An E.S.R. Study of Amine-boryl Radicals ($R_3\overset{+}{N}-\overset{-}{B}H_2^{\bullet}$) in Solution

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The e.s.r. spectrum of $Et_3\overset{+}{N}-\overset{-}{B}H_2^{\bullet}$ indicates that this species is non-planar at the boron radical centre; amine-boryl radicals abstract halogen from alkyl chlorides and bromides and the aziridine-boryl radical undergoes rapid ring opening.

The amine-boranes $R_3\overset{+}{N}-\overset{-}{B}H_3$ are isoelectronic with the alkanes R_3C-CH_3 and amine-boryl radicals $R_3\overset{+}{N}-\overset{-}{B}H_2^{\bullet}$ are similarly related to the alkyl radicals $R_3C-CH_2^{\bullet}$. Uninterpretable e.s.r. spectra attributed to pyridine complexes of the diethylboryl and diphenylboryl radicals were reported by Köster *et al.* in 1964,[1] but there have been no more recent spectroscopic studies of amine-boryl radicals, although these species have been invoked as intermediates in the reduction of 1,2-dichloroethane, CCl_4, and CCl_3Br by trimethylamine- or 4-methylpyridine-borane.[2]

We have shown previously that borane radical anions may be generated readily for e.s.r. study in solution by hydrogen atom abstraction from tetra-alkylammonium hydroborates [*e.g.* equation (1)].[3] In this communication we report that

$$Bu^tO^{\bullet} + H_4B^- \rightarrow Bu^tOH + H_3B^{-\bullet} \qquad (1)$$

amine adducts of the boryl radical ($H_2B^{\bullet}$) may be generated in a similar way from an amine-borane complex.

When a solution containing di-t-butyl peroxide (DTBP; 15% v/v) and triethylamine-borane† (10% v/v) in cyclopropane–tetrahydrofuran (THF; 3:1 v/v) was photolysed with u.v. light from a high pressure mercury discharge lamp whilst the sample was in the cavity of an e.s.r. spectrometer, the spectrum (*g* 2.0023) shown in Figure 1(a) was obtained. This spectrum can be analysed in terms of $a(^{11}B)$ 47.5, $a(2H)$ 12.9, $a(N)$ 2.2, and $a(6H)$ 2.2 G (1 G = 10^{-4} T), and we assign it to the triethylamine-boryl radical (**1**), which is isoelectronic with $Et_3\overset{+}{N}-CH_2^{\bullet}$ and $Et_3C-CH_2^{\bullet}$ [equation (2)]. The

$$Bu^tO^{\bullet} + Et_3\overset{+}{N}-\overset{-}{B}H_3 \rightarrow Bu^tOH + \underset{\textbf{(1)}}{Et_3\overset{+}{N}-\overset{-}{B}H_2^{\bullet}} \qquad (2)$$

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† The natural abundances of ^{11}B (*I* 3/2) and ^{10}B (*I* 3) are 81.2 and 18.8%, respectively. Triethylamine-borane containing these proportions of the two isotopes and material enriched in ^{11}B (97.5% + 2.5% ^{10}B) were used in these experiments.

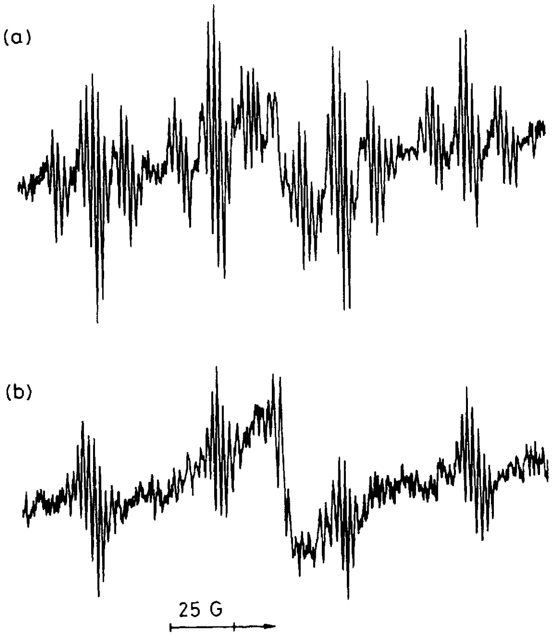

Figure 1. E.s.r. spectra at 193 K of (a) $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_2^{\bullet}}$ generated from $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_3}$ (97.5 atom% ^{11}B) in cyclopropane–THF (3:1 v/v) and (b) $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}D_2^{\bullet}}$ generated from $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}D_3}$ (81.2 atom% ^{11}B) in cyclopropane–[^{2}H$_8$]THF (3:1 v/v). Some unidentified lines are present in both spectra. No e.s.r. signals were observed during photolysis of $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_3}$ alone in cyclopropane–THF.

spectral analysis was confirmed by generating $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}D_2^{\bullet}}$ [$a(^{11}\mathrm{B})$ 48.2, a(2D) 2.0, a(N) 2.2, a(6H) 2.2 G] from $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}D_3}$ [see Figure 1(b)].

When the hyperfine splittings for (**1**) are compared with those for $\mathrm{H_3B^{\bullet -}}$ [$a(^{11}\mathrm{B})$ 19.9, a(3H) 15.2 G] and $\mathrm{H_2\dot{B}CN^-}$ [$a(^{11}\mathrm{B})$ 14.3, a(2H) 15.8, a(N) 3.0 G] at 253 K,[3] it is evident that $a(^{11}\mathrm{B})$ for the amine-boryl radical is substantially larger, corresponding[4] to *ca.* 7% unpaired electron population in the B-2s atomic orbital. Assuming orbital following, this result implies a *pyramidal* arrangement of ligands attached to boron in (**1**), in contrast with the structures of the borane and cyanoborane radical anions and of the isoelectronic carbon analogues $\mathrm{H_3C^{\bullet}}$ and $\mathrm{H_2\dot{C}CN}$, which are all effectively planar.[3,4]‡

The triethylphosphine-boryl radical (**2**) was generated by an analogous route from $\mathrm{Et_3\overset{+}{P}{-}\overset{-}{B}H_3}$ [equation (3)] and its e.s.r. parameters [$a(^{11}\mathrm{B})$ 17.6, a(2H) 16.8, $a(^{31}\mathrm{P})$ 43.6 G, g 2.0020 at 183 K in oxirane]§ indicate that this radical is *planar* at boron. A similar conclusion regarding the geometry of $\mathrm{Ph_3\overset{+}{P}{-}\overset{-}{B}H_2^{\bullet}}$, trapped in a rigid matrix, has been reached from analysis of its e.s.r. spectrum.[5]

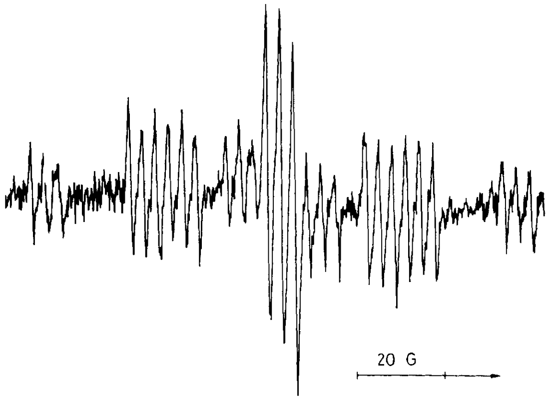

Figure 2. E.s.r. spectrum of $\mathrm{H_2B{-}N(H)CH_2CH_2^{\bullet}}$ (**4**) in cyclopropane–oxirane (1:1 v/v) at 226 K. No e.s.r. signals were observed during photolysis of aziridine-borane alone in cyclopropane–oxirane.

$$\mathrm{Bu^tO^{\bullet} + Et_3\overset{+}{P}{-}\overset{-}{B}H_3 \rightarrow Bu^tOH + \underset{(\mathbf{2})}{Et_3\overset{+}{P}{-}\overset{-}{B}H_2^{\bullet}}} \qquad (3)$$

Factors which influence the configuration of carbon-centred radicals have been much debated[6–8] and both σ-inductive (electronegativity) effects[6] and π-conjugative effects[7,8] are thought to be important. The radical $\mathrm{H_2\dot{B}X^-}$ would be expected[6] to become increasingly non-planar at boron as the relative electronegativity of X increases, although this effect can be offset by π-conjugative stabilisation of the planar geometry as in $\mathrm{H_2\dot{B}CN^-}$. The electronegativity difference between the radical centre and the non-hydrogen ligand is undoubtedly greater for (**1**) than for $\mathrm{Me_3C{-}CH_2^{\bullet}}$,[9] $\mathrm{Ph_3\overset{+}{P}{-}CH_2^{\bullet}}$,[10] or (**2**), all three of which appear to be planar or nearly so.¶ In addition, we suggest that π-conjugative destabilisation of the planar geometry of (**1**) may result from interaction between the singly-occupied B-2p$_\pi$ orbital and the *filled* π(R$_3$N) group orbital. This three electron interaction could be destabilising if the overlap integral is large,[11] as seems quite likely, and the boron radical centre should be more easily deformed from planarity than the corresponding carbon centre in $\mathrm{R_3C{-}CH_2^{\bullet}}$. Such an effect is probably unimportant for (**2**) and delocalisation of the unpaired electron from boron into an *empty* π*(R$_3$P) group orbital could be important in stabilising the planar geometry of this radical.

The borane radical anion ($\mathrm{H_3B^{\bullet -}}$) reacts rapidly with both alkyl chlorides and bromides to give alkyl radicals.[3] The ligated boryl radicals (**1**) and (**2**) behave similarly, although both appear to be somewhat less reactive than $\mathrm{H_3B^{\bullet -}}$. For example, if a cyclopropane–THF solution containing $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_3}$, DTBP, and Pr^{n}Br (*ca.* 1.5 M) is photolysed at 200—275 K, the n-propyl radical rather than (**1**) is detected implying that reaction (4) is rapid under these conditions. n-Propyl chloride is less reactive than the bromide and both (**1**) and $\mathrm{Pr^{n\bullet}}$ were detected at 200 K.

$$\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_2^{\bullet} + Pr^nBr \rightarrow Et_3\overset{+}{N}{-}\overset{-}{B}H_2Br + Pr^{n\bullet}} \qquad (4)$$

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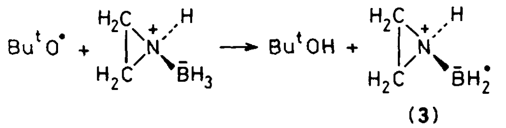
‡ Since pyramidal inversion at boron will be governed by a double minimum potential, $a(^{11}\mathrm{B})$ for $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}D_2^{\bullet}}$ would be expected to be *larger* than that for $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_2^{\bullet}}$, as observed. However, $a(^{11}\mathrm{B})$ for $\mathrm{Et_3\overset{+}{N}{-}\overset{-}{B}H_2^{\bullet}}$ varies only slightly between 185 and 230 K.

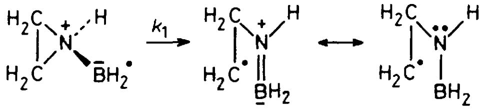
§ The tri-n-butylphosphine-boryl radical in cyclopropane shows similar e.s.r. parameters.

¶ Recent calculations (L. Bonazzola, N. Leray, and Y. Ellinger, *Chem. Phys.*, 1982, **73**, 145) predict that the radical centre in $\mathrm{H_3\overset{+}{N}{-}CH_2^{\bullet}}$ is pyramidal, in agreement with experiment, although the computed inversion barrier is very small.



(3)

(5)



(4)

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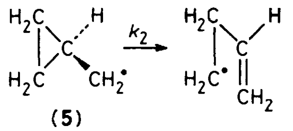

(5)

(7)

With the aim of identifying an intramolecular rearrangement of an amine-boryl radical, we investigated hydrogen atom abstraction from aziridine-borane,[12] which is isoelectronic with methylcyclopropane. Because of solubility problems, the lowest temperature attainable was 200 K in cyclopropane–oxirane (1 : 1 v/v) and in this solvent the only e.s.r. spectrum observed (see Figure 2) was one which we assign to the ring-opened radical (**4**) [$a(2H_\alpha)$ 22.3, $a(2H_\beta)$ 31.4, a(N) 3.1 G, g 2.0027 at 226 K]. The aziridine-boryl radical (**3**) [equation (5)] could not be detected, although the expected complexity of its spectrum would make detection of low concentrations very difficult.

The aziridine-boryl radical thus resembles the isoelectronic cyclopropylmethyl radical (**5**), which undergoes ready ring-opening to give the but-3-enyl radical.[13] The rate of the latter ring-opening has been measured by kinetic e.s.r. spectroscopy and at 200 K the extrapolated value of k_2 is 9.8×10^5 s^{-1}.[14] A value of k_1 in excess of *ca.* 10^3 s^{-1} would be consistent with the detection of only (**4**) at 200 K. However, the unopened radical (**3**) can evidently be trapped by alkyl halides, since the spectrum of (**4**) was partially replaced by that of the ethyl radical when hydrogen was abstracted from aziridine-borane in the presence of ethyl bromide (*ca.* 1.3 M) at 230—290 K.

Our observations imply that reaction (6) is exothermic, as is reaction (7). This is reasonable, since the energy required for *homolytic* dissociation of the π bond in an aminoborane could be similar to or even greater than the corresponding dissociation energy for an alkene.

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