First EPR characterisation of the structures and reactivities of α- and β-boryl radicals derived from boronic esters

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The first EPR observations of carbon-centred radicals with α- and β-boronic ester substituents indicated moderate thermodynamic stabilisation for the former whereas the latter had an inclination towards β-scission.

Boronic acids and esters are convenient synthetic intermediates which have been widely applied in stereocontrolled reactions.[1] Recent research has shown that α-boryl radicals, generated by addition of carbon-centred radicals to alkenyl-[2] and alkynyl-boronic esters,[3] can take part in inter- and intra-molecular chain addition reactions. α-Boryl radicals have also been generated by iodine abstraction from α-iodoboronic esters[4] and high yields of useful homoallylboronic esters were obtained in allylation reactions. These developments led us to apply EPR spectroscopy to identify the radical intermediates and examine key reaction rates for several types of carbon-centred radicals possessing a boronic ester functionality. Little is known about the EPR spectra of boron-containing species in solution, apart from the impressive spectroscopic experiments of Roberts and co-workers with amine–boryl and other ligated-boryl radicals,[5] a report on the Me$_2$BCH$_2$· radical in the solid state[6] and some aminoxyl species.[7]

The α-bromoboronic esters **1a,b** were prepared according to the protocols developed by Matteson and co-workers from B(OPr^i)$_3$, CH$_2$Br$_2$ and Bu^{n}Li for **1a**,[8] from pinacol n-hexyl boronate, CH$_2$Br$_2$ and Pr$^i_2$NLi for **1b**.[9] EPR spectra, recorded during abstraction of the bromine atoms of these boronic esters by photochemically generated Me$_3$Sn· radicals (or Et$_3$Si· radicals) in *tert*-butylbenzene, cyclopropane or propane could be positively assigned to the corresponding α-boryl radicals **2a,b** (EPR parameters in Table 1). The hyperfine splittings (hfs) from the α-Hs are somewhat smaller than in analogous unsubstituted primary and secondary alkyl radicals [*e.g.* for ·CH$_2$CH(OEt)$_2$ a(H$_α$) = 22.2 G][10] which suggests there is some electron delocalisation into the vacant boron p-orbital (**3**). This is also consistent with the comparatively large [11]B hfs.

If **3** makes a significant contribution to the ground state there should be an appreciable barrier to rotation about the C$_α$–B bond. To try and detect this we examined the EPR spectra of radicals generated from the unsymmetrical boronic esters **4a,b** prepared by transesterification of **1a,b** with (+)-pinanediol.


a R = H, **b** R = n-C$_6$H$_{13}$

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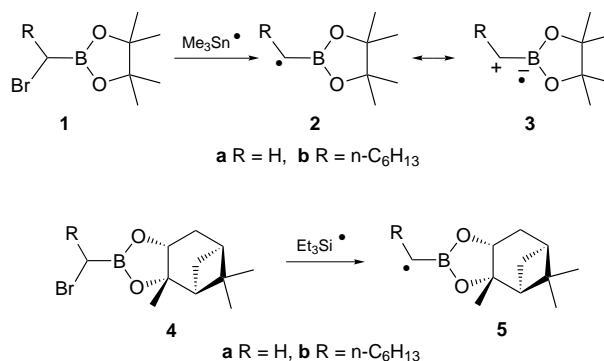
In the resulting radical **5a** the two α-Hs will be magnetically non-equivalent in the slow exchange limit. The spectrum of **5a** at 150 K [(Fig. 1(*a*)] shows hfs from [11]B, the single δ-H of the pinane ring and two equivalent H$_α$. Between 150 and 100 K selective line broadening occurred [Fig. 1(*b*)] due to restricted rotation about the C$_α$–B bond with a coalescence temperature (T_c) of < 100 K. The C$_α$–B torsion barrier (E_t) is therefore significantly greater than the analogous C$_α$–C$_β$ barrier in alkyl radicals like ·CH$_2$CHR$_2$ which show no exchange broadening.[11,12] Due to freezing of the propane solvent at lower temperatures, we were unable to determine the hfs of the non-equivalent H$_α$. However, in analogous radicals ·CH$_2$—X, (X = OH, OMe, CHR$_2$, SMe),[13–15] δa is always in the range 0.5–1.5 G. Computer simulations[16] of the exchange broadened region (160–110 K) gave best fit with δa = 0.6 G and led to log (A_t/s^{-1}) = 11.9, E_t = 12.2 ± 3.0 kJ mol^{-1}. This established that alkyl radicals with α-boronic ester substituents possess a small but significant thermodynamic stabilisation and supports the contention that boron stabilises neighbouring radical centres.

Additional data on the stabilising influence of an α-boronic ester group was obtained *via* methyl boronic ester **6**. Bu^{t}O radicals were known to displace alkyl radicals from trialkylboranes with comparative ease (homolytic substitution at boron)[17–19] and therefore a similar homolytic displacement of Me· was expected from **6**. In fact, however, photolysis (150–160 K) of a solution of **6** and Bu^{t}OOBu^t in cyclopropane

**Table 1** 9.4 GHz EPR spectral parameters of radicals derived from boronic esters[a]

			Hfs/G					
Radical	R	T/K	H(α)	H(β)	H(β)	[11]B	[10]B	Other
2a	H[b]	220[d]	20.9 (2 H)			12.3	4.1	
2b	C$_6$H$_{13}$	220[d]	20.0	23.5	23.5	12.0	4.0	0.5 (2 H)
10a	Et$_3$SiCH$_2$	195[d]	18.3	23.8	9.1	10.8	3.6	
10b	Me$_3$SnCH$_2$	235[d]	16.7	16.7	11.8	10.1	3.4	
5a	H	145[c]	21.1 (2 H)			12.4	4.2	1.1 (1 H)
5b	C$_6$H$_{13}$	220[d]	19.0	23.6	23.6	12.2	4.1	
12	Bu^n	180[c]	22.1	27.0 (2 H)	22.1 (2 H)	17.7	5.9	

[a] Hfs checked by computer simulations; 10 G = 1 mT. [b] g-Factor 2.0028; g-factors of all other radicals 2.003 ± 0.001. [c] In cyclopropane. [d] In Bu^{t}Ph.
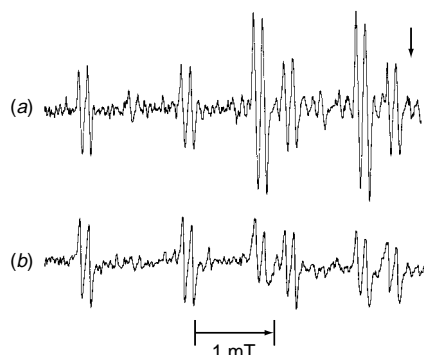
Fig. 1 Low field halves of 9.4 GHz EPR spectra of radical **5a** in *n*-propane solution at (*a*) 150 and (*b*) 110 K. Arrow indicates spectrum centre.

Scheme 1

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gave a spectrum containing Me[.], **2a** and a primary radical [a(2H) = 22.7 G] which we identify as **7**. Measurements of the relative concentrations of **2a** and CH$_3$[.] showed that abstraction of hydrogen adjacent to boron by Bu^{t}O[.] was about a factor of five more rapid than displacement of CH$_3$[.] from boron at 160 K.
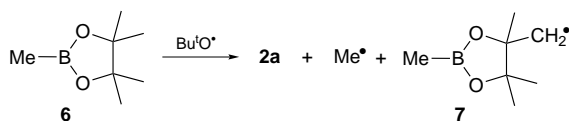
Addition to vinylborane **8** by a range of free radicals including Bu^{t}O[.], Ph[.], CCl$_3$[.], Ph$_2$N[.] and BnS[.] was examined by EPR spectroscopy. However, only the radicals Et$_3$Si[.] and Me$_3$Sn[.] added efficiently enough, under EPR conditions (200–250 K), for adduct radicals **10a,b** to be detected (see Table

a R = Et$_3$Si, **b** R = Me$_3$Sn
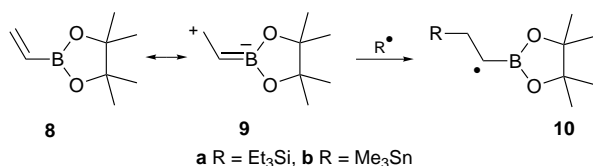
1). These observations do not conflict with reports on the production of adducts from a variety of radicals at higher temperatures, where all rates of addition will be faster, but they do suggest that nucleophilic radicals add most efficiently. This conclusion is in good accord with the idea that structures such as **9** make an appreciable contribution to the ground state.[20]

The β-bromoboronic ester **11** was prepared in good yield by bromoboration of hex-1-ene followed by esterification with pinacol. Although this reaction was reported to give mixtures of products,[21] in our hands, and under different experimental conditions, addition proceeded in good yield.§ Bromine atom abstraction from ester **11** afforded a spectrum of the β-boryl radical **12** (see Table 1) in the temperature range 180–220 K. As expected, the hfs of the β-B-atom was larger than that of an α-B-atom, due to a hyperconjugative effect. At temperatures above *ca.* 220 K the spectrum of **12** unexpectedly disappeared leaving only noise. GC–MS analysis of the photolysate at 250 K showed hex-1-ene as the major product together with minor amounts of a dimer and other unidentified components. Product analysis of a photolysis at 180 K showed the dimer to be the main product with only minor amounts of hex-1-ene. A mechanism (Scheme 1) in which dimerisation of radical **12** gives way to β-scission producing hex-1-ene and radical **13** at higher temperatures is consistent with the known facts. Boron-centred radical **13** was EPR 'silent' probably because of extensive broadening. Attempts to spin trap **13** with 2-methyl-2-nitrosopropane and *tert*-butyl hyponitrite were unsuccessful. Radical **13** might become EPR visible when ligated with a suitable donor. However, when **12** was generated in the presence of excess pyridine, no signals due to [C$_5$H$_5$N → **13**][.] were obtained.

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