Electron Spin Resonance Studies of Radicals derived from 1,3,2-Benzodioxaboroles

Jehan A. Baban, Nicholas J. Goodchild, and Brian P. Roberts *
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

The reactions of photochemically generated ethoxyl and t-butoxyl radicals with a number of 1,3,2-benzodioxaboroles and with 2-butyl-4,5-dimethyl-1,3,2-dioxaborole have been studied in solution using e.s.r. spectroscopy. With each borole, alkoxyl addition takes place at boron to give a perboryl radical adduct in which the unpaired electron occupies a π orbital delocalised over the borole residue. The perboryl adducts derived from 1,3,2-benzodioxaboroles which have a *B*-alkyl substituent (catechol boronates) break down by loss of the alkyl radical and the ease of this α-scission increases as the strength of the B–C bond decreases. The addition/fragmentation sequence corresponds to stepwise S_H2 alkoxydealkylation at boron.

Trialkylboranes undergo bimolecular homolytic substitution (S_H2) reactions very readily, especially if the attacking radical is oxygen-, sulphur-, or nitrogen-centred [equation (1)].[1,2] In view

$$X\cdot + R_3B \longrightarrow R\cdot + R_2BX \qquad (1)$$

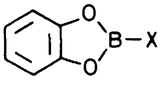
of the propensity of trivalent boron compounds to form addition complexes with Lewis bases, it seems reasonable that these homolytic displacement reactions should take place in a stepwise manner *via* an intermediate perboryl adduct of the type $[R_3BX]\cdot$. Although an optical absorption spectrum attributed to $[Ph_3BOBu^t]\cdot$ was detected after flash generation of t-butoxyl radicals in the presence of triphenylborane,[3] such intermediates have not been characterised by e.s.r. spectroscopy.

Recently, however, the e.s.r. spectrum of the simplest perboryl radical $[BH_4]\cdot$ has been detected from γ-irradiated sodium borohydride,[4,5] and we were thus encouraged to renew our search for perboryl intermediates in S_H2 reactions of organoboron compounds.

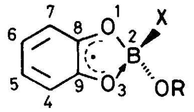
The reactivity of organoboranes towards homolytic dealkylation decreases markedly along the series $R_3B > R_2BOR > RB(OR)_2$, in parallel with the decrease in Lewis acidity of the boranes as a consequence of π bonding between oxygen and boron, as illustrated in (1). Although boronic esters $[RB(OR)_2]$

$$\underset{\textbf{(1a)}}{R_2B\text{–}\ddot{O}R} \longleftrightarrow \underset{\textbf{(1b)}}{R_2\bar{B}{=}\overset{+}{O}R}$$

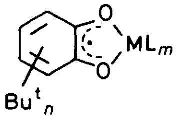
undergo alkoxydealkylation at boron only sluggishly,[1,2] we suspected that 2-alkyl-1,3,2-benzodioxaboroles (catechol boronates) (**2**; X = alkyl) would be more reactive since the π lone pairs on oxygen are partially occupied in conjugation with the benzene ring and are thus less available for interaction with boron. Furthermore, the unpaired electron in a perboryl adduct of the type (**3**)† should be delocalised onto the catechol ring system, thus stabilising this intermediate. A number of persistent radicals of the type (**4**) and related species where M is *inter alia* B, Al, In, Si, Sn, or P have been characterised previously by e.s.r. spectroscopy,[6] and it appears that the unpaired electron distribution in these radicals differs relatively little from that in the uncomplexed semi-quinones (**5**).



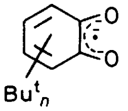
(2)



(3)



(4)



(5)

Results and Discussion

E.s.r. spectra were recorded during continuous u.v. irradiation of static liquid samples directly in the microwave cavity of the spectrometer. The primary radical source was diethyl or di-t-butyl peroxide, u.v. photolysis of which yields alkoxyl radicals [equation (2; R = Et or Bu^t)]. The concentration of peroxide

$$ROOR \xrightarrow{h\nu} 2RO\cdot \qquad (2)$$

(*ca.* 25% v/v) was generally much greater than that of the benzodioxaborole (*ca.* 5—10% v/v), to alleviate problems arising from light absorption by the latter and from the formation of u.v.–visible-absorbing reaction products. Nevertheless, sample lifetime was usually short and a yellow-brown colouration developed during irradiation. Persistent radicals, detectable for long periods after interrupting irradiation, built up slowly in most samples but were not examined further. The solvent was cyclopropane–oxirane (2:1 v/v) or cyclopropane–tetrahydrofuran (2:1 or 3:1 v/v). No e.s.r. spectra were detected in the absence of a peroxide.

Photolysis of either peroxide in the presence of (**2**; X = Bu^t) afforded a strong e.s.r. spectrum of the t-butyl radical, even at very low temperature (145 K). Although a weak central spectrum was also present with either peroxide, it was poorly defined and did not alter significantly in intensity relative to that of Bu$^t\cdot$ over a wide range of temperature, implying that the radical responsible is not the perboryl adduct (**3**; X = Bu^t), which must undergo α-scission [equation (3)] rapidly even at 145 K.

---

† Several alternative representations of the bonding in (**3**) are possible; the structure shown is not meant to imply that the oxygen atoms of the catechol residue are non-equivalent by virtue of their different σ bonding to boron.

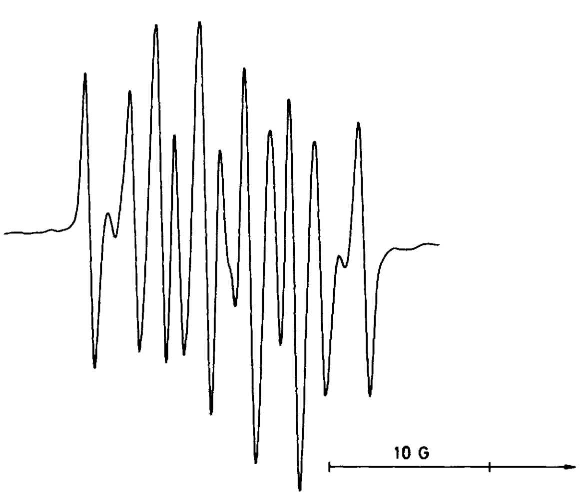
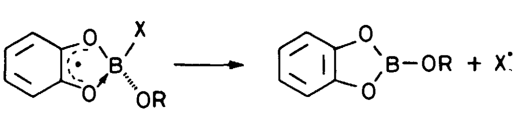


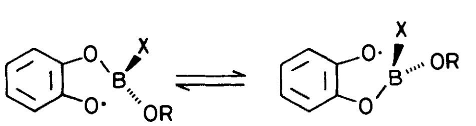
Figure 1. E.s.r. spectrum of (3; X = Me, R = Et) in cyclopropane–oxirane (2:1 v/v) at 148 K


(3)

In contrast, photolysis of either peroxide in the presence of (2; X = Me) below *ca.* 270 K did not give rise to a detectable concentration of methyl radicals, but now strong spectra assigned to the perboryl adducts (3; X = Me, R = Et or Bu^t) were observed. The spectrum of the ethoxyl radical adduct is shown in Figure 1 and it may be analysed in terms of hyperfine splittings of 2.75 G from ^{11}B (I 3/2, natural abundance 80.2%) and of 4.38 G from two magnetically equivalent protons. The contribution to the spectrum from the adduct containing ^{10}B [I 3, natural abundance 19.8%, $\gamma(^{10}\text{B})/\gamma(^{11}\text{B})$ 0.335] is also evident. The ring protons which give rise to resolvable splitting are identified as H-5 and H-6, by analogy with the assignments for the 1,2-benzoquinone radical anion[7] and for the persistent t-butyl-substituted analogues (4).[6a–c]

A MNDO–UHF semi-empirical molecular orbital calculation[8] was carried out for (3; X = Me, R = H), maintaining a planar benzodioxaborole residue and imposing C_s symmetry on the radical although, because of convergence problems, a full optimisation of the remaining geometrical variables was not possible. The predicted coupling constants obtained from an INDO calculation[9] on the resulting partially optimised geometry (ΔH_f° −607.3 kJ mol^{-1}) were $a(^{11}\text{B})$ −5.0, a(H-5, H-6) −1.7, a(H-4, H-7) −0.2, and $a(\text{C}H_3)$ −0.7 G, in qualitative agreement with the experimental values.* The e.s.r. parameters for all the perboryl radicals reported in this work are collected in the Table.

The ring protons H-5 and H-6 remain magnetically equivalent in (3; X = Me, R = Et) even at temperatures as low as 140 K, supporting an equilibrium structure with a four-co-ordinate boron rather than a rapidly interconverting pair of aryloxyl radicals containing three-co-ordinate boron as illustrated in equation (4) (compare ref. 6*b*).


(4)

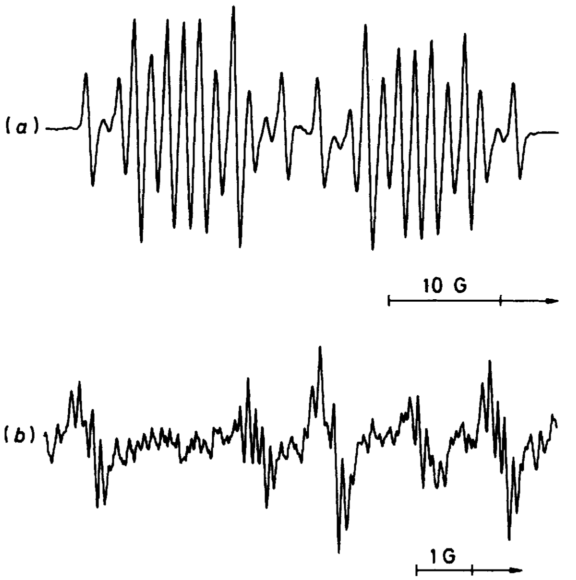
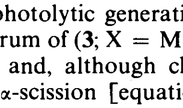
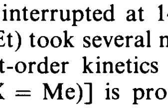


Figure 2. (*a*) E.s.r. spectrum of (3; X = H, R = Bu^t) in cyclopropane–tetrahydrofuran (2:1 v/v) at 233 K; (*b*) the first five lines in the e.s.r. spectrum of (3; X = H, R = Bu^t) under higher resolution at 234 K (the corresponding last five lines at high field were very similar in appearance)

When photolytic generation was interrupted at 145 K, the e.s.r. spectrum of (3; X = Me, R = Et) took several minutes to disappear and, although clean first-order kinetics were not followed, α-scission [equation (3; X = Me)] is probably the major pathway for decay. The lifetimes of (3; X = Me, R = Et or Bu^t) decreased as the temperature was increased and at *ca.* 280 K and above in neat di-t-butyl peroxide, the t-butoxyl adduct of (2; X = Me) undergoes α-scission sufficiently rapidly for the e.s.r. spectrum of the methyl radical to be detected.

Addition of alkoxyl radicals to the parent 1,3,2-benzodioxaborole (2; X = H) gave rise to e.s.r. spectra similar to those derived from the *B*-methyl derivative, except for an additional splitting of *ca.* 21 G from H-2 (see Figure 2). This large doublet splitting was replaced by a 1:1:1 triplet splitting of 3.2 G when the experiment was repeated with (2; X = D). An INDO calculation for the partially optimised geometry (ΔH_f° −564.0 kJ mol^{-1}) of (3; X = R = H), obtained using the MNDO method, yielded $a(^{11}\text{B})$ −6.9, a(H-2) +21.2, a(H-5, H-6) −1.7, and a(H-4, H-7) −0.1 G. The calculation also indicates the presence of a large π spin density (*ca.* 34%) on each of the two catechol oxygen atoms and hyperconjugative spin transmission to H-2 should occur effectively, as it does to the out-of-plane hydrogen atoms in a cyclohexadienyl radical.[11] The radical cation (6) is isoelectronic with the perboryl radical (7) and the former shows a splitting of 22.4 G from the out-of-plane hydrogen atoms and 5 G from two ring protons.[12] The negative boron hyperfine splittings for (3) must arise predominantly from spin polarisation of the electrons associated with the in-plane B–O σ bonds.


(6)


(7)

---

* In the absence of a more appropriate scaling factor, B-2s spin densities were multiplied by 720.8 G to convert them to splitting constants.[10]

Table. E.s.r. parameters for the perboryl radicals (**3**), (**8**), and (**10**)

Radical	Solvent[a]	T/K	g-Factor	Hyperfine splittings (G)[b] $a(^{11}B)$	a(H-5)	a(H-6)	Others[c]
(**3**; X = Me, R = Et)	A	160	2.0041	2.75	4.38	4.38	
(**3**; X = Me, R = Bu^t)	A	198	2.0042	2.70	4.19	4.19	
(**3**; X = H, R = Et)	B	233	2.0041	3.02	4.38	4.38	20.6 (1)[d]
(**3**; X = H, R = Bu^t)	B	243	2.0042	3.00	4.34	4.34	20.8 (1)[e]
(**3**; X = H, R = Bu^t)[f]	B	232		3.03	0.67[g]	0.67[g]	20.9 (1)[h]
(**3**; X = D, R = Bu^t)	B	232		3.0	4.3	4.3	3.2 (1)[g,d]
(**8**; R = Et)	B	198	2.0041	3.3	4.3		18.5 (1)
(**8**; R = Bu^t)	B	181	2.0042	3.1	3.9		21.0 (1)
(**10**; R = Et)	A	198	2.0043	2.78			9.31 (6)
(**10**; R = Bu^t)	A	186	2.0043	2.76			9.12 (6)

[a] A = cyclopropane–oxirane (2:1 v/v); B = cyclopropane–tetrahydrofuran (2:1 v/v). [b] Accurate to ±0.02 G if quoted to two decimal places; otherwise ±0.05 G. [c] Number of equivalent protons shown in parentheses. [d] Each line further split into ⩾5 components spaced by 0.13 G. [e] Each line further split into ⩾5 components spaced by 0.13 G. This splitting was also present when R = t-C_4D_9. [f] Deuteriated at the 4-, 5-, 6-, and 7-positions. [g] Deuterium splitting. [h] No further fine structure was detectable; peak-to-peak linewidth 0.18 G.

Careful examination of the spectrum of (**3**; X = H, R = Bu^t) revealed further splitting of every line into at least five components spaced by 0.13 G (see Figure 2) which cannot be accounted for by interaction with the two remaining ring protons H-4 and H-7 *alone*, assuming only one isomeric form of (**3**) is present. The same fine structure was observed when the perdeuterio peroxide was used, showing that this splitting does not arise from long-range interaction with the protons of the RO group. Similar fine structure was detectable when diethyl peroxide was the source of alkoxyl radicals, but it was absent for the radical derived from ring-deuteriated benzodioxaborole and unlabelled Bu^{t}OOBu^t. We conclude that the fine structure must result from coupling to benzene ring protons and there are two reasonable explanations for these observations. It is feasible that two different forms of (**3**) are present in similar concentration and that these have almost identical e.s.r. parameters apart from a small difference in a(H-2). The fine structure on each line could then result from a superposition of two 1:2:1 triplets, each arising from essentially equal coupling to H-4 and H-7 in both forms, to give distorted quintets. However, virtually identical fine structure was detected for (**3**; X = D, R = Bu^t) and since any difference in a(H-2) would be reduced by a factor of *ca.* 6.5 for a(D-2) this explanation can be eliminated. Thus, it appears likely that the perboryl radicals (**3**; X = H, R = Et or Bu^t) are sufficiently basic to associate with a molecule of benzodioxaborole, although the detailed structure of such a complex is not obvious. The extra fine structure could then result from coupling to the protons of a second benzene ring. Benzodioxaborole is monomeric in the vapour phase[13] and in solution,[14] although it forms addition complexes with amine Lewis bases.[15]

The spectrum of (**3**; X = H, R = Bu^t) decayed within the fall time of the spectrometer (0.3 s) when irradiation was interrupted at 240 K and the spectrum was still readily detectable at 270 K. α-Scission would give rise to hydrogen atoms [equation (3; X = H)], but we would not expect to be able to detect these under our conditions because of their high reactivity. However, α-cleavage of a B–H bond is likely to be slower than the corresponding B–C bond scission because of the greater strength of the former linkage.[16]

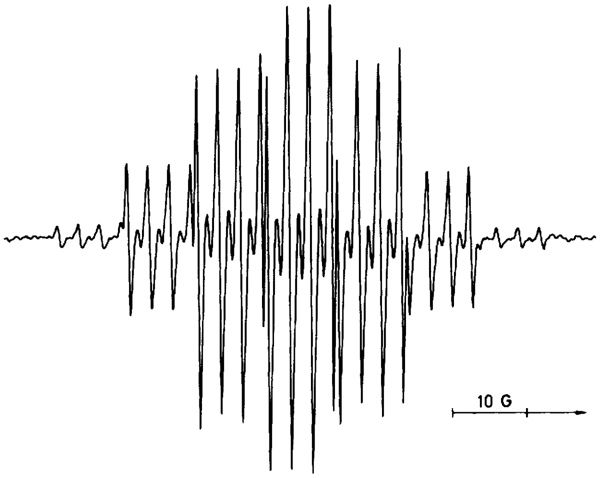
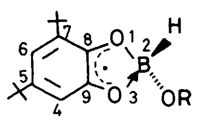


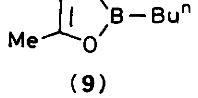
Figure 3. E.s.r. spectrum of (**10**; R = Et) in cyclopropane–oxirane (2:1 v/v) at 197 K; the contribution from the radical containing ^{10}B in natural abundance is clearly evident



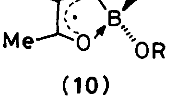
(**8**)

Addition of alkoxyl radicals to 5,7-di-t-butyl-1,3,2-benzodioxaborole gave rise to e.s.r. spectra assigned to (**8**; R = Et or Bu^t) and in which splitting from only *one* ring proton (H-6) was clearly identifiable, although further small splittings were detectable under high-resolution conditions. These small splittings probably arise from H-4 and the ring t-butyl protons, since it seems likely that the bulk of (**8**) and of the parent borole will reduce their tendency to associate. Although the spectra of (**8**; R = Et or Bu^t) were short-lived, spectra of more persistent secondary product radicals grew in rapidly as irradiation progressed, especially at higher temperatures.

For comparison, alkoxyl radical addition to 2-butyl-4,5-dimethyl-1,3,2-dioxaborole (**9**) was also studied in cyclopropane–oxirane solvent (2:1 v/v). Unlike simple dialkyl boronates, compounds of the type (**9**) undergo ready oxidation in air,[17] probably as a result of their greater Lewis acidity as compared with $RB(OR)_2$. Strong spectra of transient perboryl radical adducts (**10**) were detected (see Figure 3) and there was no indication of the ring methyl groups becoming non-equivalent on the e.s.r. timescale even at 145 K, providing support for the symmetrical structure shown.

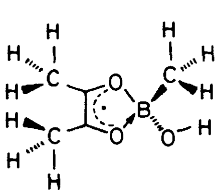


(9)



(10)

Surprisingly, no e.s.r. evidence for decay of (**10**) by loss of n-butyl radicals could be found, even at 333 K in neat di-t-butyl peroxide solvent.



(11)

An MNDO calculation[8] for the C_s structure (**11**) yielded an optimised geometry corresponding to a true energy minimum (ΔH_f° -768.9 kJ mol^{-1}). The coupling constants predicted by an INDO calculation for this structure were $a(^{11}B)$ -4.1, a(6H) $+5.7$, and a(3H) -0.6 G (the latter two averaged to simulate free rotation about the C–C and B–C bonds). The π spin populations on each ring carbon and oxygen atom were 14 and 33%, respectively.

In conclusion, S_H2 alkoxydealkylation at boron in 2-alkyl-1,3,2-benzodioxaboroles proceeds in a stepwise manner through a perboryl radical intermediate in which the unpaired electron occupies a delocalised π orbital centred on the catechol residue. The ease of breakdown of this intermediate (**3**) increases as the strength of the B–X bond decreases.

Experimental

E.s.r. Spectroscopy.—Spectra were recorded using a Varian E-109 instrument operating at *ca.* 9.2 GHz. The techniques used for sample preparation and for detection of transient photochemically generated free radicals have been described previously.[18] The light source was an Osram HBO-500 W/2 mercury discharge lamp and, after focusing with two 10 cm focal length quartz lenses and passage through an aqueous $NiSO_4$–$CoSO_4$ filter solution, the light incident on the sample was mainly in the wavelength region 240—340 nm.[19]

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 2.00271) as standard.[20] Usually, best-fit spectroscopic parameters were obtained using Preston's program ESRLSQ, which employs an exact solution of the isotropic Hamiltonian and an interative least-squares fitting procedure.[21]

Materials.—N.m.r. spectra (C_6D_6 solvent) were obtained using a Varian XL-200 instrument with tetramethylsilane internal standard (^1H, ^{13}C) or BF_3·Et_2O external standard (^{11}B). Preparation and handling of boron compounds was conducted under an atmosphere of dry nitrogen or argon.

Di-t-butyl peroxide (Fluka) was purified before use. Diethyl peroxide[22] and perdeuteriodi-t-butyl peroxide[23] were prepared as described previously. Mass spectrometric analysis of the deuteriated peroxide showed an M^+:$(M - 1)^+$ ratio of 5.7:1 and since, under the same conditions, the protio peroxide showed no peak corresponding to $(M - 1)^+$, photolysis of the deuteriated peroxide will yield t-C_4D_9O• and t-C_4D_8HO• in the ratio 12.4:1.

3,4,5,6-*Tetradeuteriocatechol.* Catechol (10.0 g) was heated under reflux for 8 h with D_2O (20 g) and D_2SO_4 (2.0 g). The solvent was removed under reduced pressure and replaced with fresh D_2O (21 g). The reflux, evaporation, replacement cycle was repeated, with addition of D_2O (22 g). After the third reflux and removal of the solvent, the residue was extracted into ether (150 cm^3), washed with saturated aqueous sodium chloride (3 × 50 cm^3), and dried ($MgSO_4$). After filtration through charcoal and Celite, the ether was removed under reduced pressure and the residual solid was recrystallised from toluene to give white crystalline tetradeuteriocatechol (8.0 g). The deuteriated catechol (0.4 g), benzyl bromide (1.3 g), and potassium carbonate (1.3 g) were heated under reflux in acetone (10 cm^3) for 1 h, then the mixture was poured into water. The yellow precipitate was separated by filtration and recrystallised, first from aqueous ethanol and then from light petroleum, to yield the dibenzyl ether as a white crystalline solid. The ^1H n.m.r. spectrum ($CDCl_3$) showed that the area of the signal from the catechol ring protons (δ 6.89) amounted to 1.5% of the area due to the benzylic protons (δ 5.13), indicating that the isotopic purity of the 3,4,5,6-tetradeuteriocatechol was $\geqslant$98.5 atom %.

Commercially available 1,3,2-benzodioxaborole (Aldrich) was purified by distillation (b.p. 38 °C at 15 Torr). It was also prepared from Me_2S·BH_3 and catechol.[24] The *B*-deuterio derivative was prepared by the reaction of BD_3 in tetrahydrofuran (THF) with catechol.[25,26] Benzene-ring deuteriated material was prepared in a similar manner[26] from 3,4,5,6-tetradeuteriocatechol.

4,6-*Di-t-butyl*-1,3,2-*benzodioxaborole* (b.p. 62—64 °C at 0.1 Torr) was prepared from 3,5-di-t-butylcatechol and THF•BH_3 following the method used[26] for benzodioxaborole (Found: C, 72.2; H, 8.7; M^+, 232. $C_{14}H_{21}BO_2$ requires C, 72.4; H, 9.1%; M, 232); ^{11}B n.m.r. δ 29.7 (br d, J_{BH} *ca.* 180 Hz).

2-t-Butyl-1,3,2-benzodioxaborole was prepared as described previously[27] [$\delta(^{11}B)$ 36.8 (s)].

2-Methyl-1,3,2-benzodioxaborole[28,29] (b.p. 59 °C at 12 Torr) was prepared by the reaction of methyl-lithium with 2-chloro-1,3,2-benzodioxaborole[30] in diethyl ether at -60 °C (Found: C, 62.8; H, 5.3; M^+), 134. Calc. for $C_7H_7BO_2$: C, 62.8; H, 5.3%; M, 134); $\delta(^{11}B)$ 35.5 (s).

2-*Butyl*-4,5-*dimethyl*-1,3,2-*dioxaborole* (b.p. 83—84 °C at 38 Torr) was prepared by azeotropic dehydration of a mixture of butylboronic acid and 3-hydroxybutan-2-one, as described[17] for the 2-isopropyl derivative (Found: C, 62.4; H, 9.6; M^+, 154. $C_8H_{15}BO_2$ requires C, 62.4; H, 9.8%; M, 154); $\delta(^{11}B)$ 33.1 (s).

Acknowledgements

We are very grateful to Mr. C. J. Cooksey for preparing and characterising the 3,4,5,6-tetradeuteriocatechol.

References

1 A. G. Davies and B. P. Roberts, in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, ch. 10.
2 K. U. Ingold and B. P. Roberts, 'Free-Radical Substitution Reactions,' Wiley-Interscience, New York, 1971, ch. 4.
3 D. Griller, K. U. Ingold, L. K. Patterson, J. C. Scaiano, and R. D. Small, jr., *J. Am. Chem. Soc.*, 1979, **101**, 3780.
4 M. C. R. Symons, T. Chen, and C. Glidewell, *J. Chem. Soc., Chem. Commun.*, 1983, 326.
5 T. A. Claxton, T. Chen, M. C. R. Symons, and C. Glidewell, *Faraday Discuss. Chem. Soc.*, 1984, **78**, 121.
6 (*a*) A. G. Milaev and O. Yu. Okhlobystin, *Russ. Chem. Rev.* (*Engl. Transl.*), 1980, **49**, 893; (*b*) A. I. Prokof'ev, T. I. Prokof'eva, I. S. Belostotskaya, N. N. Bubnov, S. P. Solodovnikov, V. V. Ershov, and

M. I. Kabachnik, *Tetrahedron*, 1979, **35**, 2471; (*c*) A. T. Prokof'ev, T. I. Prokof'eva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov, and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* (*Engl. Transl.*), 1977, **234**, 306; (*d*) A. Alberti, A. Hudson, and G. F. Pedulli, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 948; (*e*) P. E. Barker, A. Hudson, and R. A. Jackson, *J. Organomet. Chem.*, 1981, **208**, Cl; (*f*) A. G. Davies, Z. Florjańczyk, E. Lusztyk, and J. Lusztyk, *ibid.*, 1982, **229**, 215; (*g*) A. G. Davies and J. A. -A. Hawari, *ibid.*, 1983, **251**, 53.

7 K. B. Ulmschneider and H. B. Stegmann, in 'Landolt-Börnstein, New Series, Magnetic Properties of Free Radicals,' ed. H. Fischer and K.-H. Hellwege, Springer-Verlag, Berlin, 1980, vol. 9, part dl, ch. 13.

8 P. Bischof and G. Friedrich, *J. Comput. Chem.*, 1982, **3**, 486.

9 J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026; P. A. Dobosh, Quantum Chemistry Program Exchange, Program 141.

10 M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold, Wokingham, 1978, p. 176.

11 D. H. Wiffen, *Mol. Phys.*, 1963, **6**, 223.

12 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393; D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1985, 991.

13 A. C. P. Alves, J. M. Hollas, and B. R. Midmore, *J. Mol. Spectrosc.*, 1979, **77**, 124.

14 M. Zaidlewicz, in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 7, pp. 190—192. For other reviews on benzodioxaborole see G. W. Kabalka, *Org. Prep. Proced. Int.*, 1977, **9**, 133; C. F. Lane and G. W. Kabalka, *Tetrahedron*, 1976, **32**, 981.

15 R. Goetze, H. Nöth, H. Pommerening, D. Sedlak, and B. Wrackmeyer, *Chem. Ber.*, 1981, **114**, 1884.

16 J. E. Huheey, 'Inorganic Chemistry,' Harper and Row, New York, 1978, 2nd edn., pp. 842—850.

17 G. Smolinsky, *J. Org. Chem.*, 1961, **26**, 4915.

18 J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 161.

19 H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575; T. Kaiser, L. Grossi, and H. Fischer, *ibid.*, 1978, **61**, 223.

20 B. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191; R. Allendorfer, *ibid.*, 1971, **55**, 3615.

21 D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975.

22 B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Am. Chem. Soc.*, 1971, **93**, 4004.

23 P. M. Blum and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1313.

24 H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, 1977, **42**, 1392.

25 G. W. Kabalka, D. T. C. Yang, J. H. Chandler, and J. D. Baker, *Synthesis*, 1977, 124.

26 H. C. Brown, 'Organic Synthesis *via* Boranes,' Wiley-Interscience, New York, 1975, p. 63.

27 E. Negishi and H. C. Brown, *Synthesis*, 1972, 197.

28 D. Ulmschneider and J. Goubeau, *Chem. Ber.*, 1957, **90**, 2733.

29 M. Wieber and W. Künzel, *Z. Anorg. Allg. Chem.*, 1974, **403**, 107.

30 W. Gerrard, M. F. Lappert, and B. A. Mountfield, *J. Chem. Soc.*, 1959, 1529.

Received 1*st May* 1985; *Paper* 5/718