

## Homolytic Reactions of Ligated Boranes. Part 6.<sup>1</sup> Electron Spin Resonance Studies of Dialkyl Sulphide-Boryl Radicals

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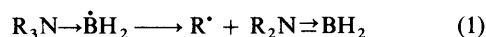
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Hydrogen-atom abstraction by  $\text{Bu}^t\text{O}^\bullet$  or  $(\text{Me}_3\text{Si})_2\text{N}^\bullet$  from dialkyl sulphide-boranes ( $\text{R}_2\text{S}\rightarrow\text{BH}_3$ ;  $\text{R} = \text{Me}$  or  $\text{Et}$ ) gives the corresponding dialkyl sulphide-boryl radicals ( $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$ ), the structures and reactions of which have been studied in solution using e.s.r. spectroscopy. The equilibrium geometry at the radical centre in  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  appears to be planar or very nearly so, as evidenced by the  $^{11}\text{B}$  and  $\text{H}_\alpha$  hyperfine coupling constants and by the effect of deuterium substitution at boron. Sulphide-boryl radicals undergo ready  $\beta$ -scission [equation (A)], in common with the amine-boryls  $\text{R}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$  but in marked contrast to



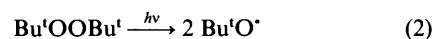
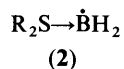
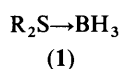
the phosphine-boryls  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$ . Sulphide-boryl radicals abstract halogen rapidly from alkyl bromides and, at 197 K, *t*-butyl bromide reacts with  $\text{Me}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  2.6-times more rapidly than *n*-propyl bromide. Approximate rate coefficients for the formation and transformation of sulphide-boryl radicals have been obtained from competition experiments. *Ab initio* molecular orbital calculations at the 6-31G\*\* level for sulphide-, phosphine-, and amine-boryl radicals and for related species provide a basis for interpretation of the experimental results.

The borane radical anion  $\text{H}_3\text{B}^{\bullet-}$ , which is isoelectronic with the methyl radical, is the simplest member of a family of ligated boryl radicals  $\text{L}\rightarrow\dot{\text{B}}\text{H}_2$ .<sup>2</sup> We have recently investigated the structural and chemical properties of a number of ligated boryl radicals in which L is a neutral Lewis base, in particular an amine<sup>3-7</sup> or a phosphine.<sup>1,7,8</sup> The borane radical anion and the amine- and phosphine-boryl radicals exhibit metalloidal properties in their reactions with molecules and often resemble silyl radicals more closely than alkyl radicals, in accord with the diagonal relationship between boron and silicon in the Periodic Table. However, unlike alkylsilyl radicals, alkylamine-boryl radicals undergo  $\beta$ -scission [equation (1)] readily<sup>1,3,4,6</sup> and



more rapidly than the isoelectronic alkyl radicals  $\text{R}_3\text{C}\rightarrow\dot{\text{C}}\text{H}_2$ . By contrast,  $\beta$ -scission of phosphine-boryl radicals  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$  is very much slower and has yet to be observed.<sup>1,8</sup>

The equilibrium geometry of the borane radical anion is planar,<sup>2,9,10</sup> like that of  $\text{H}_3\text{C}^\bullet$ , although out-of-plane deformation is not energetically demanding. Replacement of hydride by an amine to give  $\text{R}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$  is accompanied by pyramidalisation at boron,<sup>3-5</sup> whilst planarity appears to be maintained in the phosphine-boryl radicals,<sup>8</sup>  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$ . Other Lewis bases, such as dialkyl sulphides, isocyanides, and carbon monoxide, which effectively complex borane would also be expected to form stable adducts with  $\text{H}_2\text{B}^\bullet$ , and in the present paper we report e.s.r. studies of dialkyl sulphide-boryl radicals (2;  $\text{R} = \text{Me}$  or  $\text{Et}$ ), produced by hydrogen-atom abstraction from the corresponding sulphide-boranes (1).



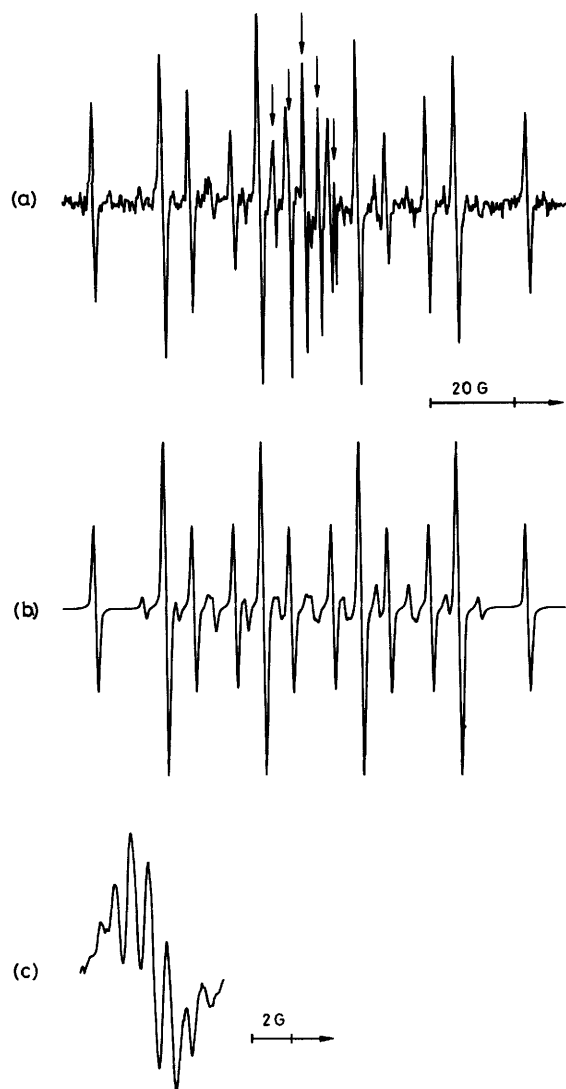
### Results

Sulphide-boranes were prepared by passing diborane into a small excess of the dialkyl sulphide. Removal of uncomplexed sulphide and any solvent under reduced pressure left the

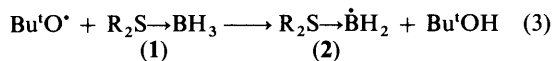
essentially pure sulphide-borane which was identified by  $^1\text{H}$  and  $^{11}\text{B}$  n.m.r. spectroscopy. Dimethyl sulphide-borane<sup>11,12</sup> is well known as a hydroborating reagent,<sup>13,14</sup> and diethyl sulphide-borane<sup>12</sup> has also been characterised previously. The sulphide-boranes used in our work contained  $^{11}\text{B}$  (*I* 3/2, 80.2 atom%) and  $^{10}\text{B}$  (*I* 3, 19.8 atom%) in natural abundance, excepting  $(\text{CD}_3)_2\text{S}\rightarrow\text{BD}_3$  which was prepared enriched in  $^{11}\text{B}$  (97.5 atom%).

E.s.r. spectra were recorded during continuous u.v. irradiation of static samples positioned in the microwave cavity of the spectrometer. Photolysis of either dimethyl or diethyl sulphide-borane in dimethyl ether-cyclopropane solvent (1.1:1 v/v) afforded no e.s.r. signals between 150 and 293 K.† Photolysis of di-*t*-butyl peroxide (DTBP) (*ca.* 15% v/v) in the presence of a dialkyl sulphide-borane (1;  $\text{R} = \text{Me}$ ,  $\text{CD}_3$ , or  $\text{Et}$ ) (*ca.* 1.5M) in cyclopropane, dimethyl ether-cyclopropane (1.1:1 v/v), or oxirane-cyclopropane (1:1 v/v) solvent below *ca.* 200 K gave rise to a strong e.s.r. spectrum of the corresponding alkyl radical  $\text{R}^\bullet$ . At the very low temperatures which could be attained without crystallisation using the mixed solvents, a second spectrum was evident for each sulphide-borane. The latter spectra showed splittings from  $^{11}\text{B}$  (21.4–23.3 G) and from two equivalent protons (16.4–16.6 G), along with further small proton splittings when  $\text{R} = \text{Me}$  or  $\text{Et}$ ; the *g*-factors were *ca.* 2.0017, somewhat less than the free-spin value (2.0023). For each sulphide-borane, the intensity of the second spectrum increased at the expense of that of  $\text{R}^\bullet$  as the temperature was decreased, supporting assignment of the former to the sulphide-boryl radical (2),  $\beta$ -scission of which provides the source of alkyl radicals [equations (2)–(4)].

† The methyl radical is detectable during u.v. irradiation of solutions containing dimethyl sulphide at low temperature; the spectrum of the ethyl radical is not observed in corresponding experiments with diethyl sulphide.<sup>15</sup> Photolysis of di-*t*-butyl peroxide in the presence of either sulphide affords the e.s.r. spectrum of  $\text{RCH}_2\text{SCHR}$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ).<sup>16</sup>



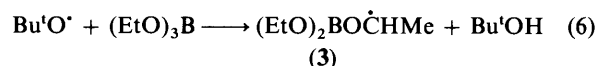
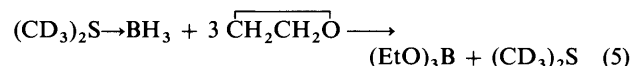
**Figure 1.** (a) E.s.r. spectrum at 154 K obtained during u.v. irradiation of DTBP and  $(\text{CD}_3)_2\text{S}\rightarrow\text{BH}_3$  in oxirane-cyclopropane (1:1 v/v). The arrows mark positions of the five most intense lines from  $\text{D}_3\text{C}^*$ . (b) Computer simulation of the spectrum of  $(\text{CD}_3)_2\text{S}\rightarrow\text{BH}_2$ , including the contribution from the  $^{10}\text{B}$ -containing radical (the weaker lines), based on the splittings given in Table 1. The linewidth is 1.0 G and the lineshape is 50% Lorentzian (50% Gaussian). (c) Expansion of the first line in the spectrum of  $\text{Me}_2\text{S}\rightarrow\text{BH}_2$  at 152 K in dimethyl ether-cyclopropane (1.1:1 v/v)



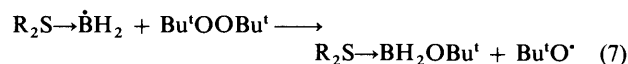
The spectrum of  $(2; \text{R} = \text{CD}_3)$  is shown in Figure 1a and its computer simulation, including the contribution from the  $^{10}\text{B}$ -containing species, is given in Figure 1b. The spectrum of  $(2; \text{R} = \text{Me})$  was less intense than that of the  $\text{C}$ -deuteriated analogue, because of the further fine structure resulting from coupling to the six equivalent methyl protons [ $a(6 \text{H}_\alpha)$  0.85 G, see Figure 1c], and was also partially obscured by that of the methyl radical. The sulphide-boryl radical  $(2; \text{R} = \text{Et})$  evidently undergoes  $\beta$ -scission more readily than  $(2; \text{R} = \text{Me}$  or  $\text{CD}_3)$  and its spectrum was less intense than that of the ethyl

radical even at very low temperatures (*ca.* 140 K). The  $\text{CH}_2\text{S}$  protons in  $(2; \text{R} = \text{Et})$  are diastereotopic and thus non-equivalent if the geometry at sulphur is pyramidal, as it almost certainly is. Because of the low intensity of the spectrum, the fine structure resulting from coupling to the methylene protons could not be conclusively identified as a 1:2:1 triplet or a 1:4:6:4:1 quintet, although the former is the more likely, implying that the splitting from one proton of each  $\text{CH}_2$  group is 1.4 G whilst that from the other is unresolved ( $\leq \text{ca. } 0.5 \text{ G}$ ). The e.s.r. parameters for all the sulphide-boryl radicals identified in this work, including the perdeuteriated species  $(\text{CD}_3)_2\text{S}\rightarrow\text{BD}_2$  which was generated by atom abstraction from  $(\text{CD}_3)_2\text{S}\rightarrow\text{BD}_3$  in order to provide further evidence for the equilibrium geometry of sulphide-boryls, are gathered in Table 1.

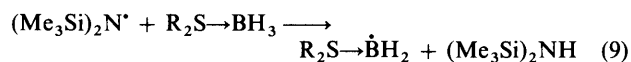
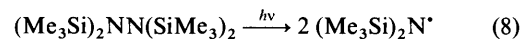
Oxirane is a good solvent for the sulphide-boranes (1) and is also relatively unreactive towards *t*-butoxyl radicals.<sup>17</sup> Epoxides are reduced by sulphide-boranes,<sup>13</sup> but the reactions between oxirane and compound (1) proved to be sufficiently slow to permit the former to be used as a solvent at low temperatures. A sample containing DTBP and compound (1;  $\text{R} = \text{CD}_3$ ) in cyclopropane-oxirane (1:1 v/v) which had been left to stand at 270 K for two days prior to photolysis afforded neither the radical  $(2; \text{R} = \text{CD}_3)$  nor  $\text{CD}_3^*$ , but instead a spectrum which we attribute to the radical (3) [ $a(1\text{H}_\alpha)$  18.7,  $a(3\text{H}_\beta)$  23.6,  $a(^{11}\text{B})$  0.45 G,  $g$  2.0030 at 227 K] formed by hydrogen abstraction from triethyl borate [equations (5) and (6)].<sup>18</sup>



Above *ca.* 200 K, spectra of the alkyl radicals derived from fragmentation of the radicals  $(2)$  were weak, sample lifetimes were short, and a gas (presumably hydrogen) was evolved. After a sample containing compound (1;  $\text{R} = \text{Et}$ ) and DTBP in cyclopropane had been irradiated with u.v. for *ca.* 10 min at 260 K, spectra of the radical  $(2; \text{R} = \text{Et})$  and  $\text{Et}^*$  were not detectable when the temperature was subsequently lowered. Instead, a relatively weak spectrum [ $a(1 \text{H})$  17.4 and  $a(3 \text{H})$  21.2 G,  $g$  2.0037 at 175 K], probably due to a radical of the type  $\text{CH}_3\dot{\text{C}}(\text{H})\text{SBX}_2$ , was observed. These results suggest the occurrence at higher temperatures of a chain process which leads to the rapid destruction of compound (1); such a reaction would ensue from reduction of DTBP by the radical  $(2)$  according to equation (7). Reaction (7) could involve electron transfer or  $\text{S}_{\text{H}}2$  displacement at oxygen; the ligated borane produced will probably lose dialkyl sulphide readily.



U.v. photolysis of tetrakis(trimethylsilyl)hydrazine<sup>19</sup> (*ca.* 10% w/v) in the presence of compound (1) at low temperatures also afforded spectra of the radical  $(2)$  and  $\text{R}^*$  [equations (8) and (9)], although the intensities were lower than those obtained from DTBP. However, spectra of the alkyl radicals  $\text{R}^*$  were observable up to much higher temperatures (295 K for  $\text{Et}^*$



derived from  $\text{Et}_2\text{S}\rightarrow\text{BH}_3$ ) than when the more easily reduced

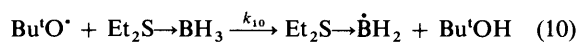
Table 1. E.s.r. parameters for dialkyl sulphide-boryl radicals

Radical	Solvent <sup>a</sup>	T/K	g-factor	Hyperfine splittings (G)			d a(X) /dT (mG K <sup>-1</sup> )
				a( <sup>11</sup> B)	a(2 H <sub>α</sub> ) <sup>b</sup>	Others	
(CD <sub>3</sub> ) <sub>2</sub> S→ $\dot{B}H_2$	A	133	2.0018	22.95	16.58		+8 ( <sup>11</sup> B), -2 (H <sub>α</sub> )
		152	2.0018	23.24	16.58		
		153	2.0018	23.12	16.55		
		178	2.0017	23.32	16.51		
(CD <sub>3</sub> ) <sub>2</sub> S→ $\dot{B}D_2$	A	132	2.0017	21.72	2.6		+11 ( <sup>11</sup> B)
		151	2.0017	21.93	2.55		
		151	2.0017	22.13	2.58		
		177	2.0017	22.22	2.55		
		195	2.0017	22.60	2.56		
Me <sub>2</sub> S→ $\dot{B}H_2$	B	149	2.0017	23.2	16.6	0.85 (6 H <sub>γ</sub> )	
Et <sub>2</sub> S→ $\dot{B}H_2$	A	150	2.0017	21.4	16.4	1.4 (2 H <sub>γ</sub> ) <sup>c</sup>	

<sup>a</sup> A = Dimethyl ether-cyclopropane (1:1 v/v); B = oxirane-cyclopropane (1:1 v/v). <sup>b</sup> Or a(2 D<sub>α</sub>). <sup>c</sup> See text.

DTBP was the primary radical source, supporting the involvement of reaction (7).

The rate of hydrogen abstraction by t-butoxyl radicals from diethyl sulphide-borane was determined relative to that for the corresponding abstraction from dimethyl ether, which also served as the solvent. When β-scission of the radical (**2**; R = Et) is sufficiently rapid that its e.s.r. spectrum is undetectable, the value of [Et<sup>•</sup>]/[MeO $\dot{C}H_2$ ], measured during continuous u.v. irradiation, will be given by equation (12), as the rate coefficients for self- and cross-reactions of the two carbon-centred radicals will be effectively equal.<sup>20,21</sup> The radical concentration ratio

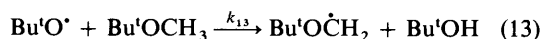


$$(k_{10}/k_{11}) = [Et^{\bullet}][Me_2O]/[MeO\dot{C}H_2][Et_2S \rightarrow BH_3] \quad (12)$$

was extrapolated to zero photolysis time to overcome problems arising from selective reagent depletion. At 165 K, with initial concentrations of Et<sub>2</sub>S→BH<sub>3</sub> and Me<sub>2</sub>O equal to 0.72 and 12.3M, respectively, the value of (k<sub>10</sub>/k<sub>11</sub>) was found to be 38.3.

The reactivity of Et<sub>2</sub>S→BD<sub>2</sub> compared with that of Me<sub>2</sub>O was determined by the same method and the deuterium isotope effect (k<sub>10</sub><sup>H</sup>/k<sub>10</sub><sup>D</sup>) was found to be 2.8 at 165 K.

The absolute value of k<sub>11</sub> at 165 K is not available, but we have recently reported measurements of k<sub>13</sub> for hydrogen abstraction from t-butyl methyl ether [see equation (14) in which R = 8.314 × 10<sup>-3</sup> kJ mol<sup>-1</sup> K<sup>-1</sup>].<sup>22</sup> If we assume that



$$\log_{10}(k_{13}/1 \text{ mol}^{-1} \text{ s}^{-1}) = (8.1 \pm 0.5) - (12.6 \pm 2.0)/2.303 RT \quad (14)$$

k<sub>11</sub> = 2 k<sub>13</sub>, it follows that k<sub>10</sub> is 9.9 × 10<sup>5</sup> l mol<sup>-1</sup> s<sup>-1</sup> at 165 K and, if we further assume that the A factors for reactions (10) and (13) are similar, the activation energy for hydrogen abstraction from Et<sub>2</sub>S→BH<sub>3</sub> must be ca. 7 kJ mol<sup>-1</sup>.

The rate coefficients for β-scission of the sulphide-boryl radicals [equation (4)] may be estimated at temperatures sufficiently low that these radicals are detectable and when attack on the solvent is unimportant. At the steady state during continuous u.v. irradiation, equation (15) should hold provided that R<sup>•</sup> is removed only by self-reaction and cross-reaction with the radical (**2**) and that the rate coefficients for these two

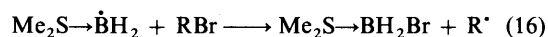
processes are effectively equal (to 2 k<sub>t</sub>).<sup>21,23</sup> Experiments were carried out in oxirane-cyclopropane solvent (1:1 v/v) for

$$k_4 = 2 k_t [R^{\bullet}] \{1 + [R^{\bullet}]/[R_2S \rightarrow \dot{B}H_2]\} \quad (15)$$

compound (**1**; R = Me, CD<sub>3</sub>, or Et) at 151 K and 2 k<sub>t</sub> for all three alkyl radicals was assumed to be equal to that for self-reaction of allyl radicals in propene-DTBP (2.0 × 10<sup>9</sup> l mol<sup>-1</sup> s<sup>-1</sup> at 151 K) derived from the data of Hefter *et al.*<sup>24</sup>

The rate coefficients for β-scission of the radicals (**2**) obtained by this method were 1.1 × 10<sup>2</sup> s<sup>-1</sup> (R = CD<sub>3</sub>), 4.8 × 10<sup>2</sup> s<sup>-1</sup> (R = Et), and 9.9 × 10<sup>1</sup> s<sup>-1</sup> (R = Me); the last result is the least reliable as every line of Me<sup>•</sup> overlaps with a line of the sulphide-boryl. If we assume that the A-factors for β-scission of the radicals (**2**) are the same as that (10<sup>12.5</sup> s<sup>-1</sup>) measured<sup>6</sup> for the analogous β-scission of Pr<sup>i</sup><sub>2</sub>EtN→ $\dot{B}H_2$ , the activation energies will be 30.2 kJ mol<sup>-1</sup> (R = CD<sub>3</sub> or Me) and 28.4 kJ mol<sup>-1</sup> (R = Et), compared with 32.7 kJ mol<sup>-1</sup> for the amine-boryl radical.

*Reactions of Sulphide-Boryl Radicals with Alkyl Halides.*—These were investigated by including the halide (1.5M) in the sample along with the sulphide-borane and DTBP; the solvent was cyclopropane-oxirane (1:1 v/v). With n-propyl or t-butyl bromide and compound (**1**; R = Me), strong spectra of Pr<sup>n</sup>• or Bu<sup>n</sup>•, respectively, were observed between 155 and 210 K; radical (**2**; R = Me) was undetectable at 155 K and only an exceedingly weak spectrum of Me<sup>•</sup> was observed with Pr<sup>n</sup>Br at 210 K. These results indicate that radical (**2**; R = Me) abstracts bromine from alkyl bromides [equation (16)] rapidly compared with the rate of its β-scission under the experimental conditions. The radicals (**2**; R = CD<sub>3</sub>) and (**2**; R = Et)



behaved similarly, although the more rapid β-scission of the latter was evidenced by a relatively high (though still very small in absolute terms) concentration of ethyl radicals in experiments with n-propyl bromide. Analogous experiments with n-propyl or t-butyl chloride and compound (**1**; R = Me) showed no evidence for halogen abstraction by the sulphide-boryl radical either at 155 or at 210 K.

The relative reactivities of Bu<sup>n</sup>Br and Pr<sup>n</sup>Br towards the radical (**2**; R = Me) were determined in competition experiments<sup>2-4</sup> and at 197 K in cyclopropane the value of [k<sub>16</sub>(Bu<sup>n</sup>Br)]/k<sub>16</sub>(Pr<sup>n</sup>Br) was found to be 2.58. U.v. irradiation

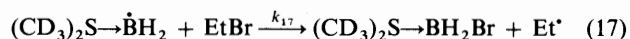
Table 2. E.s.r. parameters for ligated boryl radicals

Radical	L	Solvent <sup>a</sup>	T/K	g-factor	Hyperfine splittings (G)			d a(X) dT (mG K <sup>-1</sup> )	Ref.
					$a(^{11}\text{B})$	$a(2\text{H}_\alpha)^b$	Others		
L→ $\dot{\text{B}}\text{H}_2$	H	A	253	2.0023	19.9	15.2		+9 ( <sup>11</sup> B), -3 (H <sub>α</sub> )	c
	Me <sub>3</sub> N	B	280	2.0022	51.3	9.6	1.4 (N), 1.4 (9 H <sub>γ</sub> )		d
	Et <sub>3</sub> N	C	193	2.0023	47.5	12.9	2.2 (N), 2.2 (6 H <sub>γ</sub> )	0 ( <sup>11</sup> B), +3 (H <sub>α</sub> )	d
	Et <sub>3</sub> P	D	183	2.0020	17.6	16.8	43.6 (P)		e
	(MeO) <sub>3</sub> P	E	215	2.0019	14.7	16.6	43.9 (P)	+8 ( <sup>11</sup> B), -9 (P)	e
L→ $\dot{\text{B}}\text{D}_2$	D	A	253	2.0023	18.8	2.34		+9 ( <sup>11</sup> B)	c
	Me <sub>3</sub> N	B	280	2.0022	51.2	1.5	1.4 (N), 1.4 (9 H <sub>γ</sub> )		d
	Et <sub>3</sub> N	C	193	2.0023	48.2	2.0	2.2 (N), 2.2 (H <sub>γ</sub> )		d
	Et <sub>3</sub> P	D	183	2.0020	17.6	16.8	43.6 (P)		e
	(MeO) <sub>3</sub> P	E	215	2.0020	13.9	2.55	44.2 (P)	+10 ( <sup>11</sup> B), -5 (P)	e

<sup>a</sup> A = Me<sub>2</sub>O-Pe'OH (1.3:1 v/v); B = Bu'OH-Me<sub>2</sub>O (4:1 v/v); C = cyclopropane-tetrahydrofuran (3:1 v/v); D = oxirane; E = cyclopropane. <sup>b</sup> Or  $a(2\text{D}_\alpha)$ . <sup>c</sup> Ref. 2. <sup>d</sup> Ref. 3. <sup>e</sup> Ref. 8.

of solutions containing only sulphide-borane and alkyl bromide afforded no e.s.r. spectra.

The rate coefficient for halogen abstraction from ethyl bromide (0.61M) by the radical (2; R = CD<sub>3</sub>) [equation (17)] was determined relative to that for β-scission of the sulphide-boryl at 177 K in cyclopropane-oxirane (1:1 v/v). Making the usual assumption that the rate coefficients for self- and cross-reactions of Et<sup>•</sup> and CD<sub>3</sub><sup>•</sup> are effectively equal,<sup>20,21</sup> equation (18) should hold, in which [EtBr]<sub>0</sub> is the initial concentration of

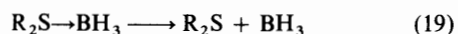


$$(k_{17}/k_4^{R=\text{CD}_3}) = [\text{Et}^{\cdot}]/[\text{CD}_3^{\cdot}][\text{EtBr}]_0 \quad (18)$$

ethyl bromide and [Et<sup>•</sup>]/[CD<sub>3</sub><sup>•</sup>] has the value corresponding to zero irradiation time. At 177 K, (k<sub>17</sub>/k<sub>4</sub><sup>R=CD<sub>3</sub></sup>) was found to be ca. 160 l mol<sup>-1</sup> and, as k<sub>4</sub><sup>R=CD<sub>3</sub></sup> is ca. 3.9 × 10<sup>3</sup> s<sup>-1</sup> at this temperature, it follows that k<sub>17</sub> is ca. 6.2 × 10<sup>5</sup> l mol<sup>-1</sup> s<sup>-1</sup>. An activation energy of ca. 12 kJ mol<sup>-1</sup> may be derived for reaction (17) if the A-factor is assumed to be the same as that (10<sup>9.3</sup> l mol<sup>-1</sup> s<sup>-1</sup>) for abstraction of bromine from n-pentyl bromide by triethylsilyl radicals.<sup>25</sup> Similar measurement of the rate coefficient for halogen abstraction from n-propyl bromide by the radical (2; R = Et) at 171 K gave a value (1.2 × 10<sup>5</sup> l mol<sup>-1</sup> s<sup>-1</sup>) which is reasonably close to that obtained for k<sub>17</sub> considering the errors and approximations involved.

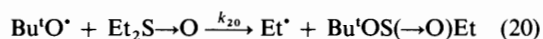
## Discussion

The sulphide-boranes (1) are less stable towards dissociation [equation (19)] than the analogous amine- or phosphine-boranes (R<sub>2</sub>N→BH<sub>3</sub> or R<sub>3</sub>P→BH<sub>3</sub>); ΔH<sub>19</sub> (R = Me or Et) is ca. +100 kJ mol<sup>-1</sup> in the gas phase.<sup>12,26</sup>

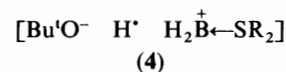


Although Paget and Smith<sup>27</sup> proposed that the reaction between compound (1; R = Me) and carbon tetrachloride to yield Me<sub>2</sub>S→BH<sub>2</sub>Cl proceeds by a radical chain mechanism and implied the intermediacy of the radical (2; R = Me), the literature appears to contain no explicit mention of sulphide-boryl radicals. The sulphide-borane R<sub>2</sub>S→BH<sub>3</sub> is isoelectronic with the sulphoxide R<sub>2</sub>S→O and with the phosphine R<sub>2</sub>P→CH<sub>3</sub>. t-Butoxyl radicals react at close to the encounter-controlled rate with trialkylphosphines<sup>28</sup> by addition to P to give an intermediate phosphoranyl radical, subsequent α-scission of which results in overall t-butoxydealkylation of the phosphine. Dialkyl sulphoxides react similarly [equation (20)] but much

more slowly, and Me<sub>2</sub>S→O undergoes t-butoxydealkylation at least 10-times more slowly than Et<sub>2</sub>S→O at 233 K.<sup>29</sup> In CF<sub>2</sub>ClCCl<sub>2</sub>F, the rate coefficient k<sub>20</sub> is ca. 1.9 × 10<sup>2</sup> l mol<sup>-1</sup> s<sup>-1</sup> at 165 K, compared with our estimate of 9.9 × 10<sup>5</sup> l mol<sup>-1</sup> s<sup>-1</sup>

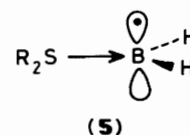


for k<sub>10</sub> at the same temperature. Attack by Bu'O<sup>•</sup> at sulphur in compound (1) is evidently much slower than abstraction of hydrogen from the BH<sub>3</sub> group. Polar factors will favour a low activation energy for reaction (10), since the alkoxy radical is highly electrophilic and the hydrogen atoms attached to boron will be relatively electron rich, and thus structure (4) should



make a significant contribution to the transition state. The relatively small isotope effect found for abstraction from diethyl sulphide-borane (k<sub>H</sub>/k<sub>D</sub> 2.8 at 165 K) is consistent with an early transition state in which there is little B-H bond breaking. Our value compares with that (2.2 at 165 K) extrapolated from the data of Griller *et al.*<sup>30</sup> for H-D-abstraction from (CH<sub>3</sub>)<sub>3</sub>N and (CD<sub>3</sub>)<sub>3</sub>N, which is also a very rapid reaction.

The <sup>11</sup>B hyperfine splittings for the radical (2) are much smaller than those for amine-boryl radicals under similar conditions (see Table 2). The value of a(<sup>11</sup>B) for radical (2; R = CD<sub>3</sub>) corresponds<sup>31</sup> to only 3.2% unpaired electron population of the B-2s orbital, such as would arise from spin-polarisation of the σ framework if the geometry at the radical centre is close to planar, as shown in structure (5). Effective planarity at boron is

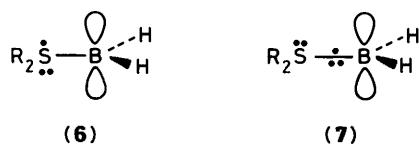


also indicated by the magnitude of a(2H<sub>α</sub>) (presumably negative in sign) which is appreciably greater than that for the pyramidal R<sub>3</sub>N→BH<sub>2</sub>. However, a(2H<sub>α</sub>) for the radical (2) is similar to the values found for R<sub>3</sub>P→BH<sub>2</sub> and H<sub>3</sub>B<sup>-</sup> (Table 2) for which it has been argued previously that the equilibrium geometries at the radical centres are planar.<sup>2,8-10,32</sup> The conformation about the SB bond could be such that the α-protons are equivalent; alternatively, if they are instantaneously non-equivalent either the difference in their splittings is too small to be resolved or rotation about the SB bond is fast on the e.s.r. timescale.

The temperature dependences of  $|a(^{11}\text{B})|$  and  $|a(2\text{H}_\alpha)|$  for the radicals (2) are similar in magnitude and have the same signs as those found for  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$  and  $\text{H}_3\text{B}^{\cdot-}$ ; they originate from the increase with temperature in the amplitude of out-of-plane motion at the radical centre. Furthermore, the smaller value of  $a(^{11}\text{B})$  found for  $(\text{CD}_3)_2\text{S}\rightarrow\dot{\text{B}}\text{D}_2$  compared with that for  $(\text{CD}_3)_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  at the same temperature is in accord with an effectively planar equilibrium geometry at boron.<sup>2,8</sup> However, the energy barrier to pyramidal distortion at boron is probably not large for either  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  or  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$ .

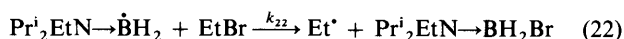
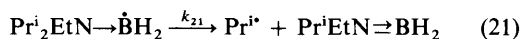
Replacement of  $\text{H}^-$  in  $\text{H}_3\text{B}^{\cdot-}$  by the more electronegative  $\text{R}_2\text{S}$  might be expected<sup>2,3,5</sup> to induce a change to a pyramidal equilibrium geometry at the boron radical centre. For the phosphine-boryl radicals, we have proposed the existence of a stabilising interaction between the unpaired electron on boron and an empty  $\pi^*$   $\text{R}_3\text{P}$  group orbital which would be maximised for the planar configuration. It appears likely that a similar interaction with an empty  $\text{R}_2\text{S}$  group orbital of appropriate symmetry could be responsible for the planar configurational preference shown by  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$ .

The sulphide-boryl radicals (2) may be regarded as 'ligand- $\pi$ ' sulphuranyl radicals by analogy with the electronic configurations identified for phosphoranyl radicals.<sup>8,33</sup> Excited states corresponding to hypervalent sulphuranyl radicals such as (6) or the  $\text{SB}\sigma^*$  species (7) may not be very far removed from the radical (5) in energy. Indeed, the remaining lone pair of



electrons on sulphur could be involved in dative  $\pi$  bonding with the empty  $2p$  orbital on boron to stabilise species (6) and (7). We have suggested that the low  $g$ -factors observed for  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$  (*ca.* 2.0020) are a consequence of the existence of an energetically accessible electronic configuration in which the unpaired electron occupies a  $\text{PB}\sigma^*$  orbital [*cf.* species (7)].<sup>8</sup> A similar explanation may be offered for the low  $g$ -factors shown by the radical (2), in which case  $g_{\text{min}}$  should be in the direction perpendicular to the S-B bond. However, it is feasible that admixture of electronic configurations in which there is unpaired electron population of P- or S- $3d$  orbitals could lead to the low  $g$ -factors observed and a similar interpretation, involving Sn- $5d$  orbitals, has been put forward to account for the low  $g$ -factor (2.0008) of  $\text{Me}_3\text{Sn}\dot{\text{C}}\text{H}_2$ .<sup>34</sup>

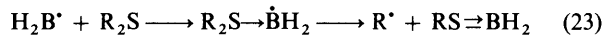
In common with other ligated boryl radicals, the sulphide-boryls abstract halogen efficiently from alkyl bromides. The preference for attack on  $\text{Bu}^1\text{Br}$  rather than on  $\text{Pr}^n\text{Br}$  is not large; this is consistent with the high absolute reactivity of  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  which appears to be comparable to that of  $\text{R}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ . Thus, our data<sup>3</sup> for the competition between  $\beta$ -scission of  $\text{Pr}^i_2\text{EtN}\rightarrow\dot{\text{B}}\text{H}_2$  and its abstraction of halogen from ethyl bromide [equations (21) and (22)] may be combined with absolute measurements<sup>6</sup> of  $k_{21}$  to give  $k_{22}$  as *ca.*  $2.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  at



255 K. If we assume that the  $A$ -factor for reaction (22) is the same as that<sup>25</sup> ( $10^{9.3} \text{ l mol}^{-1} \text{ s}^{-1}$ ) for abstraction of bromine from *n*-pentyl bromide by triethylsilyl radicals, the corresponding activation energy would be 9.7  $\text{kJ mol}^{-1}$  and the value of  $k_{22}$  extrapolated to 177 K would be  $2.8 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$  (*cf.*  $k_{17} = 6.2 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$  at 177 K). The reactivities of

$\text{R}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$  and  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  in bromine-atom abstraction are similarly high, but they are still less reactive than  $\text{Et}_3\text{Si}^{\cdot}$ , which abstracts halogen from *n*-pentyl bromide at close to the encounter-controlled rate.<sup>25</sup> Phosphine-boryl radicals are probably appreciably less reactive than the amine- and sulphide-boryls.<sup>8</sup> Abstraction of halogen from alkyl chlorides by  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  is much slower than the corresponding reaction with alkyl bromides, but the ready  $\beta$ -scission of the sulphide-boryls obscures comparison with  $\text{R}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$  and  $\text{R}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$ .

The sulphide-boryl radical (2) would presumably be an intermediate in the (unknown) homolytic dealkylation of a dialkyl sulphide by  $\text{H}_2\text{B}^{\cdot}$  [equation (23)] and the similarly



metalloidal triethylsilyl radical is known<sup>35</sup> to bring about analogous dealkylation, although intermediate sulphuranyl adducts have not been identified. The relative rates of  $\beta$ -scission of  $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$  ( $\text{R} = \text{Et} > \text{R} = \text{Me}$ ) presumably reflect the strengths of the C-S bonds undergoing cleavage.  $\beta$ -Scission of both the sulphide-boryls is somewhat faster than that of  $\text{Pr}^i_2\text{EtN}\rightarrow\dot{\text{B}}\text{H}_2$ , when a secondary C-N bond is broken, and much faster than that of  $\text{Me}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$  or  $\text{Et}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ .<sup>3</sup>  $\beta$ -Scission of  $\text{Et}_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$ , or even of  $\text{Bu}^1_3\text{P}\rightarrow\dot{\text{B}}\text{H}_2$ , does not take place at a detectable rate even at relatively high temperatures<sup>8</sup> and the rate of  $\beta$ -cleavage of  $\text{R}_n\text{D}\rightarrow\dot{\text{B}}\text{H}_2$  ( $\text{D} = \text{N, P, S}$ ) appears to increase as the fragmentation becomes more favourable thermodynamically (see below). The boron-containing products,  $\text{R}_{n-1}\text{D}\rightarrow\text{BH}_2$ , exist as dimers, trimers, or larger oligomers at ambient temperature when  $\text{R} = \text{Me}$  or  $\text{Et}$ , but when  $\text{R}$  is a bulky group the monomeric aminoborane  $\text{R}_2\text{N}\rightarrow\text{BH}_2$  is stable.<sup>36-38</sup> Dative  $p_\pi-p_\pi$  bonding between D and B is clearly important for  $\text{R}_2\text{N}\rightarrow\text{BH}_2$  and  $\text{RS}\rightarrow\text{BH}_2$ ,<sup>39-41</sup> but the part played by  $\pi$  bonding in monomeric  $\text{R}_2\text{P}\rightarrow\text{BH}_2$  does not appear to have been assessed.

**Molecular Orbital Calculations.**—To gain further insight into the structures and stabilities of sulphide-boryl radicals, and to facilitate comparisons with amine- and phosphine-boryls, we have carried out a series of *ab initio* MO calculations for protic parents using the GAUSSIAN 82 program in conjunction with the 6-31G\*\* basis set.<sup>42</sup> Molecular geometries were fully optimised, within any prescribed constraints, by minimisation of the Hartree-Fock (HF) energy. The nature of each stationary point (local minimum, transition state, *etc.*) was determined by computing the normal vibrational frequencies, and zero-point vibrational energies were evaluated for structures corresponding to local minima on the potential energy surface.\* Singlet states were investigated using spin-restricted (RHF) theory, while spin-unrestricted (UHF) theory was used for doublet states (radicals). The effects of electron correlation were assessed by single-point calculations at the HF/6-31G\*\* geometries using Møller-Plesset perturbation theory at third order (MP3). Inner shell orbitals were included in these calculations which may be denoted MP3(full)/6-31G\*\*//HF/6-31G\*\*. The results are summarised in Tables 3 and 4.

**Hydrogen Sulphide-Boryl Radical ( $\text{H}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$ ).**—At the UHF level, the  $C_1$  structure (8) is slightly more stable (by 3.3  $\text{kJ mol}^{-1}$ ) than the  $C_s$  structure (10). Both (8) and (10) are strongly pyramidal at boron ( $\phi$  63.8°) and correspond to local energy

\* Vibrational frequencies obtained from this type of calculation are generally about 11% too large and attempts are sometimes made to correct ZPVEs for this (see *e.g.* W. J. Bouma, J. M. Dawes, and L. Radom, *Org. Mass Spectrom.*, 1983, 18, 12).

**Table 3.** GAUSSIAN 82 energies and dipole moments for sulphide- and phosphine-boryl radicals and for related species

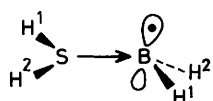
Molecule	Symmetry	HF/6-31G** energy (Hartrees) <sup>a</sup>	ZPVE (kJ mol <sup>-1</sup> )	MP3/6-31G** energy (Hartrees) <sup>a</sup>	Dipole moment (D)
(8)	C <sub>1</sub>	-424.433 389	102.7	-424.703 175	3.98
(9)	C <sub>s</sub>	-424.431 564	<i>b</i>	-424.705 394	3.86
(10)	C <sub>s</sub>	-424.432 125	101.7	-424.697 346	3.73
(11)	C <sub>s</sub>	-424.423 347	<i>b</i>	-424.694 002	4.31
(13)	C <sub>s</sub>	-368.237 339	128.8	-368.501 322	3.88
(14)	C <sub>s</sub>	-368.236 865	<i>b</i>	-368.500 984	3.87
(15)	C <sub>s</sub>	-368.236 704	<i>b</i>	-368.500 775	3.90
(12)	C <sub>s</sub>	-423.958 193	84.3	-424.217 473	1.09
(16)	C <sub>s</sub>	-367.710 357	105.1	-367.961 110	0.92
H <sub>3</sub> N→BH <sub>3</sub> <sup>c</sup>	C <sub>3v</sub>	-82.624 973	194.0 <sup>d</sup>	-82.950 418	5.54
H <sub>3</sub> P→BH <sub>3</sub>	C <sub>3v</sub>	-368.862 804	158.2	-369.153 287	4.53
H <sub>2</sub> S→BH <sub>3</sub>	C <sub>s</sub>	-425.071 575	126.2	-425.357 811	2.13
H <sup>e</sup>		-0.498 233		-0.498 233	

<sup>a</sup> 1 Hartree = 2 625.5 kJ mol<sup>-1</sup>. <sup>b</sup> One negative normal vibrational frequency. <sup>c</sup> MP3 (frozen core) calculation. <sup>d</sup> The ZPVEs for H<sub>3</sub>N→BH<sub>2</sub> and H<sub>2</sub>N→BH<sub>2</sub> are 162.9 and 133.4 kJ mol<sup>-1</sup>, respectively; these were not reported in ref. 4.

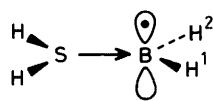
**Table 4.** GAUSSIAN 82 optimised geometries of sulphide- and phosphine-boryl radicals and of related species

Molecule	Geometry <sup>a</sup>
(8)	SB 1.998, BH <sup>1</sup> 1.189, BH <sup>2</sup> 1.189, SH <sup>1</sup> 1.327, SH <sup>2</sup> 1.337, H <sup>1</sup> BS 110.74, H <sup>2</sup> BS 106.59, H <sup>1</sup> BH <sup>2</sup> 125.76, H <sup>1</sup> SB 103.32, H <sup>2</sup> SB 111.69, H <sup>1</sup> SH <sup>2</sup> 94.12
(9)	SB 1.894, BH <sup>1</sup> 1.182, BH <sup>2</sup> 1.182, SH 1.338, H <sup>1</sup> BS 116.74, H <sup>2</sup> BS 111.20, H <sup>1</sup> BH <sup>2</sup> 132.06, HSB 109.69, HSH 92.89
(10)	SB 2.143, BH 1.192, SH 1.327, HBS 102.13, HBH 123.16, HSB 102.48, HSH 94.99
(11)	SB 1.981, BH 1.181, SH 1.331, HBS 111.18, HBH 137.64, HSB 104.68, HSH 94.68
(13)	PB 1.887, BH 1.188, PH <sup>1</sup> 1.409, PH <sup>2</sup> 1.393, HBP 115.54, HBH 126.53, H <sup>1</sup> PB 124.23, H <sup>2</sup> PB 114.50, H <sup>2</sup> PH <sup>2</sup> 102.25
(14)	PB 1.880, BH 1.187, PH <sup>1</sup> 1.407, PH <sup>2</sup> 1.394, HBP 116.19, HBH 127.63, H <sup>1</sup> PB 123.00, H <sup>2</sup> PB 115.22, H <sup>2</sup> PH <sup>2</sup> 102.33
(15)	PB 1.881, BH <sup>1</sup> 1.187, BH <sup>2</sup> 1.186, PH <sup>1</sup> 1.402, PH <sup>2</sup> 1.391, H <sup>1</sup> BP 117.46, H <sup>2</sup> BP 114.96, H <sup>1</sup> BH <sup>2</sup> 127.64, H <sup>1</sup> PB 113.09, H <sup>2</sup> PB 120.20, H <sup>1</sup> PH <sup>2</sup> 100.99, H <sup>2</sup> PH <sup>2</sup> 97.94
(12)	SB 1.791, BH <sup>1</sup> 1.183, BH <sup>2</sup> 1.184, HS 1.328, H <sup>1</sup> BS 121.20, H <sup>2</sup> BS 116.52, H <sup>1</sup> BH <sup>2</sup> 122.29, HSB 100.26
(16)	PB 1.902, BH 1.187, PH 1.400, HBP 119.82, HBH 119.99, HPB 103.15, HPH 99.49
H <sub>3</sub> N→BH <sub>3</sub> <sup>b</sup>	NB 1.680, BH 1.209, NH 1.004, HNB 110.57, HBN 104.39, HNH 108.28, HBH 114.04
H <sub>3</sub> P→BH <sub>3</sub> <sup>c</sup>	PB 2.022, BH 1.205, PH 1.393, HPB 117.34, HBP 103.14, HPH 100.58, HBH 114.99
H <sub>2</sub> S→BH <sub>3</sub> <sup>d</sup>	SB 2.682, BH <sup>1</sup> 1.190, BH <sup>2</sup> 1.190, SH 1.327, HSB 101.03, H <sup>1</sup> BS 94.62, H <sup>2</sup> BS 93.43, HSH 94.67, H <sup>1</sup> BH <sup>2</sup> 119.58, H <sup>2</sup> BH <sup>2</sup> 119.53

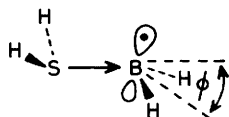
<sup>a</sup> Bond lengths in Å, bond angles in degrees. <sup>b</sup> Experimental structure; R. D. Suenram and L. R. Thorne, *Chem. Phys. Lett.*, 1981, **78**, 157. <sup>c</sup> Experimental structure: J. R. Durig, Y. S. Li, L. A. Carriera, and J. D. Odom, *J. Am. Chem. Soc.*, 1973, **95**, 2491. <sup>d</sup> The BH<sup>1</sup> bond is *anti* to the sulphur lone pair.



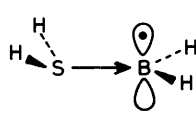
(8)



(9)



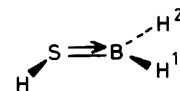
(10)



(11)

We conclude that the equilibrium geometry of H<sub>2</sub>S→BH<sub>2</sub> is probably planar or nearly planar at boron, although the amplitude of out-of-plane vibration could be quite large at normal temperatures and this motion may well be coupled to rotation about the SB bond.

*Thioborane* (HS⇌BH<sub>2</sub>).—All the atoms in the computed structure (12) were coplanar at the RHF level, in agreement

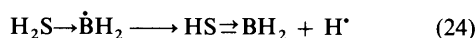


(12)

minima, unlike structures (9) and (11) which are constrained to be planar at boron and are less stable than the corresponding pyramidal structures by 4.8 and 23.0 kJ mol<sup>-1</sup>, respectively. However, inclusion of electron correlation changes the order of stability, making the C<sub>s</sub> structure (9) the most stable of the four and more stable than (8) by 5.8 kJ mol<sup>-1</sup> at the MP3 level. The pyramidal structure (10) remains more stable than (11), but by only 8.8 kJ mol<sup>-1</sup>.

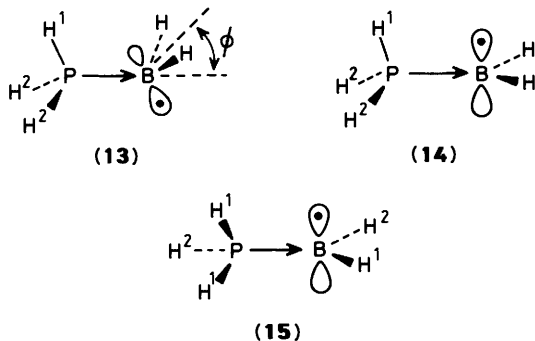
with earlier calculations using a smaller basis set;<sup>40</sup> the SB bond was shorter (by 0.10 Å) than that in H<sub>2</sub>S→BH<sub>2</sub>. The energy change associated with β-scission of radical (9) [equation (24)] was estimated to be -45.5 kJ mol<sup>-1</sup> at the MP3 level, using the 6-31G\*\* energy for the hydrogen atom and taking account of zero-point vibrational energy (ZPVE) contribu-

tions.\* As the SC bond in MeSH is 70 kJ mol<sup>-1</sup> weaker than the



SH bond,<sup>43</sup> the corresponding  $\beta$ -cleavage of  $\text{Me}_2\text{S} \rightarrow \dot{\text{B}}\text{H}_2$  should be an highly exothermic process.

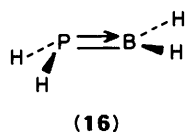
**Phosphine-Boryl Radical ( $\text{H}_3\text{P} \rightarrow \dot{\text{B}}\text{H}_2$ ).**—The 'eclipsed' conformation (13), pyramidal at boron ( $\phi$  16.6°), is the most stable of the structures examined at the UHF level, although (14), which was constrained to be planar at boron, is only marginally less stable (by 1.2 kJ mol<sup>-1</sup>). The 'staggered-planar' con-



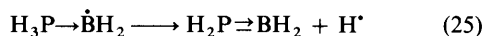
formation (15) is less stable than (14) by only 0.4 kJ mol<sup>-1</sup> at the UHF level. When electron correlation is included, the structures (13)—(15) differ in energy by at most 1.4 kJ mol<sup>-1</sup>, although (13) does remain slightly more stable than (14).

We conclude that, like  $\text{H}_2\text{S} \rightarrow \dot{\text{B}}\text{H}_2$ ,  $\text{H}_3\text{P} \rightarrow \dot{\text{B}}\text{H}_2$  is probably effectively planar at boron with a very small barrier to rotation about the PB bond. These conclusions accord with e.s.r. spectroscopic data obtained for a number of substituted phosphine-boryl radicals.<sup>8,32</sup>

**Phosphinoborane ( $\text{H}_2\text{P} \rightleftharpoons \text{BH}_2$ ).**—At the RHF level,  $\text{H}_2\text{P} \rightleftharpoons \text{BH}_2$  (16) was close to planar at boron but strongly pyramidal at phosphorus (sum of the bond angles is 305.8°). In contrast with the corresponding difference in SB bond lengths for the sulphur analogues,  $r(\text{PB})$  is marginally greater in  $\text{H}_2\text{P} \rightleftharpoons \text{BH}_2$  than in  $\text{H}_3\text{P} \rightarrow \dot{\text{B}}\text{H}_2$ , suggesting much reduced dative  $\pi$  bonding between the heavy atoms in (16) compared with (12).

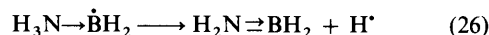


$\beta$ -Cleavage of radical (13) [equation (25)] is calculated to be endothermic by 86.5 kJ mol<sup>-1</sup> at the MP3 level, including ZPVE contributions. Although the PC bond in  $\text{Me}_3\text{P}$  is ca. 42 kJ mol<sup>-1</sup> weaker than the P-H bond in  $\text{H}_3\text{P}$ ,<sup>44</sup> the  $\beta$ -scission of  $\text{Me}_3\text{P} \rightarrow \dot{\text{B}}\text{H}_2$  should still be substantially endothermic. The corresponding  $\beta$ -scission of the ammonia-boryl radical [equation (26)] has been calculated<sup>4</sup> to be exothermic by 5.7 kJ



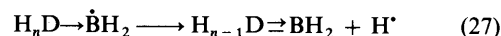
mol<sup>-1</sup> at the MP3 (frozen core) level<sup>42</sup> without taking account of ZPVE contributions and becomes exothermic by 35.2 kJ mol<sup>-1</sup> if these are included. In contrast with phosphinoborane,

\* The ZPVE of radical (9) was taken to be 102.7 kJ mol<sup>-1</sup>, the value obtained for structure (8) which corresponds to the energy minimum at the UHF level.



aminoborane is a planar molecule at the RHF/6-31G\*\* level and there is appreciable dative  $\pi$  bonding between nitrogen and boron.<sup>4,39,45</sup> As an NC bond is ca. 75 kJ mol<sup>-1</sup> weaker than an NH bond,<sup>43</sup> it follows that  $\beta$ -scission of  $\text{Me}_3\text{N} \rightarrow \dot{\text{B}}\text{H}_2$  should be highly exothermic, by an amount probably even greater than our previous estimate<sup>3</sup> of 41 kJ mol<sup>-1</sup>.

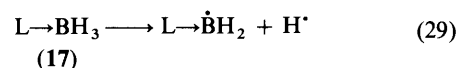
The relative rates at which sulphide-, phosphine-, and amine-boryl radicals undergo  $\beta$ -scission thus clearly reflect the thermodynamics of the three processes.  $\beta$ -Cleavage of both dialkyl sulphide- and trialkylamine-boryls is strongly exothermic and both types of radical fragment rapidly at low temperatures, while  $\beta$ -scission of trialkylphosphine-boryl radicals is probably appreciably endothermic, accounting for the relatively slow, and as yet undetected, fragmentation of these species. The favourable energetics for  $\beta$ -scission of  $\text{R}_3\text{N} \rightarrow \dot{\text{B}}\text{H}_2$  have been attributed mainly to the relative strength of the  $\text{N} \rightleftharpoons \text{B}$  bond compared with that of the  $\text{N} \rightarrow \text{B}$  linkage.<sup>3</sup> Despite the fact that sulphur is a second-row element, the situation is similar for  $\text{R}_2\text{S} \rightarrow \dot{\text{B}}\text{H}_2$ , although it is very different for  $\text{R}_3\text{P} \rightarrow \dot{\text{B}}\text{H}_2$ . In general, the energy change associated with the  $\beta$ -scission in equation (27) may be expressed by equation (28) using contributing bond-energy terms.



$$\Delta E_{27} = E(\text{D}-\text{H}) - [E(\text{D} \rightleftharpoons \text{B}) - E(\text{D} \rightarrow \text{B})] \quad (28)$$

Taking the values of  $E(\text{D}-\text{H})$  from the literature<sup>46</sup> to be 386, 363, and 322 kJ mol<sup>-1</sup> when  $\text{D} = \text{N}, \text{S},$  or  $\text{P}$ , respectively, in conjunction with our MP3 + ZPVE estimates of  $\Delta E_{27}$ , gives  $[E(\text{D} \rightleftharpoons \text{B}) - E(\text{D} \rightarrow \text{B})] = +421, +409,$  and  $+236$  kJ mol<sup>-1</sup> for  $\text{D} = \text{N}, \text{S},$  and  $\text{P}$ , respectively. The value of  $[E(\text{N} \rightleftharpoons \text{B}) - E(\text{N} \rightarrow \text{B})]$  may be compared with  $+363$  kJ mol<sup>-1</sup> derived previously by a different procedure and with the much smaller value of  $[E(\text{C}=\text{C}) - E(\text{C}-\text{C})]$  ( $+256$  kJ mol<sup>-1</sup>).<sup>3</sup> The low value of  $[E(\text{P} \rightleftharpoons \text{B}) - E(\text{P} \rightarrow \text{B})]$  is attributable mainly to the weaker dative  $\pi$  bond between phosphorus and boron; the energy required to make the phosphorus centre planar in  $\text{H}_2\text{P} \rightleftharpoons \text{BH}_2$  is not offset by the energy available from the more effective  $\pi$  bonding possible in the planar molecule. For  $\text{H}_2\text{N} \rightleftharpoons \text{BH}_2$ , the energy required to planarise the nitrogen is more than recouped by better  $\pi$  bonding. For  $\text{HS} \rightleftharpoons \text{BH}_2$ , no planarisation at the donor atom is required before the optimum geometry for sulphur-boron  $\pi$  bonding can be achieved.

Because of the profound lack of experimental thermochemical data for boron compounds, we considered it worthwhile to calculate approximate dissociation energies for B-H bonds in the ligated boranes (17;  $\text{L} = \text{H}_3\text{N}, \text{H}_3\text{P},$  or  $\text{H}_2\text{S}$ ).

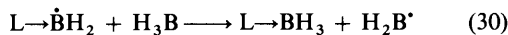


The MP3 energies and ZPVEs for compounds (17) are included in Table 3 and from these  $\Delta E_{29}$  is calculated to be  $+416, +374,$  and  $+381$  kJ mol<sup>-1</sup> when  $\text{L} = \text{H}_3\text{N}, \text{H}_3\text{P},$  and  $\text{H}_2\text{S}$ , respectively. However, we note that, unlike ammonia- and phosphine-boranes, hydrogen sulphide-borane is calculated to be only very weakly bound with respect to  $\text{H}_3\text{B}$  and the free ligand at this level of theory. For comparison  $DH^\circ(\text{C}-\text{H})$  in ethane is 411 kJ mol<sup>-1</sup> and  $DH^\circ(\text{O}-\text{H})$  in Bu'OH is 440 kJ mol<sup>-1</sup>.<sup>43</sup>

The reduction in B-H bond strength on going from  $\text{H}_3\text{N} \rightarrow \text{BH}_3$  to  $\text{H}_3\text{P} \rightarrow \text{BH}_3$  accords with the decrease, albeit small, in C-H bond strength on going from  $\text{Me}_4\text{C}$  to  $\text{Me}_4\text{Si}$ .<sup>47</sup> These reductions may be ascribed to delocalisation of the

unpaired electron into vacant orbitals of the  $H_3P$  or  $Me_3Si$  groups (*cf.* before).

The calculations also show that  $H_2B^{\cdot}$  is more tightly complexed than  $H_3B$ , irrespective of the nature of the ligand, although the difference in  $L \rightarrow B$  bond strengths is particularly large when  $L = H_3P$  or  $H_2S$ . Including ZPVE contributions, the values of  $\Delta E_{30}$  are +5.5, +47.8, and +40.7 kJ mol<sup>-1</sup> when  $L = H_3N$ ,  $H_3P$ , and  $H_2S$ , respectively.\* When  $L = H_3P$  or  $H_2S$ , the acceptor orbital in  $L \rightarrow \dot{B}H_2$  will have substantially more B-2s character than that in  $L \rightarrow BH_3$ , although the  $\sigma-\pi$



electron-promotion energy for  $H_2B^{\cdot}$  and the  $sp^2-sp^3$  re-hybridisation energy for  $H_3B$  must also be considered. Furthermore,  $\pi$  bonding between boron and the ligand will strengthen the attachment of the latter more in the radical than in its parent. These factors presumably also account for the shortening of the  $L \rightarrow B$  bond that is calculated to occur on going from  $L \rightarrow BH_3$  to  $L \rightarrow \dot{B}H_2$ .

### Experimental

E.s.r. spectra were recorded with a Varian E-109 instrument operating at *ca.* 9.2 GHz. Spectra were monitored during continuous u.v. irradiation ( $\lambda$  *ca.* 240–340 nm) of samples, sealed in evacuated Suprasil quartz tubes (3 mm o.d.  $\times$  2 mm i.d.), directly in the microwave cavity.<sup>48</sup> *g*-Factors and hyperfine splitting constants were computed from the measured microwave frequency and line positions, the latter determined using an n.m.r. gaussmeter and corrected for the field difference between the sample and the n.m.r. probe using the pyrene radical anion (*g* 2.002 71) as standard.<sup>49</sup> 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.<sup>50</sup>

Relative radical concentrations were determined by double integration of suitable lines in each spectrum and absolute radical concentrations were measured by comparison with the spectrum obtained from a standard solution of *N,N*-diphenyl-*N'*-picrylhydrazyl in carbon tetrachloride, using the signal from a piece of synthetic ruby (fixed permanently inside the microwave cavity) as an internal standard.<sup>48</sup>

**Materials.**—N.m.r. spectra ( $C_6D_6$  solvent) were obtained with a Varian XL-200 instrument, using tetramethylsilane internal standard (<sup>1</sup>H) or  $BF_3 \cdot Et_2O$  external standard (<sup>11</sup>B). Preparation and handling of sulphide-boranes were conducted under dry argon or nitrogen; all solvents were dried before use.

Commercially available dimethyl sulphide-borane (Aldrich) was freed from the excess of sulphide as described below; the material gave results indistinguishable from those obtained with the sulphide-borane synthesised from diborane and  $Me_2S$ .

**Dimethyl sulphide-borane.** Diborane, generated by addition of freshly distilled boron trifluoride-diethyl ether (14.5 g, 0.102 mol) in bis-(2-methoxyethyl) ether (30 ml) to a stirred solution of sodium borohydride (2.91 g, 0.077 mol) in the same solvent (45 ml), was carried in a slow stream of argon into a solution of dimethyl sulphide (6.40 g, 0.103 mol) in diethyl ether (15 ml) cooled to *ca.* -78 °C. After addition of the  $F_3B \cdot Et_2O$  during 30 min, the diborane generator was heated to 60–70 °C for 1 h to complete the reaction. Diethyl ether and any remaining dimethyl sulphide were removed at room temperature by pumping at 20 Torr. Dimethyl sulphide was undetectable

( $\leq 0.5\%$ ) in the <sup>1</sup>H n.m.r. spectrum of the product which showed  $\delta$  1.53 (6 H, s, Me) and 2.02 (3 H, q,  $J_{H-B}$  106.0 Hz,  $BH_3$ );  $\delta(^{11}B) - 19.7$  p.p.m. (q,  $J_{B-H}$  106.6 Hz).

**Bis(perdeuteriomethyl) sulphide-borane.** This was prepared by the same route, starting from  $(CD_3)_2S$  (Aldrich, 99.9 atom% D).

**Diethyl sulphide-borane.** This was prepared similarly; diethyl ether and uncomplexed sulphide were removed from the product at room temperature by pumping at 10 Torr,  $\delta(^1H)$  0.93 (6 H, t,  $J$  7.4 Hz, Me), 2.04 (3 H, q,  $J_{H-B}$  104.9 Hz,  $BH_3$ ), and 2.07 (4 H, q,  $J$  7.4 Hz,  $CH_2$ ); a trace of  $Et_2S$  ( $\leq 1\%$ ) may have been present;  $\delta(^{11}B) - 23.2$  p.p.m. (q,  $J_{B-H}$  104.9 Hz).

**Diethyl sulphide- $[^2H_3]$ borane.** This was prepared by the same route starting from  $NaBD_4$  (Aldrich, 98 atom% D); its <sup>1</sup>H n.m.r. spectrum was essentially identical with that of  $Et_2S \rightarrow BH_3$  apart from the absence of absorption due to the  $BH_3$  group.

**Perdeuterio(dimethyl sulphide-borane).** This was prepared in the same general way from  $(CD_3)_2S$ , except that perdeuterio-diborane was generated by addition of isotopically enriched  $BF_3 \cdot Me_2O$  (Centronic Ltd., 97.5 atom% <sup>11</sup>B) to a stirred slurry of  $LiAlD_4$  in 1,2-dimethoxyethane.<sup>3,51</sup> The product showed  $\delta(^{11}B) - 20.0$  (br s).

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\* The MP3(full)/6-31G\*\*//HF/6-31G\*\* energies for  $H_3B$  and  $H_2B^{\cdot}$  are -26.508 185 and -25.836 891 Hartrees, respectively; the corresponding ZPVEs were 72.3 and 39.9 kJ mol<sup>-1</sup>.



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