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The Influence of Boryl Substituents on the Formation and Reactivity of Adjacent and Vicinal Free Radical Centers

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Abstract: Radicals containing α-boronate substituents were generated by bromine abstraction from 1-bromoalkyldioxaborolanes (boronic esters), by addition to vinyl boronate, and by hydrogen abstraction from alkyldioxaborolanes and observed by EPR spectroscopy. Unsymmetrically substituted α-boronate radicals displayed selective line broadening in their low-temperature spectra from which barriers to internal rotation about $^{\bullet}CH_2{-}B(OR')OR$ bonds were found to be 3 ± 1 kcal mol^{-1}. Use of an empirical relationship between barrier height and bond dissociation energy led to BDE[$(RO)_2BCH_2{-}H$] = 98.6 kcal mol^{-1}. Rate constants for hydrogen abstraction from 2,4,4,5,5-pentamethyl-1,3,2-dioxaborolane by *tert*-butoxyl radicals were determined from competitive EPR and product studies and found to be relatively small, comparable to those of unactivated methyl groups. Hydrogen abstraction from bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methane was found to be extremely difficult. The structures and energetics of α-boronate radicals were computed by DFT methods (B3LYP/6-31G*). This predicted reductions in the rotation barriers of $X_2B{-}CH_2^{\bullet}$ radicals for increasing alkoxy substitution at B (X = Me or MeO) and corresponding increases in the $X_2BCH_2{-}H$ bond dissociation energies. The B3LYP-computed BDE[$(MeO)_2BCH_2{-}H$] was in excellent agreement with the analogous value derived from the experimental rotation barrier. Radicals containing *β*-boronate substituents were generated from the corresponding 2-bromoalkylboronic esters and characterized by EPR spectroscopy. At higher temperatures the main product from trialkyltin and triethylsilyl radical promoted reactions of 2-(2-bromohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was 1-hexene. This was best accounted for by a mechanism involving initial S_H2 attack on the borolane and subsequent bromine atom elimination from the displaced 2-bromohexyl radical.

Boronic acids and esters sustain a high reputation as versatile and convenient reagents for stereocontrolled syntheses[1] and for aromatic coupling processes.[2] A recent development in their chemistry, stemming from the discovery of efficient syntheses of alkenylboranes[3] and haloalkylboranes,[4] has been the emergence of promising carbon−carbon bond formation and cyclization processes mediated by boron-containing free radicals. For example, sulfonyl halides,[5] alkyl halides, and *O*-acyl-*N*-hydroxypyridine-2-thiones added efficiently to vinyl boronic esters. Likewise, suitably unsaturated haloalkylboronic esters underwent *exo*-ring closures in high yields.[6] Functionalized alkenyl diamino- and dialkoxyboranes were prepared regio- and stereoselectively by radical addition to the corresponding alkynylboranes.[7] Furthermore, α-boryl radicals derived from 1-haloalkylboronic esters were shown to add to alkenes to afford homoallylboronic esters in high yields.[8] A recent ingenious innovation employed boron-tethered radical cyclizations to provide convenient syntheses of 1,3-, 1,4-, and 1,5-diols.[9] The key intermediates in most of these processes were C-centered radicals with α- or *β*-borane, borinate, or boronate substituents. It is highly desirable that verified guidelines about the ease of formation, configuration, thermodynamic stabilization, and reactivity of such boron-containing radicals become available to steer future developments in these promising new areas.

In 1970, Matteson expertly marshalled the then known quantitative and theoretical data pertaining to neighboring-group effects of boron.[10] As far as borane-, borinate-, and boronate-substituted free radicals are concerned, quantification of reactivity has not proceeded much further since then, apart from a few ab initio computational studies. For boryl radicals ligated with amines, phosphines, sulfides, etc., the reverse is true, and

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elegant spectroscopic and kinetic studies[11] provided detailed guidelines from which the polarity reversal catalysis concept developed.[12]

It is known that boron participates strongly in π-bonding in vinylboranes and related molecules.[10] The vacant p-orbital on boron accepts a chemically significant amount of electron density from an adjacent π-system. It was expected therefore that substantial electron delocalization onto boron would prevail in α-boryl radicals of the type $^\bullet CHR-BR_2$ (R = alkyl, aryl) and hence that such species would form easily and possess sizable stabilization energies. The experimental evidence supports this presumption. Interaction of a C-centered or O-centered radical ($X^\bullet$) with trialkylborane RCH_2BR_2 (R = alkyl) normally leads to competition between two pathways:

$$X^\bullet + RCH_2BR_2 \rightarrow XH + {}^\bullet CHR-BR_2 \qquad (1)$$

$$X^\bullet + RCH_2BR_2 \rightarrow RCH_2BRX + R^\bullet \qquad (2)$$

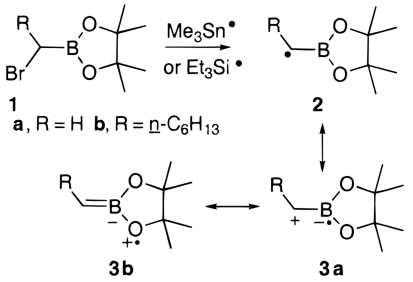
Hydrogen atom abstraction (H-abstraction) (eq 1) was found to be much faster than homolytic substitution (eq 2) when X = Br, and competitive experiments indicated that the α-boryl radicals were stabilized by 14.5 kcal mol^{-1} more than secondary alkyl radicals.[13] Similarly, H-abstraction from Et_3B by methyl radicals was found to be more than an order of magnitude faster than that from toluene and an approximate BDE of 80 kcal mol^{-1} was obtained for $Et_2BC-H_2(Me)$.[14] The preferred reaction mode for X = t-BuO$^\bullet$, and for acetone triplets, was, however, homolytic substitution (eq 2).[15] Ab initio computations support the conclusion that α-boryl substituents confer substantial stabilization on alkyl radicals. UHF computations with a 4-31G basis set gave a stabilization energy of 11 kcal mol^{-1} for the $H_2BCH_2^\bullet$ radical, the largest stabilization of a substituted methyl radical found for any simple functional group.[16] A marginally smaller stabilization energy of 9.7 kcal mol^{-1} was obtained from computations at the MP4SDTQ/6-31G* level.[17]

It was expected that the introduction of oxygen on boron in analogous borinate [$RCH^\bullet B(R)OR$] and boronate [$RCH^\bullet B(OR)_2$] radicals would decrease their stabilization because (i) donation of electron density from the nonbonding electrons on oxygen would decrease the ability of boron to delocalize the unpaired electron and (ii) the oxygen(s) would increase the electronegativity of the group also resulting in decreased radical stabilization.[16] Experimental information is, however, very meagre. The chain transfer constants of the radical-initiated reaction of CCl_4 with $CH_2{=}CHB(OBu)_2$ were very small (ca. 10^{-3}); hence it was concluded that delocalization of the unpaired electron onto boron in the propagating α-boronate radicals must be substantial.[18] However, in apparent conflict with this, H-abstraction by $Cl^\bullet$ atoms from the CH_3B group of $CH_3B(OBu\text{-}t)_2$ was barely favored (by a factor of 1.1−1.5 at 0 °C) over attack on the *C*-methyl groups.[10,19] The relative reactivities toward free radical bromination were found to decrease in the order[16] boranes > borinates > boronates, and for *tert*-butoxyl radicals, homolytic substitution was preferred over H-abstraction from methaneboronic anhydride.[15,20] Most of the qualitative and relative kinetic data seem, therefore, to suggest that stabilization of an adjacent radical center by a boronate group is small to insignificant.

The objectives of the present research were to investigate the ease of formation of α- and β-boronate radicals, to ascertain their modes of reaction, to assess the stabilization of these radicals by experimental and by ab initio theoretical methods, and to examine the kinetics of hydrogen abstraction adjacent to boronate functional groups. We recently reported the first EPR spectroscopic observations of transient radicals derived from boronic esters in solution[21] and have used this technique, integrated with product analyses, to address the above aims.

Results

Generation and EPR Spectroscopic Characterization of α-Boronate Radicals. α-Bromoalkylboronic esters **1** were prepared according to the protocols developed by Matteson and co-workers.[22,23] Bromine was readily abstracted from **1** by tin- and silicon-centered radicals to afford the corresponding α-boryl radicals **2** which were observed in cyclopropane and *tert*-butylbenzene solution by 9 GHz EPR spectroscopy (see Supporting Information for examples of the spectra).[24] The spectra of both **1a** and **1b** decayed within the spectrometer response time which indicated their half-lives were ≤ 1 ms. The intensity of the initiating UV light was varied by means of calibrated gauzes; and hence the concentration of radical **1a**, in *tert*-butylbenzene at 220 K, was shown to depend on light intensity to the power 0.68 ± 0.03. Consequently, the decay of radical **1a** was by second-order dimerization plus a first-order contribution, probably hydrogen abstraction. These results established that radical **1a** and related intermediates behave as normal transient substituted methyl radicals with no kinetic stability. The hyperfine splittings (hfs) from the α-hydrogens (Table 1) were slightly smaller than those in analogous unsubstituted primary and secondary alkyl radicals [e.g., $a(H_\alpha)$ = 22.2 G for $^\bullet CH_2CH(OEt)_2$][25] which suggested the possibility of minor electron delocalization into the boron or oxygen p-orbitals as depicted in structures **3a** and **3b**. This was also consistent with the appreciable ^{11}B and ^{10}B hfs.



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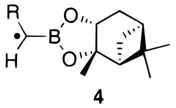
(24) The spectra were of sufficient quality for both ^{11}B and ^{10}B hfs to be resolved. For **1a**, for example, the measured $a(^{10}B)$ was equal to the measured $a(^{11}B)$ multiplied by the ratio of their magnetic moments (corrected for nuclear spin multiplicity) to within the experimental error, as expected from theory.

Table 1. Isotropic 9 GHz EPR Spectral Parameters of Radicals Derived from Boronic Esters Together with DFT Computed Values[a]

radical	R	*T*/K	$a(H_\alpha)$	$a(H_\beta)$	$a(H_\beta)$	$a(^{11}B)$	$a(^{10}B)$	*a*(other)
2a	H[b]	220[c]	20.9 (2H)			12.3	4.1	
2b	*n*-C_6H_{13}	220[c]	20.0	23.5	23.5	12.0	4.0	0.5 (2H)
4a	H	145[d]	21.1 (2H)			12.4	4.2	1.1 (1H)
4b	*n*-C_6H_{13}	220[c]	19.0	23.6	23.6	12.2	4.1	
5		165[e]	21.1			12.3	-	1.04 (3H)
6		170[e]	20.9			12.2	4.0	1.0 (1H)
9a	Et_3Si	195[c]	18.3	23.8	9.1	10.8	3.6	
9b	Me_3Sn	235[c]	16.7	16.7	11.8	10.1	3.4	
19a	*n*-Bu	180[d]	22.1	27.0 (2H)	22.1 (2H)	17.7	5.9	
19b	Me_3Si	180[d]	20.0	-	18.0 (2H)	23.3	7.8	
24		215[d]	22.1	28.2				0.9 (2H)
Computed parameters		Method[f]						
28		B3LYP	−21.4			−9.3		35.3 (C_α)
$(MeO)_2BCH_2^\bullet$		B3LYP	−21.6			−8.5		35.6 (C_α)
$MeO(Me)BCH_2^\bullet$		B3LYP	−20.7			−6.2		33.9 (C_α)
$Me_2BCH_2^\bullet$		B3LYP	−20.0			−1.1		32.0 (C_α)
29[g]		B3LYP	−23.0		15.7 (2H)	26.4		48.2 (C_α)

[a] All hfs/G checked by computer simulations. [b] *g*-factor = 2.0028; other *g*-factors 2.003 ± 0.001. [c] *t*-BuPh solvent. [d] Cyclopropane solvent. [e] *n*-Propane solvent. [f] 6-31G* basis set; computed from Fermi contact integrals. [g] Computed hfs are for the single lowest energy conformation.

If electron delocalization as depicted in **3** were significant, an appreciable barrier to rotation about the C_α−B bond would be expected. Because of its symmetry, the two α-Hs in radical **1a** will always be equivalent, irrespective of the conformation about the C_α−B bond. Three α-boryl ester radicals, **4**−**6**, each containing an element of asymmetry, were therefore generated and spectroscopically examined. In the limit of slow rotation about C_α−B, the two α-Hs will become magnetically nonequivalent and this should show up as selective line broadening in the EPR spectra of **4**−**6** at low temperatures The radicals were each generated by bromine atom abstraction by triethylsilyl radicals from the corresponding 1-bromoalkyl boronic esters in cyclopropane and propane solutions. For all three radicals, selective broadening of the central components of the triplets due to the two α-Hs was observed in the temperature range 150−100 K, with coalescence temperatures < 100K. The double doublet hyperfine structure due to two nonequivalent α-Hs could not be observed for any of the three radicals studied. This was partly because 100 K was the lowest accessible temperature and partly because indiscriminate broadening due to inefficient tumbling of radicals became significant below ca. 115 K. The hfs of nonequivalent α-Hs could not, therefore, be directly determined for any of **4**−**6**. However, in analogous radicals $^\bullet CH_2-X$ (X = OH, OMe, CHR_2, SMe),[26] the measured differences *δa* of their α-Hs were always in the range 0.5−1.5 G. Computer simulations[27] of the exchange-broadened region of radical **4** (160−110 K) employing a two-jump model accorded best fit with *δa* = 0.6 G. From comparisons of computed and experimental spectra (see Supporting Information) the following Arrhenius parameters were derived for the exchange rotation about the C_α−B bond: $\log(A_e/s^{-1}) = 11.9$, E_e/kcal mol^{-1} = 2.9 ± 0.7; the barriers obtained for radicals **5** and **6** were indistinguishable from this, i.e., both 3 ± 1 kcal mol^{-1}.



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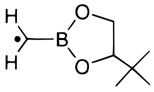

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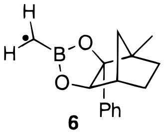

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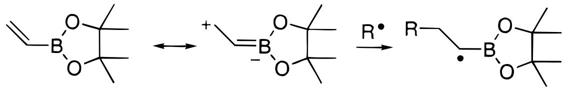
Free radical addition to vinylboronic ester **7** was also studied using EPR spectroscopy. Initiating radicals were generated photochemically from bromotrichloromethane and tetraphenylhydrazine in the presence of **7**, but only $CCl_3^\bullet$ and $Ph_2N^\bullet$ radicals were spectroscopically detected in these two experiments. Photolysis of a *tert*-butylbenzene solution of **7** and dibenzoyl peroxide produced a complex spectrum at 210 K with *a*(1H) = 36.0 G, *a*(1H) = 13.3G, *a*(1H) = 9.2 G, *a*(1H) = 8.2G, and *a*(1H) = 2.8 G. We attribute this to the 3-*tert*-butyl-1-phenylcyclohexadienyl radical formed by addition of the $Ph^\bullet$ radical to the solvent. Selective *meta*-addition of *σ*-type radicals to *tert*-butylbenzene has been reported before,[28] and the hfs are similar to those of 1-alkyl-3-*tert*-butylcyclohexadienyl radicals[28] and of the 1-phenylcyclohexadienyl radical.[29] It is evident that $Ph^\bullet$ radicals add to the aromatic solvent more easily than to vinyl boronic ester **7**. By way of contrast, $Et_3Si^\bullet$ and $Me_3Sn^\bullet$, generated from triethylsilane and hexamethylditin, respectively, in *tert*-butylbenzene, added efficiently to **7** and gave good spectra of the corresponding α-boronic ester adduct radicals **9** in the temperature range 200−250 K (Table 1). These observations do not challenge reports on the preparation of adducts from vinyl boronic esters with a variety of radicals at higher temperatures where all addition rates will be faster. They do imply, however, that nucleophilic radicals add most efficiently and are in good accord with the suggestion[10] that the polar resonance structure **8** makes an appreciable contribution to the ground state of vinyl boronic esters including **7**.



7 **8** **9**

a; R = Et_3Si, **b**; R = Me_3Sn

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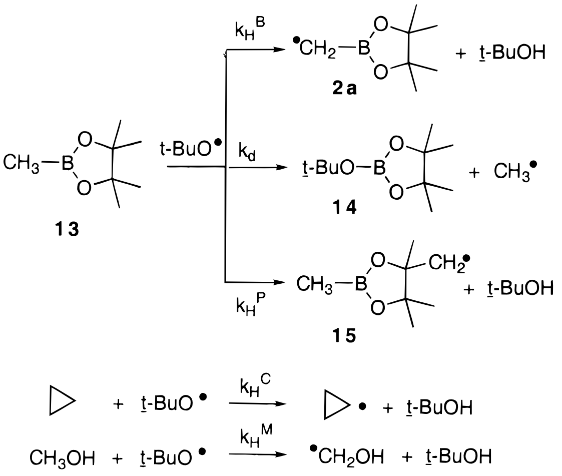
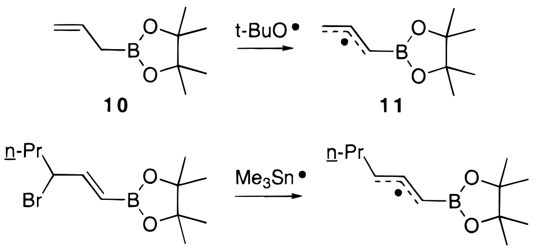
Scheme 1



Hydrogen Abstraction from Alkyl and Allyl Boronates. Kinetic data for H-abstraction has been widely used as a means of assessing the ease of radical generation and influence of adjacent functional groups on a reactive center. For allyl boronic ester **10**, *tert*-butoxyl radicals exclusively abstracted hydrogen adjacent to boron as judged by the intense EPR spectrum of the corresponding allyl radical **11** obtained [$a(1H_{exo}) = 13.9$, $a(2H_{endo}) = 13.1$, $a(1H) = 3.5$, $a(^{11}B) = 8.0$, $a(^{10}B) = 2.7$ G at 205 K in *t*-BuPh]. For comparison, a spectrum of the analogous allyl radical was obtained on bromine abstraction by $Me_3Sn^\bullet$ radicals from (3-bromohex-1-enyl)boronic ester **12** and found to have a very similar boron hfs [$a(2H_\beta) = 12.6$, $a(2H_{endo}) = 12.9$, $a(1H) = 3.4$, $a(^{11}B) = 7.9$ G at 205 K in *t*-BuPh]. No addend radical was observed in either case.



10 **11** **12**

On photolysis of a solution of methylboronate **13** and di-*tert*-butyl peroxide (DTBP) in cyclopropane, three radicals were detected by EPR spectroscopy. These were the α-borylalkyl radical **2a**, formed by H-abstraction adjacent to boron, the methyl radical generated by displacement at boron (S_H2 reaction), and the cyclopropyl radical derived from the solvent. An additional triplet signal [$a(2H_\alpha) = 22.4$ G, $g = 2.0028$ at 240 K], which we attribute to radical **15**, derived by H-abstraction from the pinacol methyls, was detected at higher temperatures ($T > \sim 230$ K) in neat DTBP (Scheme 1). The relative concentrations of radicals **2a**, $CH_3^\bullet$, and cyclopropyl [C•] were determined by computer simulation of spectra obtained at a series of temperatures for two different concentrations of **13** in cyclopropane (Table 2). These data showed that H-abstraction occurred about 10 times as readily as methyl displacement at the lower temperatures but that displacement increased in importance as temperature increased. The absolute rate constant for H-abstraction from cyclopropane by the *t*-BuO• radical was not known, and therefore this was determined from competitive experiments in which the EPR spectra of cyclopropyl and hydroxymethyl were monitored for known concentrations of DTBP and methanol in cyclopropane at a series of temperatures (see Supporting Information for details). From the known Arrhenius parameters for H-abstraction from methanol [$\log(A_H^M/s^{-1} = 9.1$, $E_H^M = 5.31$ kcal mol^{-1}]^{30} the Arrhenius parameters for H-abstraction from cyclopropane by *t*-BuO• radicals were found to be:

Table 2. Relative Concentrations of Radicals and Relative Rate Constants Obtained from Reactions of Methylboronate **13** with *tert*-Butoxyl Radicals

T/K	$[CH_3^\bullet]/[C^\bullet]$	$[\mathbf{2a}]/[C^\bullet]$	k_d/k_H^C	k_H^B/k_H^C
150[a]	0	0.32		3.3
170[a]	0	0.32		3.3
190[a]	0.044	0.43	0.46	4.5
210[a]	0.048	0.54	0.50	5.6
230[a]	0.098	0.86	1.02	8.9
250[a]	0.179	1.38	1.86	14.4
265[a]	0.258	1.97	2.68	20.5
150[b]	0	0.11		1.4
170[b]	0	0.11		1.4
190[b]	0.024	0.18	0.30	2.3
210[b]	0.038	0.23	0.48	2.9
230[b]	0.046	0.49	0.58	6.2
250[b]	0.089	0.70	1.13	8.8
265[b]	0.143	0.90	1.80	11.3

[a] [**13**] = 1.16 mol dm^{-1}, [cyclopropane] = 12.1 mol dm^{-3}. [b] [**13**] = 1.01 mol dm^{-1}, [cyclopropane] = 12.7 mol dm^{-3}.

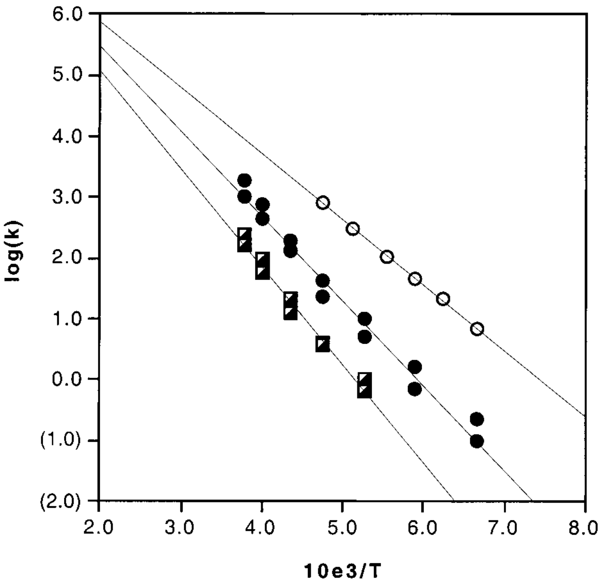


Figure 1. Arrhenius plots of rate constants for reactions of *tert*-butoxyl radicals with methyl boronate **13** and cyclopropane. Open circles: $\log(k_H^C) + 2$ for cyclopropane. Filled circles: $\log(k_H^B)$ for **13**. Half-filled squares: $\log(k_d)$ for **13**.

$$\log(k_H^C/M^{-1}\,s^{-1}) = (6.04 \pm 0.4) - (5.0 \pm 0.5)/\text{kcal mol}^{-1}/2.3RT \quad (3)$$

Application of the steady-state approximation to the mechanism shown in Scheme 1 leads to the following rate expressions: $k_H^B/k_H^C = [\mathbf{2a}][c\text{-}C_3H_6]/[C^\bullet][\mathbf{13}]$ and $k_d/k_H^C = [CH_3^\bullet][c\text{-}C_3H_6]/[C^\bullet][\mathbf{13}]$. The relative rate constants in Table 2 were obtained by use of these expressions. Incorporation of the k_H^C values, interpolated from the above Arrhenius line, led to the Arrhenius plots shown in Figure 1, from which the rate parameters in Table 3 were derived.

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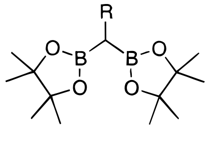
[30] Wong, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 1235–1239.

Table 3. Comparison of the Kinetic Parameters for Reactions of *tert*-Butoxyl Radicals with Methylboronate **13** with Various Substrates in Solution[a]

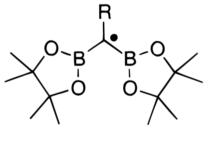
substr	mode[b]	T/K	k/M^{-1} s^{-1}	log(A/s^{-1})	E/kcal mol^{-1}	ref
c-C_5H_{10}	H	302[c]	9.6×10^5	8.5	3.5	*g*
CH_3OH	H	293[d]	1.3×10^5	9.1	5.3	*e*
$PhCH_3$	H	295[e]	2.3×10^5			*f*
c-C_3H_6	H	300[f]	2.7×10^2	6.0	4.9	*h*
13	H	300[f]	4.2×10^3	8.2	6.3	*h*
13	D	300[f]	8.7×10^2	8.3	7.3	*h*

[a] Rate parameters not corrected for number of "active" hydrogens. [b] H = H-abstraction, D = displacement of CH_3. [c] Solvent PhH/DTBP. [d] Solvent DTBP. [e] Solvent PhH/DTBP. [f] Solvent cyclopropane. [g] Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106. [e] Wong, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 1235. [f] Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520. [h] This work.

Bis-boronic esters **16a**,**b** were prepared by following literature procedures.[31] Photolyses of solutions of **16a** or **16b** in neat DTBP, and other solvents, displayed only weak and ill-defined EPR spectra. The spectra from **16a** in the temperature range 240−300 K indicated the presence of a weak triplet [$a(2H_\alpha) = 21.6$ G] which may be due to H-abstraction from the eight methyl groups. The remaining broad, weak, and ill-defined set of lines was definitely not due to radical **2a** (from homolytic displacement at boron) and could not be simulated with any set of hfs reasonably corresponding to radical **17a**. The nature of the abstracting radical was changed from the electrophilic t-BuO$^\bullet$ to the nucleophilic $Et_3NBH_2^\bullet$ by addition of amine−borane Et_3NBH_3 as polarity-reversal catalyst.[32] However, under these conditions, only a weak spectrum of the ethyl radical was detectable in the accessible temperature range.



16



17

a, R = H; **b**, R = n-C_5H_{11}

Formation and Reactions of Radicals with β-Boronate and δ-Boronate Substituents. The β-bromoboronic esters **18a**,**b** were prepared in good yield by bromoboration of the corresponding alkenes followed by esterification with pinacol. This procedure was reported to give mixtures of products,[33] but in our hands, under different experimental conditions, addition proceeded cleanly. Bromine atom abstraction from **18a** by $Me_3Sn^\bullet$ radicals in cyclopropane solution afforded the spectrum shown in Figure 2 which was well matched by a simulation based on the hfs given in Table 1. Changes in the $a(^{11}B)$ and $a(H_\beta)$ values were difficult to measure in the accessible temperature range (160−210 K) because of the comparatively large line width (see Figure 2), but a small increase of $a(H_\beta)$ from 22.0 at 160 K to 22.5 G at 205 K was discerned. The magnitudes of $a(H_\beta)$ and $a(^{11}B)$, and the temperature dependence, are consistent with those of structure **19i**,[34] in which the boron atom eclipses the SOMO, as the preferred, low temperature, conformation of radical **19a** about its $C_\alpha-C_\beta$ bond. In the preferred conformations of radicals of type $^\bullet CH_2XR_n$, where X is a second (or subsequent) row element, the XR_n group eclipses the SOMO,[34] i.e., structures are analogous to that of **19i**, but when X is C, N, or O, the staggered conformation in which XR_n is in the nodal plane of the SOMO is preferred. The spectrum obtained for radical **19b** was similar to that of **19a** (Table 1).

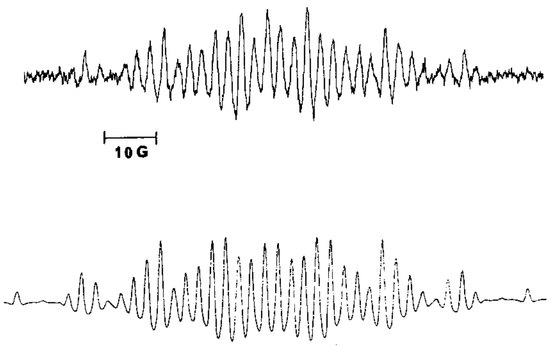
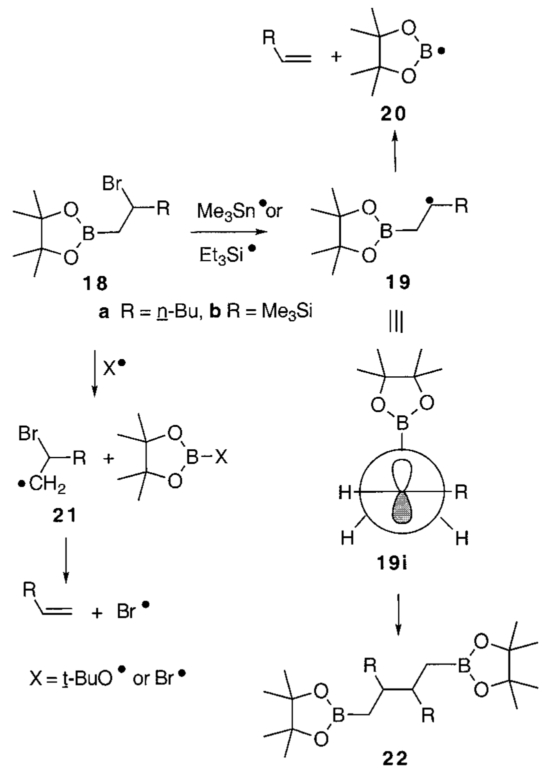


Figure 2. EPR spectrum (9 GHz) of 2-(tetramethyldioxaborolane)-ethyl radical **19a** in cyclopropane solution at 180 K; second derivative presentation. The lower spectrum is the computer simulation including ^{11}B and ^{10}B hfs (Table 1).

Scheme 2



At temperatures above ca. 220 K, the spectrum of **19a** unexpectedly became too weak for observation. This suggested it was decaying by a rapid and novel process. Product analysis of a 250 K photolysate revealed that 1-hexene was the major product together with minor amounts of a dimer and some unidentified components; the extent of reaction was low. The mixture from photolysis at 180 K on the other hand showed the dimer to be the main product accompanied by only traces of 1-hexene. The simplest mechanistic explanation of these observations would be that dimerization to produce **22** competes with a β-scission process which yields 1-hexene and boron-centered radical **20** (Scheme 2). However, the bisalkoxyboryl radical **20** was not observed by EPR spectroscopy. 2-Methyl-2-nitrosopropane and *tert*-butyl hyponitrite were added in

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(31) Castle, R.; Matteson, D. S. *J. Organomet. Chem.* **1969**, *20*, 19−28. Soundararajan, R.; Matteson, D. S. *Organometallics* **1995**, *14*, 4157−4166.

(32) Paul, V.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1953−1961.

(33) Mikhailov, B. M.; Nikolaeva, M. E. *Izv. Akad. Nauk. SSSR. Ser. Khim.* **1963**, 1368; *Chem. Abstr.* **1963**, *59*, 15296f.

(34) Kochi, J. K. *Adv. Free Radical Chem.* **1975**, *5*, 189−317.

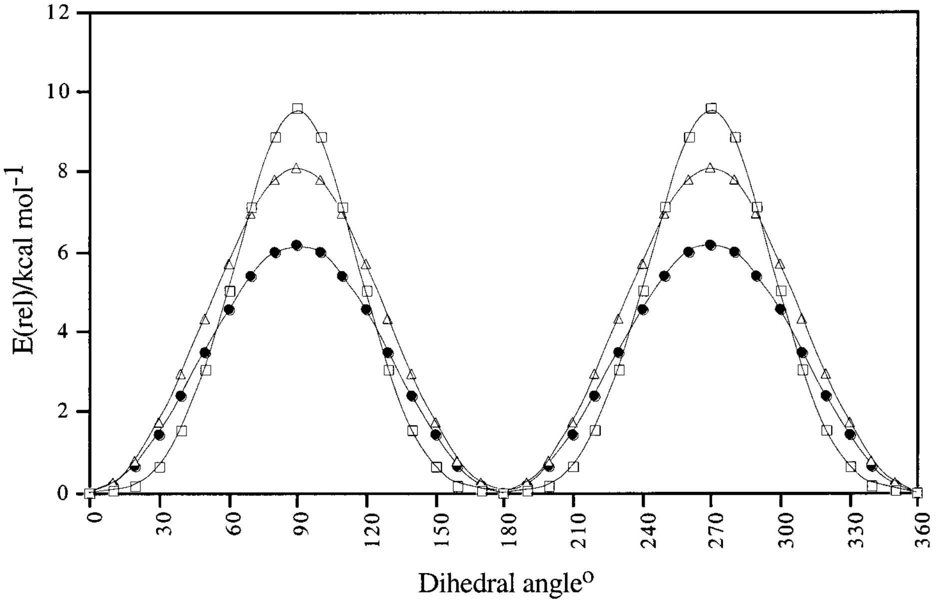
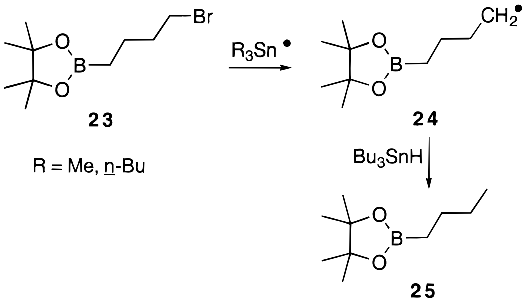


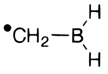
Figure 3. Plot of the relative energies of $X_2B-CH_2^•$ radicals, as computed using the B3LYP/6-31G* method, as a function of the dihedral angle $X-B-C_\alpha-H_\alpha$. Squares: radical **26**. Triangles: radical **27**. Circles: radical **28**.

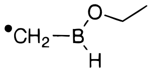
separate attempts to spin trap **20**. Although several (unidentified) spin adducts were observed, nothing corresponding to trapped **20** was detected. It was anticipated that radical **20** might show up in the spectrum when ligated with a suitable donor. However, photolysis of a mixture of **18a**, hexamethylditin, and excess pyridine gave no sign of the ligated species $[C_5H_5N \rightarrow$ **20**$]^•$. Alternatively, 1-hexene might be formed via a homolytic substitution at boron in **18** by some radical $X^•$, followed by β-scission of the resulting 2-bromoalkyl radical **21** (Scheme 2).

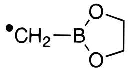
The EPR spectrum of the δ-boronato radical **24** was obtained on photolysis of a solution of 4-bromobutylboronic ester **23** and hexamethylditin in cyclopropane (Table 1). As expected, the EPR hfs were normal for a primary radical and no long-range hfs from boron was resolvable. Treatment of **23** with Ph_3SnH using photochemical initiation afforded only the orthodox reduction product 2-*n*-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **25**.



Ab Initio Density Functional Calculations on α- and β-Boronate and Related Radicals. Ab initio computations were carried out using the Gaussian 94 (revision C3) and Gaussian 98 (revision A) suites of programs.[35] Structures were fully optimized using density functional theory with no geometry constraints (B3LYP/6-31G*)[36] and employing spin-restricted (RHF) and spin-unrestricted (UHF) methods for closed shell and open shell species, respectively. Radicals **26**, **27**, and **28** were chosen as models of methyl radicals containing α-boryl, α-borinate, and α-boronate groups, respectively. For all three radicals the computed GS structures were essentially planar and the $C_\alpha-B$ bond lengths of 1.531, 1.535, and 1.531 Å for **26** to **28**, respectively, showed little effect on successive alkoxy substitution. The conformational energies about their $C_\alpha-B$ bonds were computed by incrementing the dihedral angles ($H_\alpha-C_\alpha-B-X$) by 10° and then allowing the rest of the geometry to optimize. The computed relative energies as a function of torsion angle are shown in Figure 3. Symmetrical 2-fold rotors were obtained for each radical with minima at 0° and 180° and maxima at 90° and 270°; the computed barrier heights were 9.6, 8.1, and 6.2 kcal mol^{-1} for **26**, **27**, and **28**, respectively.


26


27


28

To assess the effect of successive introduction of alkoxy substituents at boron on the strength of $H-CH_2$ bonds of adjacent methyl-B groups, the total energies, including electronic energies, zero-point vibrational energies (ZPVE), and thermal enthalpy corrections to 273 K, were computed for the model isodesmic reactions[37] shown in Table 4. The computed ground-state structures of the $R_2BCH_2^•$ radicals (R = Me or MeO) showed a negligible change of $r(B-C)$ on alkoxy substitution, but the positive charge on the boron atoms increased and the negative charge on the CH_2 groups increased with increase in alkoxy substitution. The computed enthalpy changes ($\Delta E_{tot}°$) decreased with increasing alkoxy substitution. Computed EPR hfs are listed in Table 1. The a(B) values increased, i.e., became less negative, with increasing alkyl substitution. This trend is in accord with the expected increase in electron delocalization with alkyl substitution.

To assess the feasibility of elimination from β-borylalkyl radicals such as **19a**, radical **29** which lacks the methyl and

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(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Allaham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Anders, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales C.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.

(36) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

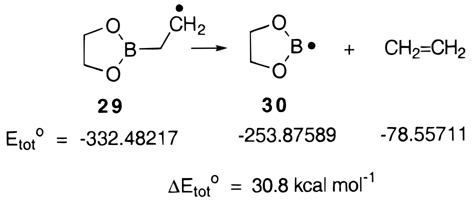
(37) Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2305−2313.

Table 4. Computed Energies of H-Transfer for Model Boryl, Borinate, and Boronate Radicals[a]

reaction E_{tot} [hartree]		$\Delta E_{tot}°$/kcal mol^{-1}	BDE(R_2BCH_2-H)[b]/kcal mol^{-1}
$Me_2BCH_2^\bullet + CH_4 \rightarrow$ -143.87803	$Me_2BCH_3 + CH_3^\bullet$ -144.52530	10.4	94.4
$MeO(Me)BCH_2^\bullet + CH_4 \rightarrow$ -219.13263	$MeO(Me)BCH_3 + CH_3^\bullet$ -219.78338	8.2	96.6
$(MeO)_2BCH_2^\bullet + CH_4 \rightarrow$ -294.38536	$(MeO)_2BCH_3 + CH_3^\bullet$ -295.03851	6.7	98.1

[a] $E_{tot}(CH_3^\bullet) = -39.82659$, $E_{tot}(CH_4) = -44.49044$ hartree. [b] R = Me or MeO; bond dissociation energies based on BDE(CH_3-H) = 104.8 (see text).

Scheme 3



butyl groups was studied as a model for β-scission. The computed total energies of each species, including ZPVE and thermal enthalpy corrections, are shown in Scheme 3. Elimination of ethene from **29** with formation of bisalkoxyboryl radical **30** was found to be 30.8 kcal mol^{-1} endothermic. Computed EPR hfs for the single lowest energy conformation of radical **29** are listed in Table 1.

Discussion

Thermodynamic Stabilization and Ease of Formation of α-Boronate Radicals. Our EPR spectroscopic study showed that alkyl radicals containing α-boronate substituents could be generated by bromine abstraction from α-bromoboronic esters by organotin and organosilyl radicals virtually as readily as unsubstituted alkyl radicals from bromoalkanes. Homolytic addition to vinyl boronic esters was facile at low temperatures for organotin and organosilyl radicals, but temperatures above ambient are presumably required for addition of most alkyl and π-radicals. On the other hand, H-abstraction by electrophilic *tert*-butoxyl radicals from methyl and methylene groups adjacent to $B(OR)_2$ was found to be slow and in competition with homolytic displacement of alkyl from boron. This was in agreement with previous findings for chlorine atom attack on alkyl boronates.[10,19] H-Abstraction does not appear to be an efficient or selective method for generation of α-boronate radicals.

The barriers to internal rotation about the $H_2C^\bullet-B(OR)_2$ bond in radicals **4a**, **5**, and **6** obtained from two-jump models of the selective EPR line broadening were quite small (3 kcal mol^{-1}). These barriers are only slightly greater than that in analogous hydrocarbon radicals such as $H_2C^\bullet$-c-C_5H_9, for which the measured barrier was[38] 0.5 kcal mol^{-1}. A linear relationship between internal rotation barriers (E_e) of primary radicals of the type $H_2C^\bullet-X$ and the standard gas-phase bond dissociation energies of the corresponding $H-CH_2X$ bonds [(BDE(C−H)] was first demonstrated[39] for a range of X and later extended.[40] Recently, recommended BDEs have increased significantly due to improved experimental methods and rationalizations between differing techniques.[41,42] Updating the thermodynamic data yields the empirical relationship

$$\text{BDE}(RCH_2-H)/\text{kcal mol}^{-1} = 101.1 - 0.86E_e \qquad (4)$$

The BDE(C−H) for boronate esters of type **13**, i.e., BDE-[$(RO)_2BCH_2-H$), derived from eq 4 is 98.6 kcal mol^{-1}. This is only 2 kcal mol^{-1} less than BDE(Et−H) and indicates that the boronate group has only a marginal activating influence on adjacent methylene groups.

Recently, Brocks et al. have reassessed and extended earlier proposals of relationships between EPR H_α and H_β hfs and BDE(C−H) values and have recommended several linear correlations.[43] For $a(H_\alpha)$ values, expressions BDE(C−H) = $1.61a(H_\alpha) + 62.4$ and BDE(C−H) = $1.93a(H_\alpha) + 57.8$ were both found to give reliable BDEs for planar or nearly planar radicals. The $a(H_\alpha)$ values of α-boronate-substituted radicals of the type [$(RO)_2BCH_2^\bullet$], i.e., **2a**, **4a**, **5**, and **6** are all 21.0 ± 0.1 G (see Table 1) and these radicals are expected to be planar. Hence, substitution into the above correlations yields 96.2 and 98.3 kcal mol^{-1} respectively for the corresponding BDE-[$(RO)_2BCH_2-H$]. Both these values, but particularly the latter, are in impressive agreement with the BDE derived from the rotation barriers and increase confidence in its reliability.

The H_2C-B torsions for radicals **26**, **27**, and **28** were all computed to be 2-fold rotors (Figure 3), which supports the use of a two-jump model in simulating the EPR exchange broadening. The computed rotation barriers decreased with successive introduction of alkoxy substituents. This agrees with the suggestion that introduction of oxygen on boron decreases the stabilization of an adjacent radical. The computed barrier height for model radical **28** was about twice the measured barriers of radicals **4a**, **5**, and **6**, but in view of the small magnitudes of both computed and experimental data, this should be considered as satisfactory agreement. Our DFT theoretical assessment of hydrogen transfer from C−H bonds adjacent to boryl, borinate, and boronate groups in model compounds predicted an increase of ca. 2 kcal mol^{-1} in C−H bond strength for introduction of each MeO group into R_2BCH_2-H compounds (Table 4). Thus, the methane-based stabilization energy of the $Me_2BCH_2^\bullet$ radical is computed to be 10.4 kcal mol^{-1}, which is close to the literature computed values for the $H_2BCH_2^\bullet$ radical quoted in the Introduction; this drops to 6.7 kcal mol^{-1} for $(MeO)_2BCH_2^\bullet$. By incorporating the experimental C−H bond dissociation energy of methane [BDE(CH_3-H) = 104.8 kcal mol^{-1}],[41] the C−H bond dissociation energies listed in column 3 of Table 4 were obtained for the model boron compounds. The excellent agreement of the computed value

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[38] Kemball, M. L.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1017−1023.

[39] Nonhebel, D. C.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 731−732.

[40] Holmes, J. L.; Lossing, F. P.; Terlouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 1086−1087.

[41] Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347−1353.

[42] Tsang, W. In *Energetics of Organic Free Radicals*; Simões, J. A. M., Greenberg, A., Liebman, J. F., Eds.; Blackie: London, 1996; pp 22−58.

[43] Brocks, J. J.; Beckhaus, H.-D.; Beckwith, A. L. J.; Rüchardt, C. *J. Org. Chem.* **1998**, *63*, 1935−1943.

for BDE[$(MeO)_2BCH_2$−H] (98.1 kcal mol^{-1}) with the analogous BDE[$(RO)_2BCH_2$−H)] value derived from the empirical relationship (eq 4) (vide supra) is very impressive and underlines the concordance of theory and experiment for these classes of compounds. The computed Mulliken atomic charges (and spin densities) on boron in radicals **26**−**28** were +0.40 (0.2), +0.45, and +0.52 (0.01), respectively, for the C_α atoms (including attached hydrogens); charges (spin densities) of −0.09 (0.90), −0.12, and −0.16 (1.0) were obtained. The computed charge (spin density) on oxygen in **28** was −0.44 (0.04). These values suggest that delocalization of the unpaired electron onto boron or oxygen as depicted in structures **3a**,**b** does not take place and that structure **2** is the most appropriate description of the radical for alkyl or alkoxy substituents on boron.

H-Abstraction from methylboronate **13** by t*ert*-butoxyl radicals took place comparatively slowly (Table 3). The measured k_H value for **13** was less, even when statistically adjusted for the number of available H atoms, than k_H for secondary hydrogens in, for example, cyclopentane. Hydrogen abstraction from **13** was faster than that from the deactivated methylene groups of cyclopropane, but the rate constant was found to be of comparable magnitude to that for primary hydrogens of unactivated methyl groups.[44] The experimental kinetic data agrees, therefore, with the above thermodynamic data that the boronate group has an insignificant activating effect on adjacent C−H bonds and implies that the activation energy for hydrogen abstraction is at least as high as that of primary hydrogens in alkanes. The failure to detect radicals **17** on reaction of bisboronate esters **16** with *tert*-butoxyl radicals provides additional support for this conclusion. The presence of two boronate groups decreased the efficiency of H-abstraction. Partly this could be due to the increased steric crowding in **16**, but even the secondary hydrogen atoms of **16a** were not abstracted and this clearly implies a high activation barrier. The rate constant for displacement of the methyl group from boron in methylboronate **13** by *tert*-butoxyl radicals (k_d, Table 3) was between three and four orders of magnitude less than the rate constant for the analogous homolytic displacement from trimethylboroxine $(MeBO)_3$.[15] Comparison of the two reactions is not straightforward because of the different ring sizes and electronic configurations of the two substrates. Our attempts to prepare suitable α-bromoborinate esters [RO(Me)BCH(Br)R] as precursors for borinate-substituted radicals were not successful so that experimental evidence of stabilization in this type of radical is lacking.

Characteristics of Radicals Containing β-Boronate Groups. The β-boronate radicals **19** were spectroscopically observable only at low temperatures (< ca. 220 K). In agreement with this, product analyses showed that at higher temperatures the dimer **22**, derived from **19a**, lessened in importance and that the major product was 1-hexene. A mechanism involving direct β-scission of **19a** to produce 1-hexene and bisalkoxyboryl radical **20** was considered (Scheme 2).[21] However, radical **20** could not be spectroscopically detected directly, by spin trapping, or on ligation with pyridine. Our good quality B3LYP computations on the model β-scission of analogous radical **29** indicated this process to be strongly endothermic (Scheme 3). This result accords well with Batey's ab initio computational results (MP2/6-31G*//UHF/6-31G*) on the $(HO)_2BCH_2CH_2^\bullet$ radical,[9] which also indicated the analogous β-scission to be highly endothermic (by 48 kcal mol^{-1}), and supports his conclusion that homolytic substitution should be favored. It is more likely therefore that the 1-hexene is produced by initial S_H2 attack on 2-bromo ester **18** by some radical X, leading to displacement of β-bromoalkyl radical **21** (Scheme 2). Elimination of a bromine atom from radical **21** is known to be a very rapid process. Once $Br^\bullet$ is formed, it could probably act as the attacking radical X. Some other species is required to set the process going. In photolyses including di-*tert*-butyl peroxide, the *tert*-butoxyl radical could be X. However, 1-hexene was also found to be the major product in the photochemical reaction of **18a** with hexamethylditin, in the absence of peroxide. Attempts to identify the coproduct [$XB(OCMe_2)_2$] were unsuccessful, but traces of halogen in the ditin may be responsible. This S_H2 reaction does not involve the intermediacy of β-boronate radicals, so β-bromo esters **18** will not be suitable β-boronate radical precursors at higher temperatures if, as seems likely, displacement is indeed their preferred homolytic reaction.

The spectroscopic data showed that the boron atom eclipses the SOMO in the lowest energy conformation (**19i**) of radical **19**. However, the magnitudes of the β-hfs and their small temperature dependencies show that the barrier to rotation about the C_α−C_β bond in **19a** is small and hence any thermodynamic stabilization of this radical by the β-boronate substituent is likely to be very small. The B3LYP computed structure of the closely related radical **29** was in good agreement with the EPR results from radical **19a**. Thus, the computed lowest energy conformation of **29** was analogous to that of **19i** with the C_β−B bond eclipsing the SOMO. The computed hfs for radical **29** are compared with the measured hfs for **19a** in Table 1. The experimental a(B) is lower than the computed value, and the experimental $a(H_\beta)$ is higher than the computed value. This is as expected because the EPR experiment measures these hfs as weighted averages of the populated torsional modes of the C_α−C_β rotation whereas the computations are for the lowest energy conformation only. Mixing in higher torsional modes would adjust both these computed hfs toward the corresponding experimental values.

Experimental Section

GC-MS analyses were run on a Finnigan Incos 50 quadrupole instrument coupled to a Hewlett-Packard HP 5890 chromatograph fitted with a 25 m HP 17 capillary column (50% phenyl methyl silicone). EPR spectra were obtained with Bruker ER 200D and Bruker EMX 10/12 spectrometers operating at 9 GHz with 100 kHz modulation. Samples of the substrate (ca. 40 mg), di-*tert*-butyl peroxide (40 μL), and triethylsilane or hexamethylditin (40 μL) were dissolved in *tert*-butylbenzene (0.5 mL) and degassed by bubbling nitrogen through the solution for 20 min. Additional samples of similar quantities were prepared in cyclopropane or *n*-propane solvent and degassed by several freeze/pump/thaw cycles. Solutions were photolyzed in the EPR resonant cavity by light from a 500 W superpressure Hg arc lamp. Hexamethylditin (Aldrich) was used as supplied.

2-(Bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a). Diisopropyl α-bromomethylboronic ester was prepared according to the protocol developed by Matteson and co-workers from triisopropylborate, dibromomethane, and *n*-butyllithium.[22] This boronate was transesterified with the appropriate diol according to the reported procedure; pinacol for **1a**, (+)-pinanediol for **4a**, and (−)-(1*R*,2*S*,3*R*,4*S*)-2-phenylbornane-2,3-diol[45] for **6**,[46] 3,3-dimethylbutan-1,2-diol for **5**. Homologation of pinacol *n*-hexylboronate with dibromomethane and lithium diisopropylamide[23] yielded **1b**. The transesterification of **1a** with (+)-pinanediol gave the ester **4b**.

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[44] Compare for example the relative rate data for toluene and *tert*-butylbenzene (Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6113−6145. Walling, C.; Mintz, M. J. *J. Am. Chem. Soc*. **1967**, *89*, 1515−1519) with the absolute data for toluene (Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520−4527).

[45] Herold, T.; Schrodt, U.; Hoffmann, R. W. *Chem. Ber*. **1981**, *114*, 359−374.

[46] We thank Dr J. Lebreton for a gift of a sample of the diol for compound **6**.

2-(Allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7) was prepared by the literature procedure from allylmagnesium chloride and triisopropylborate, followed by treatment with pinacol:[47] bp 30−35 °C/0.1 mmHg; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.25 (s, 12H), 1.70−1.75 (m, 2H), 4.92−5.02 (m, 2H), 5.82−5.91 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.0 (CH$_2$), 24.7 (CH$_3$), 83.2 (C), 114.8 (CH$_2$), 134.0 (CH).

2-(Vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10) was prepared as previously described by using triisopropylborate and vinylmagnesium bromide,[48] followed by transesterification with pinacol, bp 35−40 °C/20 mmHg.[49]

2,4,4,5,5-Pentamethyl-1,3,2-dioxaborolane (13) was prepared by esterification of the commercially available methylboronic acid (Aldrich) with pinacol:[50] bp 30−35 °C/20 mmHg; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.32 (br s, 3H), 1.28 (s, 12 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 24.8 (CH$_3$), 83.1 (C). The C atom α to the B atom was not found.

Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (16a) was synthesized by treatment of the known methyl ester, prepared according to the literature from trimethylborate, lithium, and methylene chloride,[31] with pinacol and purified by recrystallization from pentane at −20 °C: mp 53−54 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.36 (s, 2H), 1.25 (s, 12H); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 25.2 (CH$_3$), 83.4 (C). The carbon α to the boron was not found. HRMS [M$^+$]: calcd for C$_{13}$H$_{26}$^{11}B$_2$O$_4$ 268.2017, found 268.2020. Dihydroboration of hex-1-yne with dichloroborane−dimethyl sulfide yielded 1,1-bis(dichloroboryl)hexane[31] which was converted to the pinacol ester **16b**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.71 (t, 1H, J = 7.6 Hz), 0.86 (t, 3H, J = 6.8 Hz), 1.19−1.28 (m, 12H), 1.63 (d, 2H, J = 4.9 Hz); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 14.0 (CH$_3$), 22.5 (CH$_2$), 24.5 (CH$_3$), 24.9 (CH$_2$), 25.6 (CH$_2$), 31.8 (CH$_2$), 32.2 (CH$_2$), 82.8 (C). The carbon α to the boron was not found.

2-(2-Bromohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18a) and 2-(Trimethylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b). The β-bromoboronic esters **18** were prepared by bromoboration of an alk-1-ene followed by esterification with pinacol. **Typical procedure:** to a 1.4 M solution of BBr$_3$ in hexane (5 mL, 7 mmol) was added at −78 °C 7 mL of a 1 M solution of the alk-1-ene in hexane (7 mL, 7 mmol). The mixture was slowly allowed to warm to room temperature and then cooled to −10 °C. A solution of 7 mmol of pinacol in 5 mL of diethyl ether was then added. After stirring for 0.5 h, the reaction mixture was diluted with 20 mL of diethyl ether, washed with water, dried over MgSO$_4$, and concentrated. Purification by bulb to bulb distillation afforded **18a** (68%) as a colorless oil: bp 80−85/0.1 mmHg; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.91 (t, 3H, J = 7.1 Hz), 1.20−1.70 (m, 4H), 1.25 (s, 12H), 1.63 (d, 2H, J = 4.9 Hz), 1.70−1.90 (m, 2H), 4.25−4.38 (m, 1H); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 13.9 (CH$_3$), 22.0 (CH$_2$), 24.7 (CH$_3$), 29.9 (CH$_2$), 41.4 (CH$_2$), 54.7 (CH), 83.5 (C). The carbon α to the boron was not found. HRMS [M − Br]$^+$, calcd for C$_{12}$H$_{24}$^{11}BO$_2$ 211.1869, found 211.1868. **18b**: bp 45−50 °C/0.1 mmHg; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.11 (s, 9H), 1.28 (s, 12H), 1.36−1.65 (m, 2H), 3.53−3.62 (dd, 1H, J = 5.8 and 10.8 Hz); HRMS [M − CH$_3$]$^+$ calcd for C$_{10}$H$_{21}$^{11}B^{81}BrO$_2$Si 293.0567, found 293.0579.

2-(4-Bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23) was prepared by hydroboration of 4-bromobut-1-ene with dibromoborane−dimethyl sulfide complex in methylene chloride as described previously[51] (78%): bp 50−55/0.1 mmHg; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.80 (t, 2H, J = 7.4), 1.22 (s, 12H), 1.43−1.67 (m, 4H), 3.40 (t, 2H, J = 6.9); ^{13}C NMR (75.5 MHz, CDCl$_3$) 10.4 (br, CH$_2$), 22.3 (CH$_2$), 24.8 (CH$_3$), 33.6 (CH$_2$), 35.3 (CH$_2$), 83.0 (C).

Photolytic Reaction of 18a with Hexamethylditin. Bromo ester **18a** (30 mg) and hexamethylditin (30 mg) in *tert*-butylbenzene (0.5 mL) were photolyzed with unfiltered light from a 500 W superpressure Hg lamp in a quartz tube at 250 K for 3 h. GC-MS analysis showed unreacted **18a**, several tin compounds plus peak no. 110, 1-hexene (major product), together with peak no. 629, dimer **22** (minor): EIMS m/z 365 [(M − Bu)$^+$, 1], 153, (18), 101 (32), 85 (50), 84 (100), 83 (75), 69 (40), 55 (45), 43 (40), 41 (48). The photolysis was also carried out on a similar scale at 180 K in cyclopropane with DTBP (30 mg). The product chromatogram showed the dimer **22** as the main product with minor amounts of 1-hexene and a boron-containing product which was probably n-C$_6$H$_{13}$B(OCMe$_2$)$_2$. No t-BuOB(OCMe$_2$)$_2$ was detected.

Photolytic Reaction of 18a with Triethylsilane and DTBP. Bromo ester **18a** (30 mg), triethylsilane (30 mg), and DTBP (50 mg) in cyclopropane (ca. 0.5 mL) were photolyzed with light from a 500 W superpressure Hg lamp for 5 h at 180 K. The GC-MS analysis showed unreacted **18a**, (Et$_3$Si)$_2$O, several related silicon compounds, 1-hexene (minor), a boron-containing product which was probably n-C$_6$H$_{13}$B(OCMe$_2$)$_2$ (minor), and dimer **22** (major).

Photolytic Reaction of 23 with Triphenyltin Hydride. 4-Bromobutyl ester **23** (0.051 g, 0.19 mmol) and triphenytin hydride (0.086 g, 0.25 mmol) in benzene (5 mL) were degassed and photolyzed in a quartz tube at 60 °C for 2.5 h with light from a 400 W medium-pressure Hg lamp. This yielded 2-n-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[52] (**25**) as the sole tin-free product (81%): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.78 (2H, t, J = 7.5 Hz), 0.88 (3H, t, J = 7.1 Hz), 1.17−1.45 (4H, m), 1.24 (12H, s); EIMS m/z (%) 169 ([M − Me]$^+$, 11), 129 (10), 85 (24), 59 (18), 55 (19), 43 (78), 42 (55), 41 (92), 39 (40), 29 (100).

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Supporting Information Available: Sample 9 GHz EPR spectra of radicals **2a**, **5**, and **6**. Experimental and computed exchange-broadened spectra of radical **4a** as functions of temperature and exchange rate constant, respectively, with a Table of best fit rate constants. Sample EPR spectra of radicals **9a** and **9b**. Table of rate constants for H-abstraction from cyclopropane by t-BuO$^\bullet$ radicals. B3LYP/6-31G* computation outputs for $^\bullet$CH$_2$B(OCH$_2$)$_2$ and $^\bullet$CH$_2$CH$_2$B(OCH$_2$)$_2$ radicals and a table of computed total energies for each species studied. (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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