomethane and the borohydrides was not known.

(iv) *Reaction with alkyl isocyanides.* t-Butoxyl radicals add to alkyl isocyanides to form imidoyl radicals (17) which

$$Bu^tO\cdot + RN{=}C \longrightarrow \underset{(17)}{RN{=}\dot{C}OBu^t} \longrightarrow RNCO + Bu^t\cdot \tag{xiv}$$

$$Et_3Si\cdot + RN{=}C \longrightarrow \underset{(18)}{RN{=}\dot{C}SiEt_3} \longrightarrow Et_3SiCN + R\cdot \tag{xv}$$

$$H_3B^{\bar{\cdot}} + RN{=}C \longrightarrow R\cdot + H_3\bar{B}CN \tag{xvi}$$

$$H_2\dot{B}CN^- + RN{=}C \longrightarrow R\cdot + H_2\bar{B}(CN)_2 \tag{xvii}$$

undergo rapid β-scission above *ca.* 220 K to give t-butyl radicals and an alkyl isocyanate.[22] Trialkylsilyl radicals add in a similar way, but the imidoyl radical (18) undergoes very ready β-scission to give trialkylsilyl cyanide and an alkyl radical.

Photolysis of Bu^tOOBu^t in the presence of TBAB (0.5M) and methyl isocyanide (1.5M) in Me_2O–Pe^tOH afforded only the spectrum of the methyl radical, even at 170 K, and neither $MeN{=}\dot{C}OBu^t$ nor $Bu^t\cdot$ were detected. Similarly, with n-butyl isocyanide $Bu^n\cdot$ was detected between 170 and 290 K. During the reaction of $H_3B^{-\cdot}$ with Bu^tNC, spectra of both $Bu^t\cdot$ and $H_3B^{-\cdot}$ were observable between 160 and 200 K, whilst above 200 K only the spectrum of $Bu^t\cdot$ was apparent. These results indicate that $H_3B^{-\cdot}$ reacts with the isocyanides to give an alkyl radical, and presumably, cyanoborohydride. Any intermediate imidoyl radical $RN{=}\dot{C}\bar{B}H_3$, if formed, must be very short-lived. Assuming that (17) does not rapidly abstract hydrogen from H_4B^- at 170 K, the results also imply that $Bu^tO\cdot$ reacts more rapidly with H_4B^- than with RNC.

When Bu^tOOBu^t was photolysed in the presence of TBAC and MeNC spectra of both $Me\cdot$ and $H_2\dot{B}CN^-$ could be observed. At 168 K only $H_2\dot{B}CN^-$ was detectable, whereas at higher temperatures both radicals were present until at *ca.* 250 K only $Me\cdot$ was detected. Photolysis of Bu^tOOBu^t or Pe^tOOPe^t in the presence of TBAC and Bu^tNC gave rise to both $H_2\dot{B}CN^-$ and $Bu^t\cdot$, with the latter radical predominant above 240 K. These results show that $H_2\dot{B}CN^-$ also displaces $R\cdot$ from RNC [equation (xvii)]. With Bu^tNC after prolonged photolysis at 290 K, when the temperature was subsequently reduced to 250 K, a spectrum showing $a(^{11}B)$ 12.9, a(2N) 2.4, and a(1H) 16.1 G was observed. We tentatively assign this spectrum to $H\dot{B}(CN)_2^-$, formed by abstraction of hydrogen from $H_2\bar{B}(CN)_2$.

(v) *Reaction with alkyl halides.* The reactions of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ with a number of alkyl halides (each *ca.* 2M) were investigated in Me_2O–Pe^tOH solvent, usually between 170 and 290 K.

Both $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ failed to react with n-propyl or n-octyl fluoride at rates sufficient to give detectable concentrations of the appropriate alkyl radical and only the borane radical anions were detected. Similarly, $H_2\dot{B}CN^-$ failed to react with primary, secondary, or tertiary alkyl chlorides (Pr^nCl, Pr^iCl, Bu^tCl) up to 295 K. In contrast, when $H_3B^{-\cdot}$ was generated in the presence of Pr^nCl, only $Pr^n\cdot$ was detected, even at 170 K, and hence reaction (xviii) is rapid at this temperature.

$$H_3B^{\bar{\cdot}} + Pr^nCl \longrightarrow Pr^n\cdot + H_3\bar{B}Cl \tag{xviii}$$

$$H_3\bar{B}Cl \rightleftharpoons BH_3 + Cl^- \tag{xix}$$

$$H_3B^{\bar{\cdot}} + R^1Hal \xrightarrow{k_1} R^1\cdot + H_3\bar{B}Hal \tag{xx}$$

$$H_3B^{\bar{\cdot}} + R^2Hal \xrightarrow{k_2} R^2\cdot + H_3\bar{B}Hal \tag{xxi}$$

$$(k_1/k_2) = [R^1\cdot][R^2Hal]/[R^2\cdot][R^1Hal] \tag{xxii}$$

$$R^1\cdot + R^2Br \longrightarrow R^2\cdot + R^1Br \tag{xxiii}$$

$$Bu^tO\cdot + Pr^n{}_3B \longrightarrow Pr^n\cdot + Pr^n{}_2BOBu^t \tag{xxiv}$$

$$Me_3Si\cdot + RHal \longrightarrow R\cdot + Me_3SiHal \tag{xxv}$$

Over the usual temperature range, both $H_3B^{\cdot}$ and $H_2\dot{B}CN^-$ reacted with Pr^nBr and Pr^nI sufficiently rapidly that the spectra of the radical anions were completely quenched and only $Pr^n\cdot$ was detected. Reaction of $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$ with ethyl, isopropyl, t-butyl, or cyclopentyl bromide also afforded the appropriate alkyl radical and the spectra of the borane anions were completely quenched at all temperatures.

Competition experiments were carried out to determine the relative reactivities of primary, secondary, and tertiary alkyl bromides and chlorides towards $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$. Ethyl, n-propyl, isopropyl, and t-butyl halides were studied and the n-propyl halide was used as the standard competitor since there is little overlap of the spectrum of $Pr^n\cdot$ with those of the other alkyl radicals.

The relative reactivity (k_1/k_2) of two halides towards $H_3B^{\cdot}$ [equations (xx) and (xxi)] will be related by equation (xxii) to the alkyl radical concentrations obtained during continuous photolysis, provided that $R^1\cdot$ and $R^2\cdot$ are removed only by radical–radical reactions which have effectively equal diffusion-controlled rate constants.[23] Reaction mixtures were kept at 77 K prior to photolysis and radical concentration ratios were extrapolated to zero photolysis time to circumvent problems arising from selective consumption of one halide by thermally or photochemically induced reactions with

Table 5. Relative rate constants [a] for abstraction of halogen from pairs of alkyl halides in Me_2O–Pe^tOH (1.3 : 1 v/v) at 203 K

Attacking radical	Bromides k_{Et}/k_{Pr^n}	k_{Pr^i}/k_{Pr^n}	k_{Bu^t}/k_{Pr^n}	Chlorides k_{Bu^t}/k_{Pr^n}
$H_3B^{-\cdot}$	1.0	1.0	1.2	2.4
$H_2\dot{B}CN^-$	1.5	2.0	5.1	
$Me_3Si\cdot$	1.1	1.7	3.4	14.0

[a] Estimated accuracy ±10%.

borohydride or borane anion. The relative rate constants obtained at 203 K are given in Table 5.

In order to eliminate some possible sources of error, a number of further experiments were carried out. Photolysis of a solution containing Pr^nBr, Bu^tOOBu^t, and norbornene (as a trap for bromine atoms, if formed) did not yield a detectable concentration of $Pr^n\cdot$ and the only spectrum observed was that of $MeO\dot{C}H_2$, formed by abstraction of hydrogen from Me_2O by $Bu^tO\cdot$. Thus, photochemical decomposition (direct or sensitized) of the alkyl bromide is unimportant. To show that the feasible bromine atom exchange reaction (xxiii) did not influence the steady-state concentrations of alkyl radicals, a mixture of $Pr^n{}_3B$ and Bu^tOOBu^t [together a source of $Pr^n\cdot$, see equation (xxiv)[24]] and Bu^tBr was photolysed in Me_2O–Pe^tOH. Only $Pr^n\cdot$ was detected at 203 K.

In experiments with Pr^nBr and Bu^tBr, variation by a factor of two of the total alkyl halide concentration for a fixed molar ratio had no significant effect on the relative concentrations of $Pr^n\cdot$ and $Bu^t\cdot$. With the same two halides, (k_1/k_2) was independent of $[Pr^nBr]/[Bu^tBr]$ in the range 1.0—3.0.

For comparison, similar competition experiments were carried out for the reactions of $Me_3Si\cdot$ with alkyl halides[25] [equation (xxv)] and the results obtained in Me_2O–Pe^tOH solvent are included in Table 5. The same reactivity of Pr^nBr relative to Bu^tBr was obtained in cyclopropane at 203 K.

Discussion

Formation of Borane Radical Anions.—The borohydride ion is isoelectronic with methane in which the C–H bond is relatively strong [$D(H_3C{-}H)$ 438 kJ mol^{-1}].[26] However, calculations have indicated that there is a steady decrease in $D(H_3M{-}H)$ across the isoelectronic series from H_4N^+ to H_4C to H_4B^- and $D(H_3\bar{B}{-}H)$ was predicted to be *ca.* 7 kJ mol^{-1} less than $D(H_3C{-}H)$, although the calculated absolute values of the bond dissociation enthalpies were too low.[27] Since $D(Bu^tO{-}H)$ is 440 kJ mol^{-1},[28] hydrogen abstraction from H_4B^- by $Bu^tO\cdot$ is probably exothermic by *ca.* 9 kJ mol^{-1}. The negative charge would be expected to facilitate hydrogen abstraction by an electrophilic radical because of favourable polar effects, which may be represented by a contribution from (19b) to the transition state.

$$Bu^tO\cdot\ \ H{-}\bar{B}H_3 \longleftrightarrow Bu^t\bar{O}{:}\ \ H\cdot\ BH_3$$

(19a) (19b)

A high rate of abstraction is in accord with our qualitative observations, since no competitive abstraction of hydrogen from the dimethyl ether co-solvent was detected when $[Me_2O]/[H_4\bar{B}]$ was *ca.* 14. Quantitative studies of hydrogen abstraction from various hydroborates are planned.

The extent of delocalisation of the unpaired electron in H_2BCN^- is similar to that in H_2CCN (see below) and it seems likely that $D(H_3\bar{B}{-}H) - D(H{-}\bar{B}H_2CN) \simeq D(H_3C{-}H) - D(H{-}CH_2CN) \simeq 49$ kJ mol^{-1}.[29] Thus, abstraction of hydrogen from $H_3\bar{B}CN$ will be more exothermic than from H_4B^- by *ca.* 49 kJ mol^{-1} although the polar effect represented by structure (19b) for attack on H_4B^- would be reduced by the presence of the electron-withdrawing CN group.

Methyl radicals probably abstract hydrogen from H_4B^- and $H_3\bar{B}CN$ relatively rapidly ($k > 10^3$ l mol^{-1} s^{-1}) above 270 K, but further studies of the reactions of different types of radical with H_4B^- and substituted analogues are clearly needed.

E.s.r. Spectra.—(i) *Borane radical anions.* The e.s.r. spectrum of $H_3B^{-\cdot}$ generated by γ-irradiation of borohydrides, has been observed previously in rigid matrices.[1,2] On the basis of the magnitudes of the boron and proton splittings, it was concluded that $H_3B^{-\cdot}$ is planar, as are the isoelectronic radicals $H_3C\cdot$ and $H_3N^{+\cdot}$.[1,2]

The contribution of the central atom 2*s* orbital to the SOMO is approximately constant (*ca.* 3%) for the radicals $H_3B^{-\cdot}$, $H_3C\cdot$, and $H_3N^{+\cdot}$, consistent with planar equilibrium geometries for all three species.[1,2] The magnitude of a(3H) increases steadily on going from $H_3B^{-\cdot}$ to $H_3N^{+\cdot}$, although the spin population of the H-1*s* orbital, which arises primarily from σ–π polarisation, remains approximately constant. This variation of a(3H) is thought to be due to an 'excess charge effect' that is, to a decrease in $|\psi(0)|^2$ for the H-1*s* orbital as the negative charge on hydrogen increases on going from $H_3N^{+\cdot}$ to $H_3B^{-\cdot}$.[30]

The energy required for pyramidal distortion of $H_3B^{-\cdot}$ would be expected[31] to be less than for $H_3C\cdot$ or $H_3N^{+\cdot}$ and thus the previous report[2] that $a(^{11}B)$ and a(3H) do not vary between 80 and 300 K is surprising, although the minimum linewidth was 3.5 G for the radical anion trapped in the solid state. Our solution spectra of $H_3B^{-\cdot}$ and $D_3B^{-\cdot}$ are much better resolved and permit accurate determination of the temperature dependence of the coupling constants.

Inspection of Table 1 and Figure 2 shows that $|a(^{11}B)|$ increases and $|a(3H)|$ decreases with increasing temperature and that $|a(^{11}B)|$ for $H_3B^{-\cdot}$ is larger than for $D_3B^{-\cdot}$ at the same temperature. Parallel trends are shown by $|a(^{13}C)|$ and $|a(3H)|$ for $H_3{}^{13}C\cdot$ and $D_3{}^{13}C\cdot$[32,33] and result from increased population of out-of-plane vibrational states, thus introducing H-1*s* and $^{11}B(^{13}C)$-2*s* character into the SOMO, as the temperature increases.

The fact that $H_3B^{-\cdot}$ carries a negative charge might be expected to result in significant sensitivity of its e.s.r. spectrum to environmental effects. Such effects are evident from the results given in Table 1 and Figure 2, but their magnitudes are small. The differences in coupling constants observed in Me_2O–Pe^tOH and Me_2O–EtOH solvent systems presumably arise from differences in hydrogen bonding of $H_3B^{-\cdot}$ to ROH and/or in anion–cation association.

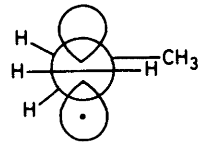
The cyanoborane radical anion is isoelectronic with $H_2\dot{C}CN$ and the e.s.r. parameters for both are consistent with a planar arrangement at the radical centre. Compared with $H_3B^{-\cdot}$, $a(^{11}B)$ is smaller and a(H) is slightly larger in $H_2\dot{B}CN^-$ and these differences probably reflect delocalisation of the unpaired electron onto nitrogen in the latter radical, as shown in (20; M = B^-), coupled with a reduction in the negative charge at H as a result of the presence of the electronegative CN group. Analogous delocalisation occurs in the cyanomethyl radical (20; M = C) and the similar magnitudes of a(N) for $H_2\dot{B}CN^-$ and $H_2\dot{C}CN$ suggest a similar extent of delocalisation for both.

$$H_2\dot{M}{-}C{\equiv}N \longleftrightarrow H_2M{=}C{=}N^{\cdot}$$

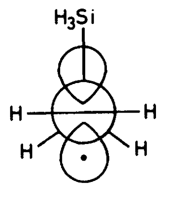
(20a) (20b)

The e.s.r. parameters [$a(^{11}B)$ 153, a(3F) 178 G] reported[3] for $F_3B^{-\cdot}$ indicate that this radical is strongly pyramidal like $F_3C\cdot$ [$a(^{13}C)$ 271.3, a(3F) 145.3 G][34] as a result of the presence of the three highly electronegative fluorine ligands and their associated non-bonding electron pairs.[35] Very recently, it has been reported[5] that $a(^{11}B)$ for $R_3B^{-\cdot}$ is strongly dependent on the nature of R [28.0 G (R = Bu^tCH_2), 38.5 G (R = Bu^t)] and this has been interpreted[5] as confirming that $X_3B^{-\cdot}$ is more easily pyramidalised than $X_3C\cdot$.

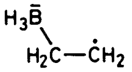
(ii) *β-Borylalkyl radicals and* 1-*borylcyclohexadienyl radicals.* The β-substituted ethyl radical produced by addition of $H_3B^{-\cdot}$ to ethylene adopts the eclipsed conformation (2). In contrast, the isoelectronic propyl radical prefers the staggered conformation (21)[36] and such a conformation is also adopted by the isoelectronic negatively charged radical $\bar{O}CH_2\dot{C}H_2$.[37] In fact, we know of no previous example of a β-substituted ethyl radical $XCH_2CH_2\cdot$ which preferentially adopts an eclipsed conformation when X is a first-row element. However, when X is a higher period element, the eclipsed conformation is generally favoured and the β-silylethyl radical adopts the conformation (22) analogous to (2).[36]



(21)

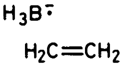


(22)



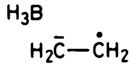
$\overset{H_3\bar{B}}{H_2C}-\dot{C}H_2$

(23a)



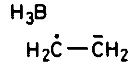
$\overset{H_3B^{\cdot-}}{H_2C=CH_2}$

(23b)



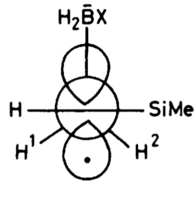
$\overset{H_3B}{H_2\bar{C}-\dot{C}H_2}$

(23c)

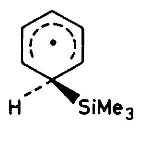


$\overset{H_3B}{H_2\dot{C}-\bar{C}H_2}$

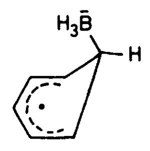
(23d)



(24)



(25)



(26)

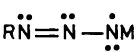
It is likely that the eclipsed conformation (2) is preferred because of an effective σ–π hyperconjugative interaction between the electrons forming the C–B bond and the unpaired electron formally centred on C_α.* This stabilising interaction would be maximised in the eclipsed conformation and would lead to transfer of spin density from C_α into the sp^3 hybrid orbital on boron and to transfer of negative charge to C_α and C_β, as illustrated by canonical structures (23a—d). The value of $a(^{11}B)$ corresponds to *ca.* 13% occupation of the B-sp^3 orbital by the unpaired electron.[38]

A similarly effective hyperconjugative interaction between the C–Si bond and the radical centre is probably responsible for the preferred eclipsed conformation of $H_3SiCH_2\dot{C}H_2$. In contrast, the hyperconjugative interaction with the β-C–C bond in the propyl radical is less effective and the balance between hyperconjugative and steric effects results in preference for the staggered conformation. These differences in hyperconjugative stabilisation energies can be related to the relative energies of the C_α-$2p_\pi$ orbital and the β-C–M σ bonding orbital (M = H_3C, H_3B^-, or H_3Si).

The e.s.r. parameters for the adducts (3) of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ to trimethylvinylsilane are also indicative of an eclipsed conformation (24; X = H or CN). At 225 K, rotation about the C_α–C_β bond averages the environments of H^1 and H^2 in (24), but at lower temperatures the central line of the β-proton triplet broadens relative to the outer lines, showing that rotational averaging is becoming slow on the e.s.r. time scale.

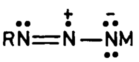
The adducts of $H_3B^{-\cdot}$ to benzene, pyridine, and substituted analogues exhibit spectra typical of cyclohexadienyl or azacyclohexadienyl radicals, characterised by large splittings from the proton and boron attached to C_1 and ring proton splittings that decrease in the order $a(H_p) > a(H_o) \gg a(H_m)$. The e.s.r. spectrum of (4) is very similar to that of (25)[39] and t-butyl, trimethylsilyl, and trifluoromethyl ring substituents have little effect on the spin distribution in (4). INDO calculations[40] predict that the ring is planar in the unsubstituted cyclohexadienyl radical, but that it is very easily deformed from planarity and 1-substituted cyclohexadienyl radicals appear to favour a conformation in which the ring is non-planar. A hyperconjugative interaction of the type described above for $H_3\bar{B}CH_2\dot{C}H_2$ should lead to a preference for the conformation (26) for (4) and a similar conformation has been suggested for the trimethylsilyl analogue (25) on the basis of *ab initio* molecular orbital calculations.[41]

(iii) *Triazenyl radicals.* The spectroscopic parameters of the triazenyl radicals (15) formed by addition of $H_3B^{-\cdot}$ or H_2BCN^- to alkyl azides are similar to those of $CH_3\overset{\frown}{NNN}CH_3$ (27)[42] and $CH_3\overset{\frown}{NNN}SiR_3$ (28)[21] which have been reported previously (see Table 3) and for which it is known that the central nitrogen gives rise to the largest splitting. The implication is that (15), like (27) and (28), is a σ radical in which the unpaired electron resides in a three-centre antibonding orbital in the plane of the three nitrogen atoms and is principally associated with the central atom.[42] The contributions from the canonical structures (29d and f) would be expected to be particularly important when M is a σ-donor–π-donor X_3B^- group. Coupling to only two of the three nitrogen nuclei was resolved for (15) and, on account of the relatively large splittings from the protons attached to boron, it seems reasonable to conclude that the coupling to the alkylated



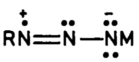
$R\ddot{N}=\ddot{N}-\underset{\cdot\cdot}{\dot{N}}M$

(29a)



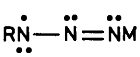
$R\ddot{N}=\overset{+}{\dot{N}}-\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}M$

(29c)



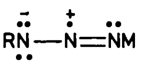
$R\overset{+}{\dot{N}}=\ddot{N}-\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}M$

(29e)



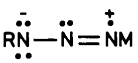
$R\underset{\cdot\cdot}{\dot{N}}-\ddot{N}=\ddot{N}M$

(29b)



$R\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}-\overset{+}{\dot{N}}=\ddot{N}M$

(29d)



$R\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}-\ddot{N}=\overset{+}{\dot{N}}M$

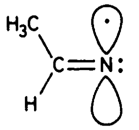
(29f)

---

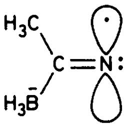
* We cannot eliminate the possibility that steric effects are also partly responsible for the conformational preference, because the effective bulk of the $H_3\bar{B}$ substituent may be increased by solvent and ion association.

nitrogen is unresolved. When M is a σ-donor–π-acceptor R_3Si group, (29c) would be predicted to be particularly important, because of the ability of silicon to stabilise the negative charge on an adjacent nitrogen, leading to an increase in spin density on the central nitrogen compared with that in $R\overbrace{NNN}^{\cdot}R$.

(iv) *Iminyl radicals.* The SOMO of an iminyl radical is a σ-orbital to which an N-2*p* atomic orbital makes the major contribution. There is appreciable hyperconjugative spin transfer into the β-bonds, which eclipse the N-$2p_\sigma$ orbital, and the value of $a(H_\beta)$ in (30) indicates *ca.* 15% transfer into the H-1*s* orbital. Assuming sp^3 hybridisation of the β-carbon and -boron in (31), the ^{13}C and ^{11}B coupling constants imply *ca.* 18% and 12% transfer onto C and B, respectively.[38] These results are somewhat surprising since both MINDO/3–UHF calculations [43] and qualitative ideas about the abilities of $C{-}CH_3$ and $C{-}\bar{B}H_3$ bonds to enter into hyperconjugation (see above) suggest that (31) might adopt a distorted structure in which $\widehat{BCN}$ is significantly less than $\widehat{CCN}$, with a consequently larger spin density on boron than on the methyl carbon. The e.s.r. parameters for $D_3\bar{B}(H_3C)C{=}N\cdot$ are similar in Me_2O–Pe^tOH and in the aprotic Me_2O–$MeOCH_2CH_2OMe$ (see Table 4), indicating that solvent effects are not of crucial importance.



(30)



(31)

Reactivities of Borane Radical Anions.—The decay mechanisms of the borane radical anions in the absence of added reactants are not known with certainty. Since a gas (presumably hydrogen) was evolved during photolysis, especially at higher temperatures, the basicity of the solution probably increases progressively.

Methyl radicals undergo dimerisation to give ethane at the diffusion controlled rate in solution. The analogous dimerisation * of $H_3B^{-\cdot}$ would yield the diborane dianion $[B_2H_6]^{2-}$ which, although not well authenticated, has been proposed previously as an intermediate in the reaction of sodium with diborane.[44] In a medium capable of providing a proton, particularly in the presence of an alcohol, $H_3B^{-\cdot}$ could decay *via* the unstable species $H_4B\cdot$ [45] which might give $H_2B\cdot$ and H_2 or transfer a hydrogen atom leaving BH_3.

In the reactions of borane radical anions with alkenes, arenes, and alkyl azides, cyanides, isocyanides, and halides the unifying theme throughout is the similarity in reactivities of $H_3B^{-\cdot}$ and $H_3Si\cdot$ (where known) or $R_3Si\cdot$ and the lower reactivity shown by $H_3C\cdot$. Similarities between $X_3B^{-\cdot}$ and $X_3Si\cdot$ might be expected in view of the similarly high strengths of the bonds which boron and silicon form to electronegative elements. The ionisation potential of $H_3B^{-\cdot}$, although unknown and likely to be dependent on environmental factors, must be relatively low and certainly much smaller than that of $H_3C\cdot$ (9.8 eV).[46] Thus, borane radical anions would be expected to show marked nucleophilic character, as do trialkylsilyl radicals.[46] Differences in behaviour between $H_3B^{-\cdot}$ and $R_3Si\cdot$ might arise because the H_3B^- group will be a π-donor, whilst the R_3Si ligand is a π-acceptor.

The majority of the adducts of borane radical anions were short-lived and their detection by e.s.r. spectroscopy implies a high efficiency of production. Quantitative kinetic studies of the reactions of borane radical anions will be reported in subsequent papers.

Whilst $H_3B^{-\cdot}$ adds readily to both ethylene and trimethylvinylsilane, $H_2\dot{B}CN^-$ adds only to the latter. Addition of $H_3B^{-\cdot}$ is probably more exothermic than addition of the stabilised $H_2\dot{B}CN^-$ (see above). Addition to trimethylvinylsilane will be more exothermic than addition to ethylene and the π-electron-withdrawing Me_3Si group would be expected to facilitate addition of the nucleophilic borane anions. Methyl radicals do not add to ethylene or to trimethylvinylsilane under the same conditions,[47] whilst $H_3Si\cdot$ adds readily to ethylene [36,48] and, presumably, to trimethylvinylsilane. Trimethylsilyl radicals add readily to both alkenes.[36,47]

Whilst $H_3B^{-\cdot}$ and $Me_3Si\cdot$ [39] add readily to benzene, $H_3C\cdot$ does not add under the same conditions. Addition of $H_3B^{-\cdot}$ to benzene will be more exothermic than addition of $H_2\dot{B}CN^-$ and the latter reaction was not detected. Electron-withdrawing substituents accelerate and electron-donating substituents retard addition to the benzene ring, as expected, and the rate of addition of $H_3B^{-\cdot}$ increases in the order $PhCMe_3 < PhH < PhCF_3$. The nucleophilic character of $H_3B^{-\cdot}$ is also evidenced by its regioselective addition to the *meta*-position of $PhCMe_3$, but to the *para*-position of $PhCF_3$. Addition of the nucleophilic dimethyl-n-propylsilyl radical to $PhCF_3$ takes place at the *meta*- and *para*-positions (40 and 60%, respectively), but not at the *ortho*-position, and it has been suggested that the rate of *para*-addition compared with that of *meta*-addition increases with the addendum nucleophilicity.[49] The Me_3Si group is a π-electron-withdrawing substituent and, as expected, addition of $H_3B^{-\cdot}$ to $PhSiMe_3$ is more rapid than to $PhCMe_3$ and appears to afford mainly the *para*-adduct.

Polar effects are also apparent in the addition of $H_3B^{-\cdot}$ to pyridine, which occurs more rapidly than the reaction with benzene. Addition takes place most rapidly at the electron deficient 4-position and, when this is blocked by a t-butyl group, at the 2-position. Methyl radicals do not add to pyridine under the same conditions. The *N*-silylpyridinyl radical was detected by e.s.r. spectroscopy as the product of reaction of $Me_3Si\cdot$ with pyridine. This difference in behaviour of $Me_3Si\cdot$ and $H_3B^{-\cdot}$ may be related to the fact that the silyl group is a π-acceptor while the H_3B^- substituent will be a π-donor. Steric effects prevent addition of $Me_3Si\cdot$ to nitrogen in 2,6-di-t-butylpyridine and addition to carbon takes place at the 4-position.

Addition of $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$ to the terminal nitrogen of an alkyl azide gives a 1,3-triazenyl radical. Trialkylsilyl radicals add in a similar fashion,[21] but addition of alkyl radicals is not detectable under the same conditions. It seems likely that electron donation to the electrophilic azide (SOMO–LUMO interaction [46]) is important in the transition state for addition of the more nucleophilic radicals. Similarly, whilst $H_3B^{-\cdot}$ adds readily to nitriles to give iminyl radicals, addition of methyl radicals is undetectable by e.s.r. spectroscopy. Addition of $H_2\dot{B}CN^-$ is slower than that of $H_3B^{-\cdot}$ and this would be predicted on the basis of both polar and thermodynamic considerations. The rate of β-scission of (32) [equation (xxvi)] increases in the order R = Me < Et < Bu^t as the strength of the R–C bond decreases.

It is possible that $H_3B^{-\cdot}$ is involved in the reactions of borohydrides with nitroso-compounds to give nitroxides of the type $RN(\dot{O})\bar{B}H_3$.[50]

Both $H_3B^{-\cdot}$ and $R_3Si\cdot$ react rapidly with alkyl isocyanides to bring about displacement of an alkyl radical and an

---

* Because of electrostatic repulsion, self-reaction of two negatively charged radicals will be slower than the corresponding reaction of two neutral radicals.

intermediate imidoyl adduct is detectable in the reactions with $R_3Si\cdot$.[22] Again, $H_2\dot{B}CN^-$ is less reactive than $H_3B^{-\cdot}$ and steric effects are apparent since Bu^{t}NC reacts less readily than MeNC. Alkyl radicals do not react with isocyanides under the same conditions.[22] It is likely that a transient imidoyl adduct $RN{=}\dot{C}\bar{B}H_2X$ is involved in the reactions of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ with RNC, although the reactions could be formulated as electron transfer processes leading to an unstable isocyanide radical anion which rapidly breaks down.


$$R(H_3\bar{B})C{=}N^{\bullet} \longrightarrow R^{\bullet} + H_3\bar{B}CN \qquad \text{(xxvi)}$$

(32)

Electron transfer from $H_3B^{-\cdot}$ or $H_2\dot{B}CN^-$ to the reactant must also be important in the reactions of the borane radical anions with alkyl halides. The reductions of organic halides to hydrocarbons using borohydrides or borohydride derivatives are well known reactions, most of which are thought to proceed by heterolytic hydride transfer pathways.[9,10,51] However, a radical chain mechanism has been proposed to account for the reduction of *gem*-dibromonorcarane (33) to a mixture of *cis*- and *trans*-7-bromonorcarane (35) (see Scheme).[7] It was also suggested that the borohydride reduction of carbon tetrachloride to chloroform and dichloromethane might proceed by a homolytic mechanism.[7]

The reduction of chloro-, bromo-, or iodo- (but not fluoro-) benzene by sodium borohydride may be initiated photochemically (254 nm) in aqueous acetonitrile at room temperature. Benzene is produced in high yield with a quantum efficiency often considerably in excess of unity. A similar radical chain sequence was proposed involving reactions (xxvii) and (xxiii).[6] Because of favourable polar and thermodynamic factors, both the phenyl radical [equation (xxiii)] and the α-bromocyclopropyl radical (34) (see Scheme) probably abstract hydrogen from H_4B^- more rapidly than do simple alkyl radicals.

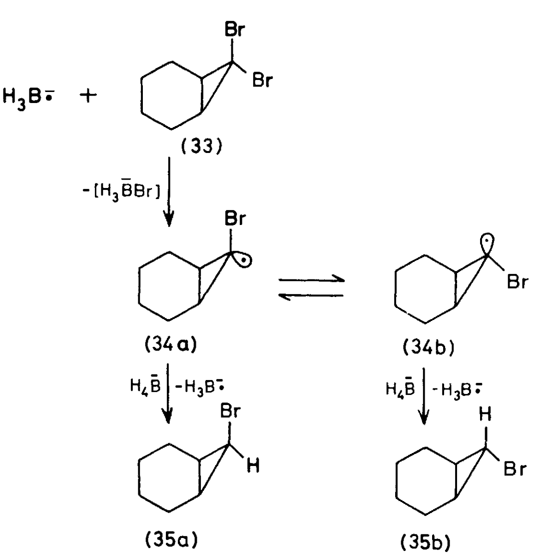
$$H_3B^{-\cdot} + PhX \longrightarrow Ph^{\bullet} + H_3\bar{B}X \qquad \text{(xxvii)}$$

$$Ph^{\bullet} + H_4B^- \longrightarrow PhH + H_3B^{-\cdot} \qquad \text{(xxviii)}$$

$$H_3B^{-\cdot} + RBr + {:}S \longrightarrow R^{\bullet} + Br^- + H_3BS \qquad \text{(xxix)}$$

Our e.s.r. experiments have confirmed that $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ react rapidly with alkyl bromides and iodides to give the corresponding alkyl radicals, although neither react with primary alkyl fluorides. Whilst $H_3B^{-\cdot}$ reacts similarly with primary, secondary, or tertiary alkyl chlorides, $H_2\dot{B}CN^-$ does not. Again, there is a parallel between the reactivities of the borane radical anions and silyl radicals: alkyl radicals do not abstract halogen from alkyl halides (except from iodides [52]) under similar conditions.

The reaction of $H_3B^{-\cdot}$ with primary, secondary, and tertiary alkyl bromides is very unselective, whilst $H_2\dot{B}CN^-$ exhibits a selectivity similar to that of $Me_3Si\cdot$. Consistent with its low selectivity, our qualitative observations indicate that the reactions of $H_3B^{-\cdot}$ with alkyl chlorides, bromides, and iodides are very rapid. Halogen abstraction by trialkylstannyl radicals is also rapid and relatively unselective and it has been proposed that there is an appreciable degree of electron transfer to the alkyl halide in the transition state for these reactions.[53,54] However, the differences between ' single electron transfer ' processes and ' atom abstraction ' reactions are often rather subtle,[55] and, although there is undoubtedly a significant degree of electron transfer in the transition state for the reactions of $H_3B^{-\cdot}$ and $H_2\dot{B}CN^-$ with alkyl halides, the extent of B-Hal bond formation is difficult to determine. It is possible, especially in the donor solvents employed, that the solvent plays a part in the reaction and that the initial product is a solvent–borane complex [see equation (xxix)].



Scheme

The reactions of $H_2\dot{B}CN^-$ with RHal to give R· and $H_2\bar{B}$(CN)Hal or H_2BCN + Hal^- will be less exothermic than the corresponding reactions of $H_3B^{-\cdot}$ because of the lower *homolytic* dissociation enthalpy of the B-Hal bond, as a consequence of conjugative stabilisation of $H_2\dot{B}CN^-$ relative to $H_3B^{-\cdot}$, or because of the higher ionisation potential of $H_2\dot{B}CN^-$, respectively.

Conclusions.—The chemistry of complex hydrides is of enormous practical importance, as judged from the rapidly increasing volume of literature concerning the uses in synthesis of boro- and alumino-hydrides.[56] The vast majority of these reactions are considered to be heterolytic in nature, but the question posed by our present results is to what extent are borane and alane [57] radical anions involved in these reactions? An understanding of reaction mechanism is essential for the design of new reagents of potential synthetic importance. Much work remains to be done to establish qualitative and quantitative reactivities of different borane and alane [57] radical anions and to determine the rates of their formation by reaction of various types of radical with hydro-borates and -aluminates.

Experimental

E.s.r. Spectrscopy.—Spectra were recorded using Varian E-4 or E-109 spectrometers operating at *ca.* 9.2 GHz. The techniques used for sample preparation and for the detection of transient free radicals generated photochemically or thermally in the spectrometer cavity have been described previously.[11] Decay kinetics for photochemically generated radicals were measured by computer-averaging of a large number of signal decay curves produced by positioning a rotating sectored disc in the light path.[14]

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 a standard.[58] When second-order effects were significant, 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.[13]

Materials.—Tetra-n-butylammonium borohydride [9] and cyanoborohydride [10] were prepared by published methods from the sodium salts. $Bu^n{}_4NBD_4$ was prepared in a similar way from $NaBD_4$ in D_2O–NaOD. Lithium borohydride (BDH) and trimethylsilane (PCR) were used as received.

Di-t-butyl peroxide was purified [59] before use and di-t-pentyl peroxide,[60] di-t-butyl hyponitrite,[12] azomethane,[61] and tri-n-propylborane [62] were prepared using published methods.

The solvents, alkenes, arenes, pyridines, nitriles, and n- and t-butyl isocyanides were commercial materials which were purified if necessary. The alkyl chlorides, bromides, and iodides were carefully distilled middle fractions; n-octyl fluoride (Fluka) was used as received and n-propyl fluoride was prepared as described in the literature,[63] as were methyl isocyanide,[64] 1-adamantyl,[65] t-butyl,[21,66] n-hexyl,[67] isopropyl,[67] and methyl azides.[68]

Acknowledgements

We are very grateful to Dr. K. F. Preston (N.R.C. Ottawa) for providing us with a copy of his computer program ESRLSQ and to Dr. J. E. Parkin (U.C.L.) for adapting this program to run on the University of London CDC 7600 computer. We thank the S.E.R.C. for support and the Royal Society and the University of London Central Research Fund Committee for grants to purchase equipment.

References

1 R. C. Catton, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc. A*, 1969, 2622.
2 E. D. Sprague and F. Williams, *Mol. Phys.*, 1971, **20**, 375.
3 R. L. Hudson and F. Williams, *J. Chem. Phys.*, 1976, **65**, 3381.
4 J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan, and D. S. Miller, *J. Am. Chem. Soc.*, 1970, **92**, 6825.
5 A. Berndt, H. Klusik, and K. Schlüter, *J. Organomet. Chem.*, 1981, **222**, C25.
6 J. A. Barltrop and D. Bradbury, *J. Am. Chem. Soc.*, 1973, **95**, 5085.
7 J. T. Groves and K. W. Ma, *J. Am. Chem. Soc.*, 1974, **96**, 6527.
8 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 360.
9 A. Brändström, U. Junggren, and B. Lamm, *Tetrahedron Lett.*, 1972, 3173.
10 R. O. Hutchins and D. Kandasamy, *J. Am. Chem. Soc.*, 1973, **95**, 6131.
11 J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 161 and references contained therein.
12 H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 1966, 6163.
13 D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975.
14 K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Am. Chem. Soc.*, 1971, **93**, 902; R. W. Dennis and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1975, 140.
15 J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189.
16 H. Zeldes, R. Livingston, and J. S. Bernstein, *J. Magn. Reson.*, 1976, **21**, 9.
17 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938; S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organomet. Chem.*, 1969, **16**, P36.
18 B. Schroeder, W. P. Neumann, J. Hollaender, and H.-P. Becker, *Angew. Chem. Int. Ed. Engl.*, 1972, **11**, 850; S. V. Ponomarev, H.-P. Becker, W. P. Neumann, and B. Schroeder, *Liebig's Ann. Chem.*, 1975, 1895.
19 T. N. Mitchell, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1149.
20 D. Griller, K. Dimroth, T. M. Fyles, and K. U. Ingold, *J. Am. Chem. Soc.*, 1975, **97**, 5526.
21 B. P. Roberts and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1353.
22 P. M. Blum and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1313.
23 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1971, 1823.
24 A. G. Davies and B. P. Roberts, *Chem. Commun.*, 1969, 699; P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3942.
25 A. Hudson and R. A. Jackson, *Chem. Commun.*, 1969, 1323.
26 M. H. Baghal-Vayjooee, A. J. Colussi, and S. W. Benson, *J. Am. Chem. Soc.*, 1978, **100**, 3214.
27 M.-B. Krogh-Jespersen, J. Chandrasekhur, E.-U. Würthwein, J. B. Collins, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1980, **102**, 2263.
28 J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 5417.
29 K. D. King and R. D. Goddard, *J. Phys. Chem.*, 1976, **80**, 546.
30 M. C. R. Symons, *Nature (London)*, 1969, **224**, 686; T. A. Claxton, *ibid.*, 1970, **226**, 1242.
31 T. A. Claxton in 'Electron Spin Resonance,' ed. R. O. C. Norman, The Chemical Society, London, 1973, vol. 1, p. 199.
32 R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74.
33 I. A. Zlochower, W. R. Miller, jun., and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 3339; H. Fischer and H. Hefter, *Z. Naturforsch., Teil A*, 1968, **23**, 1763.
34 R. W. Fessenden, *J. Magn. Reson.*, 1969, **1**, 277.
35 L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767; P. J. Krusic and R. C. Bingham, *J. Am. Chem. Soc.*, 1976, **98**, 230.
36 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 846.
37 Y. Kirino, *J. Phys. Chem.*, 1975, **79**, 1296.
38 P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.
39 M. Kira and H. Sakurai, *Chem. Lett.*, 1981, 927.
40 M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, 1975, **97**, 1004.
41 M. Kira and H. Sakurai, *Chem. Lett.*, 1982, 221.
42 J. C. Brand and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 748.
43 P. Bischof, *J. Am. Chem. Soc.*, 1976, **98**, 6844.
44 W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Am. Chem. Soc.*, 1956, **78**, 689; 1958, **80**, 1828; E. L. Muetterties, 'The Chemistry of Boron and its Compounds,' Wiley, New York, 1967, p. 252.
45 J. H. Baxendale, A. Breccia, and M. D. Ward, *Int. J. Rad. Phys. Chem.*, 1970, **2**, 167; M. C. R. Symons, *ibid.*, 1976, **8**, 381.
46 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, London, 1976, ch. 5.
47 J. A. Baban, Ph.D. Thesis, London, 1979.
48 K. Y. Choo and P. P. Gaspar, *J. Am. Chem. Soc.*, 1974, **96**, 1284.
49 H. Sakurai in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch. 25.
50 M. Crozet and P. Tordo, *J. Am. Chem. Soc.*, 1980, **102**, 5696; *Inorg. Chim. Acta*, 1981, **53**, L57.
51 H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, 1969, **34**, 3923; F. Rolla, *ibid.*, 1981, **46**, 3909; R. O. Hutchins, D. Kandasamy, C. A. Maryanoff, D. Masilamini, and B. E. Maryanoff, *ibid.*, 1977, **42**, 82; R. O. Hutchins and N. R. Natale, *Org. Prep. Procedures Int.*, 1979, **11**, 201; H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, 1973, **95**, 1670 and references cited in these papers.
52 A. L. Castelhano, P. R. Marriott, and D. Griller, *J. Am. Chem. Soc.*, 1981, **103**, 4262.
53 J. J. Barber and G. M. Whitesides, *J. Am. Chem. Soc.*, 1980, **102**, 239.
54 E. V. Blackburn and D. D. Tanner, *J. Am. Chem. Soc.*, 1980, **102**, 692.
55 J. K. Kochi, *Pure Appl. Chem.*, 1980, **52**, 571.
56 See 'Ventron Alembic,' ed. R. C. Wade, Thiokol/Ventron, Danvers, issues 1—23.
57 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 1167.
58 B. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191; R. Allendorfer, *ibid.*, 1971, **55**, 165.
59 J. Q. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 5363.
60 N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, 1946, **68**, 643.

61 R. Renaud and L. C. Leitch, *Can. J. Chem.*, 1952, **32**, 545.
62 L. H. Long and D. Dollimore, *J. Chem. Soc.*, 1953, 3902.
63 W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, 1955, **77**, 4899.
64 R. E. Schuster, J. E. Scott, and J. Casanova, jun., *Org. Synth.*, 1966, **46**, 75.
65 T. Sasaki, S. Eguchi, T. Katada, and O. Hiroaki, *J. Org. Chem.*, 1977, **42**, 3741.
66 J. A. Miller, *Tetrahedron Lett.*, 1975, 2959.
67 E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, 1957, **22**, 654.
68 J. Bragin, S. Chan, E. Mazzola, and H. Goldwhite, *J. Phys. Chem.*, 1973, **77**, 1506.

Received 12*th March* 1982; *Paper* 2/435