all will ultimately rest on the structural data given here.

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Supplementary Material Available: Tables IV and V, listings of $10|F_o|$ vs. $10|F_c|$ for 1 and 5, respectively, and Tables VI and VII, root-mean-square amplitudes of vibration for 1 and 5, respectively (37 pages). Ordering information is given on any current masthead page.

Deprotonation of 1,1-Diboronic Esters and Reactions of the Carbanions with Alkyl Halides and Carbonyl Compounds

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The efficient deprotonation of 1,1-diboronic esters has been accomplished with lithium 2,2,6,6-tetramethylpiperidide in the presence of tetramethylethylenediamine in tetrahydrofuran. Bis(1,3,2-dioxaborin-2-yl)methane, $(C_3H_6O_2B)_2CH_2$, is slightly more acidic than triphenylmethane and has been deprotonated to a diborylmethide salt, $(C_3H_6O_2B)_2CH^-Li^+$, which has been alkylated by alkyl halides, RX, to form 1,1-bis(1,3,2-dioxaborin-2-yl)alkanes, $(C_3H_6O_2B)_2CHR$, which in turn have been deprotonated and alkylated with a second alkyl halide to form fully substituted *gem*-diboronic esters, $(C_3H_6O_2B)_2CRR'$. The carbanionic intermediates have also been condensed with carbonyl compounds to form alkeneboronic esters, useful intermediates for synthesizing carbonyl compounds homologous to the original. The carbanions, $(C_3H_6O_2B)_2C^-R$, condense with carboxylic esters, $R'CO_2CH_3$, with elimination of boron to form ketones, RCH_2COR'. The synthesis of 1,1-diboronic esters, $(C_3H_6O_2B)_2CHR$, from methanediboronic ester anion and alkyl halide is possible only if the alkyl group, R, is primary, but an alternative route involving catalytic hydrogenation of alkene-1,1-diboronic esters, $(C_3H_6O_2B)_2C{=}CR_2'$, has been developed, and the deprotonation of these more hindered alkane-1,1-diboronic esters has been demonstrated.

Introduction

Lithium bis(dialkoxyboryl)methides, $Li^{+-}CH[B(OR)_2]_2$, are known to react with alkyl halides to form alkane-1,1-diboronic esters[1-4] and with aldehydes or ketones to form 1-alkene-1-boronic esters.[1,4-6] The latter reaction is the key step in an efficient conversion of carbonyl compounds to the homologous aldehydes.[7]

The synthetic utility of these reactions was formerly limited by the requirement that a boronic ester group be replaced in order to form the carbanion.[4]

$$R'C[B(OR)_2]_3 + R''Li \rightarrow Li^{+-}CR'[B(OR)_2]_2 + R''B(OR)_2$$

The method of synthesis of tris(dialkoxyboryl)methanes, $R'C[B(OR)_2]_3$, was successful where R′ = $(RO)_2B$, H, C_6H_5, or CH_3, with decreasing yields in the sequence listed,[4,8] and would be impractical for more complex R′ groups. Attempts to alkylate lithium tris(dimethoxyboryl)methides, $Li^{+-}C[B(OR)_2]_3$, with alkyl halides, R′X, resulted in disproportionation and formation of a mixture of $R'_2C[B(OCH_3)_2]_2$ and $R'C[B(OCH_3)_2]_3$.[2] When the more hindered propanediol boronic ester group was used in the hope of avoiding the disproportionation, methyl iodide with $Li^{+-}C(CO_2C_3H_6)_3$ efficiently yielded $CH_3C(BO_2C_3H_6)_3$ but ethyl iodide was converted to ethylene, confirmed by conversion to ethylene dibromide.[9]

Several synthetic routes to alkane-1,1-diboronic esters [1,1-bis(dialkoxyboryl)alkanes], $R'CH[B(OR)_2]_2$, have been reported,[2-4,8,10-12] and it appeared that these would be useful synthetic intermediates if a base could be found which would attack the α-proton in preference to the boron atoms. The report of the deprotonation of 9-methyl-9-borabicyclo[3.3.1]nonane with lithium 2,2,6,6-tetramethylpiperidide by Rathke and Kow[13] prompted us to

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[1] (a) Preliminary communication: Matteson, D. S.; Moody, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 3196–3197. (b) We thank the National Science Foundation for support (Grants no. MPS75-19557 and CHE77-11283).

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[12] Matteson, D. S.; Cheng, T.-C. *J. Organomet. Chem.* **1966**, *6*, 100–101.

[13] Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854–6855.

Table I. Exploration of Conditions for Deprotonation of Methanediboronic Esters (1) without Chelating Agent for Li^+, Using Homologation of Aldehydes as Probe

boronic ester	solvent[a]	base	mol of base[b]	time,[c] h	reactant	product[d]	% yield (GLC)
1a	THF	LiTMP	2	14	benzaldehyde	phenylacetaldehyde	29
1a	THF	LiTMP	1	3	benzaldehyde	phenylacetaldehyde	6
1a	THF	LiTMP	1	14	benzaldehyde	phenylacetaldehyde	0
1a	THF	$LiCPh_3$	1	2.5	benzaldehyde	phenylacetaldehyde	6
1a	THF	LDA	1	14	benzaldehyde	phenylacetaldehyde	0
1a	THF	*t*-BuLi	1	2.5	benzaldehyde	phenylacetaldehyde	0
1b	THF	LiTMP	2	4	benzaldehyde	phenylacetaldehyde	12
1b	THF	LiTMP	2	10	benzaldehyde	phenylacetaldehyde	trace
1c	THF	LiTMP	2	10	benzaldehyde	phenylacetaldehyde	0
1e	THF	LiTMP	2	12	heptanal	octanal	12
1b	benzene	LiTMP	2	12	heptanal	octanal	37
1d	benzene	LiTMP	2	24	heptanal	octanal	40

[a] 30 mL of solvent used for 3.5 mmol of boronic ester **1**. [b] Per mol of **1**. Lithium tetramethylpiperidide, diisopropylamide, or triphenylmethide was prepared at 0-25 °C and cooled to −78 °C (or 0 °C for LiTMP in benzene) before addition of the boronic ester. [c] Time stirred at 20-25 °C before cooling to −78 °C and adding 1 mol of aldehyde/mol of **1**. [d] The intermediate alkeneboronic ester was oxidized with a slight excess of sodium perborate 0.5-1 h, except that with **1d** slow oxidation was noted, time 6 h.

Table II. Exploration of Conditions for Deprotonation of Bis(1,3,2-dioxaborin-2-yl)methane (1b) by Lithium 2,2,6,6-Tetramethylpiperidide in the Presence of Li^+ Complexing Agent and for Homologation of Heptanal and Cyclohexanone[a]

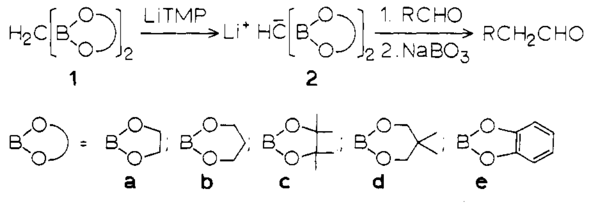
mol of LiTMP[b]	complexing agent	mol[b] of complexing agent	solvent	carbonyl reactant	other reagents	product	% yield (GLC)
1	TMEDA	1	THF	heptanal		octanal	62
1	TMEDA	2	THF	heptanal		octanal	60
2	TMEDA	2	THF	heptanal		octanal	59
1	TMEDA	0.5	THF	heptanal		octanal	49
1	DABCO	1	THF	heptanal		octanal	46
1	HMPA	1	THF	heptanal		octanal	11
1	TMEDA	1	2:3 THF/Et_2O	heptanal		octanal	55
1	TMEDA	1	1:1 THF/CH_2Cl_2	heptanal		octanal	0
1	TMEDA	1	THF	heptanal	CH_2Cl_2[c]	octanal	59
1.15[d]	TMEDA	1.15	THF	heptanal		octanal	55
1.15[d]	TMEDA	1.15	THF	heptanal	$MgBr_2$[e]	octanal	4
1	TMEDA	1	THF	heptanal	$MgBr_2$[f]	octanal	34
1	TMEDA	1	THF[g]	heptanal	CH_2Cl_2[g]	octanal	84[g]
1	TMEDA	1	THF	cyclohexanone		$C_6H_{11}CHO$	66
1	TMEDA	1	THF	cyclohexanone	$B(OMe)_3$[h]	$C_6H_{11}CHO$	69
1	TMEDA	1	THF	cyclohexanone	$B(OMe)_3$ + CH_2Cl_2	$C_6H_{11}CHO$	55

[a] See Experimental Section for general conditions. [b] Per mol of **1b** and carbonyl compounds. [c] Added with the heptanal, equal vol to THF (20 mL). [d] And 1.15 mol of **1b**/mol of heptanal. [e] From Br_2 + Mg in ether, added to **2b** at 0 °C. [f] Added after **2b** cooled to −78 °C. [g] The precipitated **2b** was filtered, and the heptanal in 4:3 THF/CH_2Cl_2 was added. Oxidation time 4 h; duplicate yields within 1%; found 2% heptanal in one run, none in the other. [h] Added 1 mol just before cyclohexanone.

try the same reagent for deprotonation of a methanediboronic ester.

Results

Exploration of Deprotonation Conditions. The first attempt at deprotonation was made with ethylene glycol methanediboronate [bis(1,3,2-dioxaborol-2-yl)methane][14] (**1a**) under conditions similar to those used for 9-methyl-9-BBN by Rathke and Kow,[13] 2 mol of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in tetrahydrofuran (THF) at room temperature. Reaction with benzaldehyde, oxidation with sodium perborate,[7] and GLC analysis indicated a 29% yield of phenylacetaldehyde.



This initial success encouraged us to search for more efficient conditions for the deprotonation of ethylene glycol methanediboronate (**1a**), with the dismal results summarized in Table I. It appeared likely that **1a** has insufficient steric hindrance to prevent competing attack of base at a boron atom to form a complex resistant to deprotonation, and we therefore tested propanediol methanediboronate [bis(1,3,2-dioxaborin-2-yl)methane] (**1b**) as well as the pinacol (**1c**), 2,2-dimethylpropanediol (**1d**), and catechol (**1e**) esters. Results were still poor (Table I), though some improvement was noted when heptanal was used in place of benzaldehyde as the carbonyl reactant, perhaps because the rather sluggish peroxide oxidation under basic conditions destroyed more of the product phenylacetaldehyde than the less sensitive octanol.

In parallel work with pinacol (phenylthio)methaneboronate, it appeared that yields of deprotonation product were significantly improved by the inclusion of tetra-

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[14] The older system of naming boronic esters according to the customs of organic chemists is self-explanatory and easy to read when the structures are complicated and will be used informally in this article in preference to the current systematic style, shown in brackets. Another name for the 1,3,2-dioxaborol-2-yl group is "ethylenedioxyboryl".

Table III. Alkylation of Alkane-1,1-diboronic Ester Anions

anion	R-X	product	% yield GLC	 isolated
2b	$CH_3(CH_2)_3I$	$CH_3(CH_2)_3CHO$	86	
2b	$CH_3(CH_2)_3Br$	$CH_3(CH_2)_3CHO$	79	
2b	$CH_3(CH_2)_3Cl$	$CH_3(CH_2)_3CHO$	23[a]	
2b	$CH_3(CH_2)_4Br$	$CH_3(CH_2)_4CHO$	80	62
2b	$CH_3(CH_2)_4Br$	$CH_3(CH_2)_4CH(BO_2C_3H_6)_2$ (**3**)		71
2b	$CH_3(CH_2)_6I$	$CH_3(CH_2)_6CHO$	82	
2a	$CH_3(CH_2)_6I$	$CH_3(CH_2)_6CHO$	55	
2b	$CH_3(CH_2)_6OSO_2C_6H_4CH_3$	$CH_3(CH_2)_6CHO$	76	
2b	$C_6H_5CH_2Br$	$C_6H_5CH_2CHO$	71	
2b	$Cl(CH_2)_4I$	$Cl(CH_2)_4CHO$	83	
2b	$CH_3O_2C(CH_2)_5Br$	none		0
2b	*cyclo*-$C_6H_{11}Br$	none	0	
2b	$CH_3(CH_2)_4CHBrCH_3$	$CH_3(CH_2)_4CH(CH_3)CHO$	6[b]	
2b	$(C_2H_5)_2CHI$	$(C_2H_5)_2CHCHO$	8	
2b	$NC(CH_2)_4Br$	$NC(CH_2)_4CH(BO_2C_3H_6)_2$ (**5**)		49
2b	$CH_3C(O_2C_2H_4)(CH_2)_3I$	$CH_3C(O_2C_2H_4)(CH_2)_3CH(BO_2C_3H_6)_2$ (**4**)		57
6	CH_3I	$CH_3(CH_2)_4COCH_3$	78	
6	$C_6H_5CH_2CH_2I$	$C_6H_5CH_2CH_2C(BO_2C_3H_6)_2C_5H_{11}$		70

[a] Longer reaction time not tested. [b] Octanal used as integration standard.

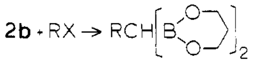
methylethylenediamine (TMEDA),[15] presumably because the TMEDA coordinates with lithium ion and thereby increases the nucleophilicity of the amide anion. Accordingly, the effect of TMEDA on the reaction of propanediol methanediboronate (**1b**) with LiTMP was tested, with immediately improved results (Table II). The lithium bis(trimethylenedioxyboryl)methide (**2b**) was observed to precipitate after the reactants, initially mixed at −78 °C, were warmed to 0 °C.

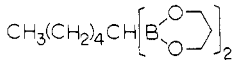
The **2b** prepared by deprotonation of **1b** still remained inferior to **2a** prepared by deboronation of ethylene glycol methanetriboronate [tris(1,3,2-dioxaboral-2-yl)methane] as a reagent for the homologation of aldehydes.[7] Accordingly, other factors affecting the reaction were explored. Diazabicyclooctane (DABCO) and hexamethylphosphoramide (HMPA) proved less successful than TMEDA as lithium ion complexing agents. The use of lithium diisopropylamide in place of LiTMP yielded only 6% octanal from heptanal. Dichloromethane, a beneficial cosolvent (and perhaps reactant) in the deboronation route to carbanions,[6,7] proved incompatible with the deprotonation of **1b** to **2b** and failed to improve the yield when added at a later stage. Since it was thought that the reaction medium used for the deprotonation process might be sufficiently more basic than that remaining after the deboronation reaction to promote side reactions such as enolization, attempts were made to reduce the basicity by adding magnesium bromide or trimethyl borate, but the former proved deleterious and the latter ineffective (Table II). When the ethylene glycol ester **2a** was prepared from **1a** under the best conditions found for the propanediol ester **2b**, it homologated heptanal to octanal in 43% yield.

Evidence that the formation of **2b** by deprotonation of **1b** was indeed highly efficient was first obtained when **2b** was allowed to react with 1-iodoheptane, which led to octanal in 82% yield. Subsequently, it was found that the homologation of heptanal to octanal could be carried out with similar high efficiency, provided the precipitated lithium bis(1,3,2-dioxaborin-2-yl)methide (**2b**) was isolated by filtration in a Schlenk apparatus before reaction with the heptanal (Table II). It was also found necessary to allow longer for the peroxidic deboronation of the propanediol alkeneboronate intermediates than for that of the corresponding ethylene glycol esters.

Attempted reaction of camphor, a sterically hindered ketone, with **2b** failed. The general synthetic utility of **2a** and, implicitly, **2b** in comparison with other methods for homologating carbonyl compounds has been discussed in a previous article.[7]

Alkylation of Diborylcarbanions. The alkylation of lithium bis(1,3,2-dioxaborin-2-yl)methide (**2b**) was initially





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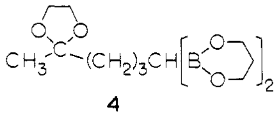

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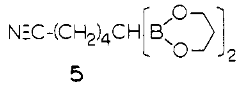

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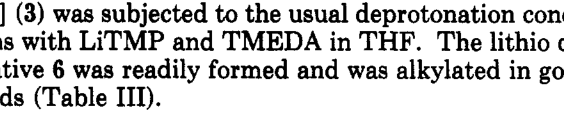
explored with the aid of gas chromatography of the aldehydes resulting from in situ perborate oxidation of the alkylation products. Good yields were obtained with primary iodides, bromides, and a tosylate, but secondary halides yielded little or no alkylation product (Table III). Isolation of the initially formed alkane-1,1-diboronic esters was also found to be straightforward. Examples included propanediol hexane-1,1-diboronate (**3**), the ethylene ketal of propanediol 5-oxohexane-1,1-diboronate (**4**), and propanediol 5-cyanopentane-1,1-diboronate (**5**).

For a test of the possibility of deprotonating a 1,1-diboronic ester produced by alkylation of **2b**, propanediol hexane-1,1-diboronate [1,1-bis(1,3,2-dioxaborin-2-yl)hexane] (**3**) was subjected to the usual deprotonation conditions with LiTMP and TMEDA in THF. The lithio derivative **6** was readily formed and was alkylated in good yields (Table III).



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Reactions of a Diborylcarbanion with Carbonyl Compounds. It was expected that 1-lithio-1,1-bis(1,3,2-dioxaborin-2-yl)hexane (**6**) would react with aldehydes in a manner analogous to that of the diborylmethide (**2b**). This was confirmed by reaction of **6** with benzaldehyde and in situ perborate oxidation of the intermediate 1-phenyl-1-heptene-2-boronic ester (**7**) to form 1-phenyl-2-heptanone (Table IV).

The reaction of lithium bis(1,3,2-dioxaborol-2-yl)methide (**2a**) with benzoyl chloride or methyl benzoate to form

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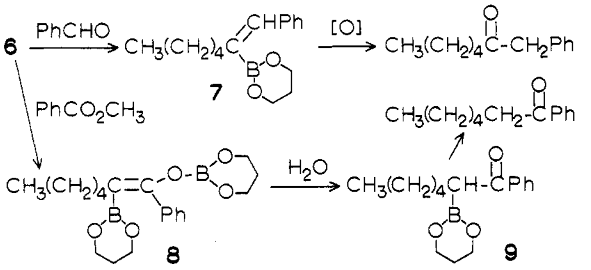
[15] (a) Matteson, D. S.; Arne, K. *J. Am. Chem. Soc.*, **1978**, *100*, 1325–1326. (b) Matteson, D. S.; Arne, K., *Organometallics*, in press.

Table IV. Reactions of 1-Lithio-1,1-bis(1,3,2-dioxaborin-2-yl)hexane (6) with Carbonyl Compounds

carbonyl compd	product	% yield (GLC)
C_6H_5CHO	$C_6H_5CH_2CO(CH_2)_4CH_3$	84
$C_6H_5CO_2CH_3$	$C_6H_5CO(CH_2)_5CH_3$	99[a]
C_6H_5COCl	$C_6H_5CO(CH_2)_5CH_3$	37
$CH_3CO_2C_2H_5$	$CH_3CO(CH_2)_5CH_3$	37
$CH_3(CH_2)_2CO_2CH_3$	$CH_3(CH_2)_2CO(CH_2)_5CH_3$	66

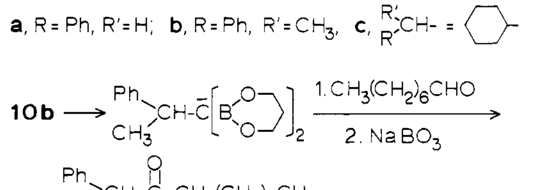
[a] 2,4-DNP derivative isolated, 71%.

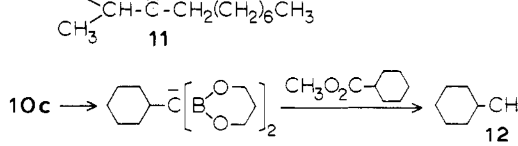
acetophenone has been noted previously.[7] This type of reaction becomes of considerably greater synthetic interest with more complex boronic ester anions such as **6**. Thus, methyl benzoate and **6** quantitatively yielded 1-phenylheptanone, presumably by way of a boron enolate intermediate (**8**) and an unstable α-boryl ketone (**9**).

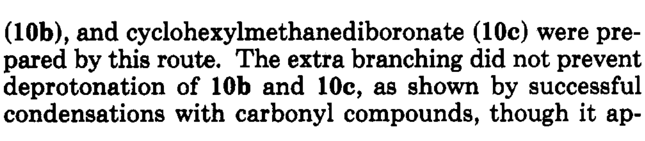


The low efficiency of reaction of benzoyl chloride with **6** (Table IV) was unexpected on the basis of previous experience.[7] The low yield with ethyl acetate may be attributed to competition of the acidic α-protons for the carbanion. Methyl butyrate gave a satisfactory yield of acylation product (Table IV).

Alkane-1,1-diboronic Esters from Hydrogenation of Alkene-1,1-diboronic Esters. Because alkylation of lithium bis(1,3,2-dioxaborin-2-yl)methide (**2b**) is inefficient with secondary halides, alkane-1,1-diboronic esters branched at the 2-carbon are unavailable by this route. An alternative approach was devised, involving hydrogenation of alkene-1,1-diboronic esters over a palladium catalyst. These boronic esters are easily prepared from lithium tris(1,3,2-dioxaborin-2-yl)methide and either aldehydes or ketones.[16] As examples, propanediol 2-phenylethane-1,1-diboronate (**10a**), 2-phenylpropane-1,1-diboronate (**10b**), and cyclohexylmethanediboronate (**10c**) were prepared by this route. The extra branching did not prevent deprotonation of **10b** and **10c**, as shown by successful condensations with carbonyl compounds, though it appeared that **10b** reacted slowly.







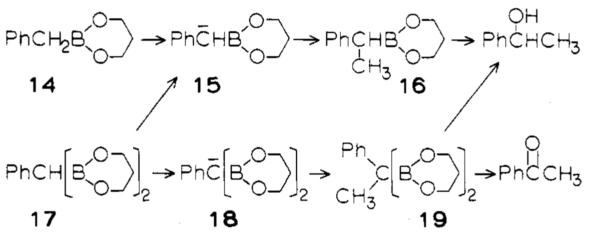
Acidity of Bis(1,3,2-dioxaborin-2-yl)methane (1b). Treatment of **1b** with LiTMP and TMEDA in THF precipitates lithium bis(1,3,2-dioxaborin-2-yl)methide (**2b**), which has been isolated by filtration in a Schlenk apparatus. The air-sensitive solid **2b** appeared to contain 0.3–0.5 mol of THF on the basis of NMR and elemental analysis, though pure material was not obtained.

An early experiment indicated at least 6% deprotonation of ethylene glycol methanediboronate (**1a**) by lithium triphenylmethide (Table I). Since the pK_a of the latter is known with some precision,[17] the deprotonation of propanediol methanediboronate (**1b**) by lithium triphenylmethide was investigated briefly. With the kinetic aid of TMEDA in THF, equimolar amounts of these reactants at 0 °C led to immediate dissolution of the red precipitate of lithium triphenylmethide and gradual precipitation of white lithium bis(1,3,2-dioxaborin-2-yl)methide (**2b**), confirmed by alkylation with 1-bromopentane followed by perborate oxidation of the resulting hexane-1,1-diboronic ester (**3**) and isolation of the hexanal as the 2,4-dinitrophenylhydrazone in 32% yield. Similar results were obtained when triglyme [1,2-bis(2-methoxyethoxy)ethane] was used in place of TMEDA as the lithium ion complexing agent. The THF solution retained a deep red color of the triphenylmethide anion up to the point where the 1-bromopentane was added. When a few milligrams of triphenylmethane was added to a suspension of **2b** prepared from LiTMP and **1b**, the precipitate turned pink but the solution remained clear and colorless. These results suggest that the methanediboronic ester **1b** is a stronger acid than triphenylmethane.

Structural Limits of Deprotonation. We explored some of the practical limits to the structures of boronic esters which can be deprotonated. Propanediol methaneboronate (**13**) treated with LiTMP under our usual conditions, followed by 1-bromopentane, oxidation with sodium perborate, and GLC analysis, yielded less than 1% 1-hexanol. With LiTMP under the conditions described by Rathke and Kow,[13] the yield of 1-hexanol was 2%. The use of *sec*-butyllithium in cyclohexane/THF or LiTMP in TMEDA as solvent also yielded 1–2% 1-hexanol. Thus, practical deprotonation of **13** has not been accomplished and appears unpromising.

13

Propanediol benzylboronate (**14**) was readily deprotonated by LiTMP to form the anion **15**, which with methyl iodide yielded propanediol 1-phenylethane-1-boronate (**16**), characterized by oxidation to 1-phenylethanol (66%). Unexpectedly, bis(propanediol) benzyldiboronate (**17**) also yielded anion **15**, the deboronation product, together with



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[16] Matteson, D. S.; Hagelee, L. A. *J. Organomet. Chem.* **1975**, *93*, 21–32.

[17] (a) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321–325. (b) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; Drucker, J. E.; Gerhold, J.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Mathews, W. S. *Ibid.* **1977**, *42*, 326–332.

lesser amounts of the deprotonation product (**18**).

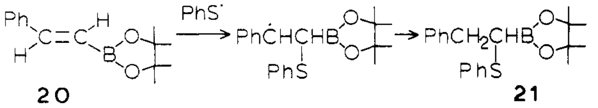
The 1-phenylethane-1,1-diboronic ester (**19**) would be expected to undergo some protodeboronation during the oxidation process,[18] but the proportion of 1-phenylethanol derived from **17** was very high (73–85% yields), and the proton NMR spectrum of the crude boronic ester intermediates showed both the methyl doublet corresponding to **16** and the singlet corresponding to **19**.[18]

In view of the successful generation of an allylic anion from an alkenyldialkylborane and LiTMP by Kow and Rathke,[19] we attempted the deprotonation of pinacol (*E*)-1-propene-1-boronate and trapping of the anion by silylation with chlorotrimethylsilane, but no trimethylsilyl peak could be seen in the NMR spectrum of the crude reaction product after evaporation of the solvent.

Deprotonations of other substituted methaneboronic pinacol esters, $XCH_2BO_2C_2(CH_3)_4$, found concurrently with or subsequent to this work, include X = PhS,[15] X = $(CH_3)_3Si$,[20] X = $CH_2{=}CH$,[21] and X = Ph_3P^+.[21]

Free Radical Stabilities. Interpretation of carbanion stabilities should take stabilities of the corresponding radicals into account, since the free energy of ionic dissociation must equal the sum of the free energies of homolytic dissociation and one-electron transfer. Our early work indicated that a boronic ester group stabilizes an adjacent radical somewhat less effectively than does a phenyl group,[22] and the result of Pasto and co-workers on the radical bromination of a 2-phenylethane-1-boronic ester to form a 2-bromo-2-phenylethane-1-boronic ester agrees.[18] However, there is a discrepancy in the reported addition of hydrogen bromide under "free radical conditions" to ethylene glycol 2-phenylethene-1-boronate to form the 2-bromo-2-phenylethane-1-boronic ester,[18] or at least its degradation products,[3] which would imply that the boronic ester group was more effective than the phenyl in stabilizing an adjacent radical.

We have carried out the radical initiated addition of thiophenol to pinacol 2-phenylethene-1-boronate (**20**) and



20 21

obtained pinacol 1-(phenylthio)-2-phenylethane-1-boronate (**21**), which shows clearly that the phenyl is more effective than the boronic ester group in stabilizing the adjacent radical. The possibility that the anomalous hydrogen bromide addition might be an ionic[18] process is thus confirmed.[23]

Discussion

Synthetic Utility. Anions from deprotonation of *gem*-diboronic esters function as synthetic equivalents of carbonyl anions or as substituted Wittig reagents. Demonstrated useful transformations are summarized in eq 1–8.

$$RCHO + {}^{-}CH(BO_2C_3H_6)_2 \rightarrow trans\text{-}RCH{=}CHBO_2C_3H_6 \rightarrow RCH_2{-}CHO \tag{1}$$

$$RBr + {}^{-}CH(BO_2C_3H_6)_2 \rightarrow R{-}CH(BO_2C_3H_6)_2 \rightarrow R{-}{}^{-}C(BO_2C_3H_6)_2 \tag{2}$$

$$R{-}CH(BO_2C_3H_6)_2 \rightarrow R{-}CHO \tag{3}$$

$$R'Br + R{-}{}^{-}C(BO_2C_3H_6)_2 \rightarrow \;\rightarrow R{-}CO{-}R' \tag{4}$$

$$R'CHO + R{-}{}^{-}C(BO_2C_3H_6)_2 \rightarrow \;\rightarrow R{-}CO{-}CH_2R' \tag{5}$$

$$R'CO_2CH_3 + R{-}{}^{-}C(BO_2C_3H_6)_2 \rightarrow \;\rightarrow RCH_2{-}CO{-}R' \tag{6}$$

$$R'COR'' + R{-}{}^{-}C(BO_2C_3H_6)_2 \rightarrow R'R''C{=}CR(BO_2C_3H_6) \rightarrow R'R''CHCOR \tag{7}$$

$$R'COR'' + {}^{-}C(BO_2C_3H_6)_3 \rightarrow R'R''C{=}C(BO_2C_3H_6)_2 \rightarrow R'R''CHCH(BO_2C_3H_6)_2$$

equivalent to $R{-}CH(BO_2C_3H_6)_2$ in further transformations (8)

Several other types of transformations are implicit in eq 1–8. For example, *trans*-RCH=CHB(OR″)$_2$ (eq 1) is known to be readily convertible to *cis*-RCH=CHR′ by R′Li followed by iodine and sodium hydroxide,[24] to *cis*-RCH=CHBr by bromine and sodium hydroxide,[25] or to *trans*-RCH=CHI by iodine and sodium hydroxide.[26] Unfortunately, the stereochemistry of the alkeneboronic esters derived from ketones (eq 7) is uncontrolled, limiting the possible utility of these intermediates. Alkeneboronic esters and *gem*-diboronic esters can be converted to the corresponding organomercurials,[10a,27] and boron-substituted carbanions are known to alkylate triphenyltin chloride and similar reagents.[4,5] Such possibilities as conjugate addition of these boron-substituted carbanions to α,β-unsaturated carbonyl compounds or reactions with epoxides have not been explored.

The major drawback to *gem*-diboronic esters as synthetic intermediates is the mediocre yield of the precursor, tetramethyl methanediboronate, $CH_2[B(OCH_3)_2]_2$, and the required use of lithium dispersion in its preparation, which involves the hazards of exothermic reaction and flammable materials. However, the preparation involves only one step, can be carried out on a substantial scale (80 g), and has proved more reliable than the analogous preparation of hexamethyl methanetriboronate, $HC[B(OCH_3)_2]_3$, in our experience.[4] Accordingly, we would recommend the deprotonation of the diboronic ester (**1b**) in preference to deboronation of the triboronic ester for general synthetic purposes.

We have made several attempts to improve the synthesis of **1b**. These included direct reaction of propanediol boron chloride with dichloromethane and lithium, which apparently yielded 20% of **1b** in a mixture from which it was not easily separated. Preparation of dilithiomethane[28] followed by treatment with methyl borate in ether failed, and the reported route to bis[bis(dimethylamino)boryl]-

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[18] Pasto, D. J.; Chow, J.; Arora, S. K. *Tetrahedron* **1969**, *25*, 1557–1569.

[19] Kow, R.; Rathke, M. W. *J. Am. Chem. Soc.* **1973**, *95*, 2715–2716.

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[22] (a) Matteson, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 4228–4233. (b) Matteson, D. S. *J. Org. Chem.* **1964**, *29*, 3399–3400.

[23] Ionic additions of hydrogen bromide to alkeneboronic acids have been reported: (a) Matteson, D. S.; Liedtke, J. D. *Chem. Ind. (London)* **1963**, 1241. (b) Matteson, D. S.; Schaumberg, G. D. *J. Org. Chem.* **1966**, *31*, 726–731.

[24] (a) Evans, D. A.; Crawford, T. C.; Thomas, R. C.; Walker, J. A. *J. Org. Chem.* **1976**, *41*, 3947–3953. (b) Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 3652–3653.

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[27] Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *152*, 1–5.

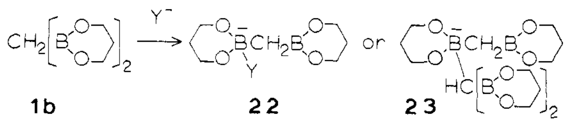
[28] Krohmer, P.; Goubeau, J. *Chem. Ber.* **1971**, *104*, 1347–1361.

methane[28] offers no advantage. The uneconomic but fairly efficient route based on an organomercurial[12] suggests future possibilities of alternate routes.

Several possible routes exist to substituted *gem*-diboronic esters, $R{-}CH(BO_2C_3H_6)_2$, in addition to alkylation of the diborylmethide ion **2b** with RBr (where R must be primary). That represented by eq 8 is probably the most general and reliable alternative and is necessary if R is to be secondary. The methanetetraboronic ester precursor is the most efficiently produced of the series.[4,8] The coupling of *gem*-dichloroalkanes with dimethoxyboron chloride by lithium dispersion has been explored only for R = phenyl, though 1,1,1-trichloroethane has yielded the ethane-1,1,1-triboronic ester.[8] Dihydroboration of acetylenes has been reported to yield 1,1-diboryl compounds which can be converted to boronic esters,[11] but no proof was offered that the 1,2-isomer was absent, and we obtained the 1,2-isomer as the major product of dihydroboration of phenylacetylene.[3] Hydroboration of 1-alkeneboronic esters generally yields mainly 1,1-diboronic esters after alcoholysis, accompanied by lesser amounts of 1,2-isomers, which are difficult to separate.[10]

Acidity of Methanediboronic Ester 1b. The experimental observations suggest, but do not quite prove, that propanediol methanediboronate (**1b**) is a somewhat stronger acid than triphenylmethane in THF. Referred to Bordwell's scale, this corresponds to a pK < 30.6 in dimethyl sulfoxide.[17,29] It is not possible to suggest a lower limit, but it seems unlikely that there could be many orders of magnitude of difference.

There are several obstacles in the way of obtaining an accurate pK measurement for the methanediboronic ester **1b**. The lithium salt **2b** is a slightly soluble precipitate in THF, which tends falsely to increase the apparent acidity of **1b**. A different boronic ester or solvent might solve this problem. However, there remains the strong possibility of reaction of bases Y^- at the boron atom to form borate complexes (22), including the possibility of self-condensation of the diborylmethide salt **2b** with its parent acid (**1b**) to form complex borate salts (**23**). These reactions tend falsely to decrease the apparent proton acidity of **1b**. It is the predominance of formation of anions such as **22** with bases that are not very hindered that accounts for the difficulty of deprotonating methanediboronic esters in the first place. In view of these likely complications, it would be a major effort to determine an accurate pK for a methanediboronic ester, and no serious attempt was made.



1b 22 23

Hückel Calculations. Even with the limitations of the available measurements, it is clear that the boronic ester group has a greater effect than phenyl in strengthening the acidity of an adjacent methylene group (diphenylmethane pK = 32.6 in dimethyl sulfoxide).[17] It is therefore of interest to compare results of simple Hückel molecular orbital calculations on the delocalization energies of phenyl and dialkoxyboryl compounds, summarized in Table V. Calculated electron densities and bond orders of the boron species are listed in Table VI. For the dialkoxyboryl groups, the parameters used were the Pariser–Parr–Pople-based set recently published by Van-Catledge.[30] The tabulated delocalization energies represent the change in π-bond energy in going from $PhCH_3$ to $PhCH_2^-$, etc.

Table V. Hückel Delocalization Energies of Anions and Radicals[a]

structure	anion DE, β	radical DE, β
$PhCH_2$	0.7206	0.7206
$(HO)_2BCH_2$	0.9948	0.5064
Ph_2CH	1.3006	1.3006
$[(HO)_2B]_2CH$	1.5653	0.8025
Ph_3C	1.8002	1.8002
$[(HO)_2B]_3C$	2.0124	1.0391

[a] Parameters: $h_B = -0.45$; $h_O = +2.09$; $k_{CB} = 0.73$; $k_{BO} = 0.35$.[30]

The Hückel calculations correctly reflect the qualitative energy relationships found. Methanediboronic esters are correctly predicted to be more acidic than diphenylmethane, though incorrectly not as acidic as triphenylmethane. However, the triphenylmethide ion is almost as basic as diphenylmethide because the third phenyl group cannot be coplanar with the first two.[17] A similar phenomenon must occur in the boronic ester series, since redistribution reactions we have observed previously imply that diborylmethide ions cannot be much, if any, more basic than triborylmethide ions.[2]

The delocalization energies also correctly reflect the relative radical stabilities, the boronic ester group being significantly less effective than phenyl in stabilizing an adjacent radical. The reason for the difference between radicals and anions is that the highest occupied molecular orbital (HOMO) of the phenyl series is nonbonding, but the HOMO of the boronic ester series is bonding (essentially a carbon–boron π bond, see Table VI). Thus, the electron affinity of a boryl-substituted radical is higher than that of a phenyl-substituted radical. These results are all qualitatively in accord with the known radical chemistry of boronic esters,[20] including the observations that the boronic ester group assists formation of an adjacent radical by the addition of a radical to an alkeneboronic ester much more effectively than by abstraction of hydrogen from a methaneboronic ester with an oxidizing radical such as *tert*-butoxyl.[22]

In a previous publication, we used Hückel theory to account for the failure of a vinylboronic ester to undergo conjugate addition of a Grignard reagent, with a vinyl carboxylic ester used for comparison.[30] This is in no way contradictory to the present conclusions, the deciding factor being, as always, the relative stability of the tetrahedral borate complex (analogous to **22**) compared with the α-boryl carbanion or the relative stabilities of the transition states leading to these species.

Experimental Section

All reactions involving carbanions or other air-sensitive compounds were run under an argon atmosphere. Tetrahydrofuran (THF) was dried over sodium/potassium alloy and distilled under argon. Tetramethylethylenediamine (TMEDA) was distilled from calcium hydride. 2,2,6,6-Tetramethylpiperidine was dried over calcium sulfate and distilled. These amines were stored over 5-Å molecular sieves in bottles capped with rubber septums. Cyclohexane was distilled from sodium. Glassware was oven dried and cooled under argon, and reagents were transferred with hypodermic syringes and injected through rubber septums. Bu-

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(29) Our previous report that lithium tris(1,3,2-dioxaborin-2-yl)methide is protonated by dimethyl sulfoxide[16] may be attributed to inadequate exclusion of moisture, though it is also possible that this observation was correct and that proton transfer from Me_2SO to the triborylmethide anion is followed by irreversible complexing of the dimsyl anion to the boronic ester, analogous to structure **23**.

(30) Van-Catledge, F. A. *J. Org. Chem.* **1980**, *45*, 4801–4802.

(31) Matteson, D. S.; Mah, R. W. H. *J. Org. Chem.* **1963**, *28*, 2171–2174.

Table VI. Hückel Electron Densities, Bond Orders, and Energies of Boron-Substituted Carbanions and Radicals[a]

structure	π-electron density			π-bond order		π-bond energy, β
	C	B	O	C–B	B–O	
$(HO)_2BCH_2^-$	1.351	0.682	1.984	0.925	0.147	9.541
$[(HO)_2B]_2CH^-$	1.255	0.420	1.976	0.677	0.191	18.657
$[(HO)_2B]_3C^-$	1.209	0.316	1.974	0.559	0.209	27.651
$(HO)_2BCH_2\cdot$	0.680	0.382	1.969	0.476	0.213	9.053
$[(HO)_2B]_2CH\cdot$	0.639	0.251	1.965	0.355	0.236	17.895
$[(HO)_2B]_3C\cdot$	0.624	0.201	1.962	0.299	0.245	26.677

[a] Parameters: see Table V.

Table VII. Diol Methanediboronic Esters

compds[a]	mp, °C	^{1}H NMR,[b] δ		% yield
		CH_2B_2	other	
$CH_2[B(-OCH_2-)_2]_2$ (**1a**)	29–32	0.43	4.29	
$CH_2[B(-OCH_2-)_2CH_2]_2$ (**1b**)	42–43	0.13	1.943, 4.08	78
$CH_2[B(-OCMe_2-)_2]_2$ (**1c**)	53–54	0.35	1.28	74
$CH_2[B(-OCH_2-)_2CMe_2]_2$ (**1d**)	67–68	0.23	0.97, 3.68	86
$CH_2(BO_2C_6H_4)_2$ (**1e**)	89–90	1.43	7.2 (m)	73
$C_6H_5CH[B(-OCH_2-)_2CH_2]_2$ (**17**)	150–151		1.92,[c] 4.05, 7.3	

[a] All compounds yielded correct analyses. Anal. Calcd for **1a**, $C_5H_{10}B_2O_4$: C, 38.46; H, 6.41; B, 14.10. Found: C, 38.21; H, 6.60; B, 13.74. Anal. Calcd for **1b**, $C_7H_{14}B_2O_4$: C, 45.65; H, 7.61; B, 11.96. Found: C, 45.71; H, 7.73; B, 11.79. Anal. Calcd for **1c**, $C_{13}H_{26}B_2O_4$: C, 58.21; H, 9.70; B, 8.21. Found: C, 58.36; H, 9.77; B, 8.08. Anal. Calcd for **1d**, $C_{11}H_{22}B_2O_4$: C, 55.00; H, 9.17; B, 9.17. Found: C, 55.16; H, 9.24; B, 8.94. Anal. Calcd for **1e**, $C_{13}H_{10}B_2O_4$: C, 61.91; H, 3.97; B, 8.73. Found: C, 61.80; H, 4.12; B, 8.64. Anal. Calcd for **17**, $C_{13}H_{18}B_2O_4$: C, 60.00; H, 6.92; B, 84.6. Found: C, 60.17; H, 7.20; B, 8.23. [b] The CH_2B peaks were characteristically broadened singlets, and the peaks due to the diol moieties had the expected multiplicities and integrals. [c] Believed to include overlapping peaks of $C_6H_5CHB_2$ and $CH_2CH_2CH_2$ quintet.

tyllithium was standardized against 2-propanol to the 9,10-phenanthroline end point. Proton NMR spectra were recorded at 60 MHz with a Varian EM-360 instrument. For gas chromatography, the column was 10% SE-30 on Chrom W(NAW) in a 3.1 m × 3 mm stainless-steel tube, and the identities of all major products were verified by comparison of retention times with those of authentic samples as well as coinjection. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

Diol Methanediboronic Esters (1). To 30 g (0.188 mol) of bis(dimethoxyboryl)methane in 200 mL of THF under argon was added 0.376 mol of the diol in 150 mL of THF, and the mixture was kept overnight at 25 °C. Vacuum distillation of the solvent followed by recrystallization of the residue from 4:1 ether/pentane yielded the bis(diol) methanediboronic ester. Bis(propanediol) phenylmethanediboronate (**17**) was similarly prepared. Physical properties of these compounds are summarized in Table VII.

Lithiobis(1,3,2-dioxaborin-2-yl)methane (2b). A solution of 3.5 mmol of *n*-butyllithium (2.4 M) in hexane was added dropwise to a stirred solution of 0.41 g (3.5 mmol) of 2,2,6,6-tetramethylpiperidine and 0.49 g (3.5 mmol) of TMEDA in 10 mL of THF stirred at 0 °C. The solution was stirred 15 min at 0 °C and 15 min at 20–25 °C and then cooled with a Dry Ice/acetone bath to −78 °C. In another flask, a solution of 0.644 g (3.5 mmol) of bis(1,3,2-dioxaborin-2-yl)methane (**1b**) in 10 mL of THF was cooled to −78 °C and transferred into the first flask by means of a large-bore double-ended hollow needle and argon pressure. After the solution was stirred 1 h at −78 °C and 1 h at 0 °C, a precipitate of lithiobis(1,3,2-dioxaborin-2-yl)methane (**2b**) was obtained. For most reactions, this was used directly as a slurry. For a check on the nature of the precipitate, it was filtered in a Schlenk apparatus under argon. After being dried under vacuum, the air-sensitive solid had the approximate composition $LiCH(BO_2C_3H_6)_2\cdot 0.5THF$. Anal. Calcd for $C_9H_{17}B_2LiO_{4.5}$: C, 47.88; H, 7.59; B, 9.58; Li, 3.07. Found: C, 45.85; H, 7.36; B, 9.25; Li, 3.28.

Preparation of Aldehydes from Lithiobis(1,3,2-dioxaborin-2-yl)methane (2b) and Carbonyl Compounds or Alkyl Halides. The slurry of **2b** described in the preceding paragraph was cooled to −78 °C, and 3.3 mmol of the selected aldehyde, ketone, alkyl halide, or alkyl tosylate was injected. After being warmed to 20–25 °C and stirred 3 h, the solution was concentrated under vacuum and the residue was treated with 20 mL of water and 20 mL of dichloromethane followed by 2.25 g (14.6 mmol) of sodium perborate tetrahydrate. After the mixture was stirred 15 min, a suitable reference compound was injected to serve as a quantitative internal standard for gas chromatography, the phases were separated, and the product was extracted with additional dichloromethane (50 mL). The dichloromethane solution was washed with 1.5 M hydrochloric acid to remove amines and then dried over magnesium sulfate before gas chromatographic analysis. In one run, the scale was increased by a factor of 3, and **2b** with 1-bromopentane yielded 62% of hexanal, isolated by bulb to bulb distillation and confirmed by ^{1}H NMR and gas chromatographic analysis. Results are summarized in Tables II and III.

Isolation of *gem*-Diboronic Esters from Alkylations. The general procedure outlined in the preceding paragraph for the preparation of aldehydes was followed on a 10-mmol scale, except that after concentration of the THF solution, the diboronic ester residue was dissolved in dichloromethane/pentane (1:1) and chromatographed on a short column of silica gel powder (60–200) mesh). Further purification was carried out by bulb to bulb distillation. The following compounds were prepared by this method. **Bis(propanediol) hexane-1,1-diboronate** (**3**): bp 93–102 °C (0.07 torr); 71%; ^{1}H NMR ($CDCl_3$) δ 0.43 (t, 1, CHB_2), 0.9–1.3 (m, 11, $CH_3(CH_2)_4$), 1.84 (quintet, 4, $CH_2CH_2CH_2$), 4.03 (t, 8, OCH_2CH_2). Anal. Calcd for $C_{12}H_{24}B_2O_4$: C, 56.76; H, 9.53; B, 8.51. Found: C, 56.73; H, 9.60; B, 8.65. **Ethylene ketal of bis(propanediol) 5-ketohexane-1,1-diboronate** (**4**): bp 125–134 °C (0.07 torr); 57%; NMR ($CDCl_3$) δ 0.42 (t, 1, CHB_2), 1.29 (s, 3, CH_3C), 1.4 (br m, 6, $(CH_2)_3$), 1.94 (q, 4, $CH_2CH_2CH_2$), 3.97 (s, 4, OCH_2CH_2O), 4.05 (t, 8, OCH_2CH_2). Anal. Calcd for $C_{14}H_{26}B_2O_6$: C, 53.90; H, 8.40; B, 6.93. Found: C, 53.99; H, 8.33; B, 6.85. **Bis(propanediol) 5-cyanopentane-1,1-diboronate** (**5**): bp 120–132 °C (0.07 torr); 49%; NMR ($CDCl_3$) δ 0.40 (t, 1, CHB_2), 1.5 (br m, 6, $(CH_2)_3$), 1.94 (q, 4, $CH_2CH_2CH_2$), 2.38 (t, 2, CH_2CN), 4.08 (t, 8, OCH_2CH_2). Anal. Calcd for $C_{12}H_{21}B_2NO_4$: C, 54.41; H, 7.99; B, 8.16; N, 5.29. Found: C, 54.53; H, 7.87; B, 8.19; N, 5.10.

1-Phenyloctane-3,3-diboronic Acid. 1-Lithio-1,1-bis(1,3,2-dioxaborin-2-yl)hexane (**6**) was prepared from **3** under the same conditions used to prepare **2b** from **1b**. Compound II **6** did not precipitate from THF. Treatment with 2-phenylethyl iodide and isolation of the boronic ester as described in the preceding paragraph yielded 70% propanediol 1-phenyloctane-3,3-diboronate, not analytically pure: NMR ($CDCl_3$) δ 0.9 (m, 3, CH_3), 1.33 (m,

~10, $(CH_2)_4 + CH_2CB_2$), 1.83 (m, ~4, $OCH_2CH_2CH_2O$), 2.5 (m, 2, $PhCH_2$), 4.01 (t, 8, OCH_2CH_2), 7.37 (s, 5, C_6H_5). Treatment with water yielded 1-phenyloctane-3,3-diboronic acid: mp 66 °C dec; NMR (CD_3SOCD_3) similar to propanediol ester but lacking $OCH_2CH_2CH_2O$ multiplets at δ 1.83 and 4.01 and having a broad OH peak at δ 5.2. Anal. Calcd for $C_{14}H_{24}B_2O_4$: C, 60.49; H, 8.70; B, 7.78. Found: C, 60.28; H, 8.78; B, 8.08.

Cyclohexyl Cyclohexylmethyl Ketone (12). Lithium tetramethylpiperidide was prepared from 5.5 mmol of butyllithium and 6 mmol of tetramethylpiperidine in 5 mL of THF and 618 mg of TMEDA, and 1.344 g (5.05 mmol) of bis(1,3,2-dioxaborin-2-yl)cyclohexylmethane (**10c**) in 5 mL of THF was added. The THF was evaporated until a pressure of 0.1 torr at 25 °C was attained, and the residue was treated with 760 mg (5.7 mmol) of methyl cyclohexanecarboxylate in 5 mL of cyclohexane, which resulted in an exothermic reaction. The mixture was refluxed 1 h. Workup with aqueous acid and extraction with ether followed by distillation yielded 771 mg of cyclohexyl cyclohexylmethyl ketone, bp 85–100 °C (0.2 torr) (lit.[32] bp 164–165 °C (16 torr)), containing 2.4% of methyl cyclohexanecarboxylate and 3.3% of starting boronic ester by NMR, contained yield of product, 70%: NMR ($CDCl_3$) δ 1.0–2.0 (m, 22, cyclohexyl CH), 2.35 (m, 3, $CHCOCH_2$), 3.77 (s, CH_3O, 3.5 mol %), 4.04 (t, $[BO_2(CH_2)_2CH_2]_2$, 2.6 mol %). The semicarbazone was prepared; mp 190–193 °C (lit.[32] mp 190–191 °C).

1-Phenyl-1-heptanone, 2-octanone, and 4-decanone were prepared from **6** and methyl benzoate, ethyl acetate, or methyl butyrate, respectively, under conditions similar to those described for the preparation of cyclohexyl cyclohexylmethyl ketone in the preceding paragraph, except that the period of refluxing in cyclohexane was overnight and the yields (Table IV) and identities of the products were established by gas chromatography. It has not been proved whether it is necessary to reflux these reaction mixtures at all, but a low yield was obtained in an early attempt when the THF and volatile byproducts were not distilled from **6** and no reflux was used.

2-Phenyl-3-undecanone (1b). LiTMP was prepared from 10.5 mmol of 2,2,6,6-tetramethylpiperidine, 10.2 mmol of TMEDA, and 10.4 mmol of 1.6 M butyllithium in 10 mL of THF. The solution was cooled with an ice bath, and 2.71 g (9.41 mmol) of propanediol 2-phenylpropane-1,1-diboronate (**9**) was added. The mixture was stirred 22 h at 20–25 °C, yielding a substantial amount of precipitate, and then cooled to −78 °C, and 10.5 mmol of octanal was infected. The mixture was stirred overnight at 20–25 °C, concentrated, and treated with 20 mL of water, 35 mL of ether, 2 g of sodium perborate, and 1 g of sodium hydroxide, and the solution was stirred overnight. The product was extracted into ether, and the mixture was washed with water and distilled: bp 88–101 °C (0.01 torr); 69%; redistilled, bp 109–116 °C (0.025 torr), mp 0–7 °C; NMR ($CDCl_3$) δ 0.91 (m, 3, CH_3), 1.26 (m, 12, $(CH_2)_6$), 1.41 (d, J = 7 Hz, 3, $CHCH_3$), 2.40 (t, J = 7 Hz, 2 $COCH_2$), 3.85 (q, J = 7 Hz, 1, $COCHCH_3$), 7.44 (s, 5, C_6H_5). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 83.09; H, 10.52.

1-Phenyl-2-heptanone was prepared from lithiated propanediol hexane-1,1-diboronate (**6**) and benzaldehyde under conditions similar to those described for 2-phenyl-3-undecanone in the preceding paragraph, but with characterization of the product by gas chromatography (Table IV).

Triphenylmethyllithium as Base for Preparation of Diborylmethide Anion. Triphenylmethyllithium was prepared from 1.25 g (5.12 mmol) of triphenylmethane and 5.25 mmol of butyllithium in 10 mL of THF and 0.8 mL of TMEDA at 0 °C, which resulted in a red precipitate. A solution of 943 mg (5.12 mmol) of bis(trimethylenedioxyboryl)methane in 5 mL of THF was injected, resulting in immediate dissolving of the red precipitate, but a red solution remained. After 2 h and being warmed to 17 °C the solution was still red, and there was precipitate on the flask walls. The mixture was cooled to 0 °C and 843 mg (5.7 mmol) of 1-bromopentane was injected, with fading of the red color within 1 min, and stirring was continued at room temperature overnight. The mixture was concentrated under vacuum, and the residue was treated with 50 mL of petroleum ether. Distillation (104–115 °C (0.1 torr)) yielded 401 mg of a liquid mixture estimated by NMR to contain 74% (73 mol %) of propanediol hexane-1,1-diboronate (**3**) and the remainder triphenylmethane, 22.7% estimated yield of contained boronic ester. There was also a solid fraction, probably mostly triphenylmethane but also containing some **3**. Both the liquid and the solid fractions were combined and treated with 805 mg of 2,4-dinitrophenylhydrazine in sulfuric acid/methanol and 625 mg of sodium perborate tetrahydrate. The crystals obtained from two crops were chromatographed on silica gel, eluting the triphenylmethane with petroleum ether and the 2,4-DNP with 1:1 ether/petroleum ether: yield of hexanal 2,4-DNP, 414 mg, mp 105–106 °C; second crop, 47 mg, 99–102 °C, total 32%. An authentic sample, mp 99–102 °C, gave no depression on mixing.

Hydrogenation of 1-Alkene-1,1-diboronic Esters to Alkane-1,1-diboronic Esters (10). The appropriate alkene-1,1-diboronic esters[16] were hydrogenated over a 5% palladium/charcoal catalyst in ethyl acetate at 1 atm, 25 °C, until saturated (8 h to yield **10a**, 2 days for **10b** and **10c**), and the products were distilled. **Bis(propanediol) 2-phenylethane-1,1-diboronate (10a)**, bp 112–127 °C (0.06 torr); 97%; ^1H NMR ($CDCl_3$) δ 0.83 (t, J = 8 Hz, 1, CHB_2), 1.79 (quintet, 4, $OCH_2CH_2CH_2O$), 2.78 (d, J = 8 Hz, 2, $PhCH_2CHB_2$), 3.96 (t, 8, OCH_2CH_2), 7.28 (s, 5, C_6H_5). Anal. Calcd for $C_{14}H_{20}B_2O_4$: C, 61.39; H, 7.36; B, 7.89. Found: C, 61.15; H, 7.17; B, 8.17. **Bis(propanediol) 2-phenylpropane-1,1-diboronate (10b)**: bp 120–134 °C (0.03 torr); 89%; NMR ($CDCl_3$) δ 0.85 (d, J = 10 Hz, 1, CHB_2), 1.23 (d, J = 7 Hz, 3, CH_3CH), 1.49 (q, 2, $OCH_2CH_2CH_2O$), 1.91 (q, 2, $OCH_2CH_2'CH_2O$), 3.11 (m, J = 7 and 10 Hz, 1, $CH_3CH(Ph)CHB_2$), 3.72 (t, 4, OCH_2CH_2), 4.04 (t, 4, $OCH_2'CH_2$), 7.28 (s, 5, C_6H_5). Anal. Calcd for $C_{15}H_{22}B_2O_4$: C, 62.57; H, 7.70; B, 7.51. Found: C, 62.71; H, 7.68; B, 7.49. **Bis(propanediol) cyclohexylmethane-1,1-diboronate (10c)**: bp 95–110 °C (0.06 torr); 79%; NMR ($CDCl_3$) δ 0.28 (d, J = 10 Hz, 1, CHB_2), 1–2 (m, 15, cyclo-C_6H_{11} + $CH_2CH_2CH_2$), 4.03 (t, 8, OCH_2CH_2). Anal. Calcd for $C_{13}H_{24}B_2O_4$: C, 58.71; H, 9.10; B, 8.13. Found: C, 58.67; H, 9.06; B, 8.10.

Propanediol Methaneboronate (13). Methaneboronic anhydride pyridine complex was prepared by the published procedure.[22b] *Caution*! The published procedure failed to note *spontaneous combustion* of the organic extracts if exposed to air a few seconds during workup. It is essential to maintain a blanket of argon over the ether/butanol solutions of methaneboronic acid at all times, and the preparation must be regarded as extremely hazardous on the scale described.[22b] Trimethylborane is a probable byproduct that would account for the spontaneous flammability. Methaneboronic anhydride[22b] and an equivalent amount of propanediol were stirred over magnesium sulfate overnight, the product (**13**) was distilled below room temperature under vacuum and redistilled through a short fractionating column: bp 104–105 °C (700 torr); NMR ($CDCl_3$) δ 0.12 (s, 3, CH_3B), 1.95 (quintet, 2, $CH_2CH_2CH_2$), 4.03 (t, 4, OCH_2CH_2). Anal. Calcd for $C_4H_9BO_2$: C, 48.08; H, 9.08; B, 10.82. Found: C, 47.87; H, 9.04; B, 11.09.

Propanediol Benzylboronate. Dimethyl benzylboronate[33] was converted to the propanediol ester: bp 258–259 °C; NMR ($CDCl_3$) δ 1.76 (q, 2, $CH_2CH_2CH_2$), 2.19 (br s, $PhCH_2B$), 3.90 (t, 4, OCH_2CH_2), 7.26 (s, 5, C_6H_5). Anal. Calcd for $C_{10}H_{13}BO_2$: C, 68.24; H, 7.44; B, 6.14. Found: C, 68.23; H, 7.27; B, 6.10.

Pinacol β-Styreneboronate (20). β-Styreneboronic acid[8] was prepared from methyl borate and β-styrylmagnesium bromide (preferably in THF) and was esterified with pinacol in toluene with azeotropic removal of the water. The product (**20**) was distilled: bp 89–93 °C (0.05 torr); NMR showed expected relationship to known ethylene glycol ester.[5] Anal. Calcd for $C_{14}H_{19}BO_2$: C, 73.07; H, 8.32; B, 4.70. Found: C, 73.06; H, 8.21; B, 4.89.

Pinacol 2-Phenyl-1-(phenylthio)ethane-1-boronate (21). A mixture of 2.05 g of pinacol β-styreneboronate (**20**), 3 mL of thiophenol, and 150 mg of azobisisobutyronitrile was heated 3.5 h at 100 °C. Distillation yielded 2.66 g (88%) of **21**: bp 136–140 °C (0.01 torr); ^1H NMR identical with that of the authentic sample.[15]

Registry No. 1a, 29173-15-7; **1b**, 63035-38-1; **1c**, 78782-17-9; **1d**, 78782-18-0; **1e**, 78782-19-1; **2a**, 57404-82-7; **2b**, 63035-39-2; **3**, 63035-

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42-7; **4**, 63074-46-4; **5**, 63035-43-8; **6**, 63035-40-5; **9**, 78782-20-4; **10a**, 78782-21-5; **10b**, 78782-22-6; **10c**, 78782-23-7; **12**, 6713-49-1; **13**, 51901-48-5; **14**, 62930-28-3; **16**, 78782-24-8; **17**, 78782-25-9; **19**, 78782-26-0; **20**, 78782-27-1; **21**, 66080-30-6; LiTMP, 38227-87-1; triphenylmethyllithium, 733-90-4; $CH_3(CH_2)_3I$, 542-69-8; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_3Cl$, 109-69-3; $CH_3(CH_2)_4Br$, 110-53-2; $CH_3(CH_2)_6I$, 4282-40-0; $CH_3(CH_2)_6OSO_2C_6H_4CH_3$, 24767-82-6; $C_6H_5CH_2Br$, 100-39-0; $Cl(CH_2)_4I$, 10297-05-9; $CH_3(CH_2)_4CHBrCH_3$, 1974-04-5; $(C_2H_5)_2CHI$, 1809-05-8; $NC(CH_2)_4Br$, 5414-21-1; $CH_3C(O_2C_2H_4)(CH_2)_3I$, 3695-28-1; CH_3I, 74-88-4; $C_6H_5CH_2CH_2I$, 17376-04-4; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_4CHO$, 66-25-1; $C_6H_5CH_2CHO$, 122-78-1; $Cl(CH_2)_4CHO$, 638-29-9; $CH_3(CH_2)_4CH(CH_3)CHO$, 16630-91-4; $(C_2H_5)_2CHCHO$, 97-96-1; $CH_3(CH_2)_4COCH_3$, 110-43-0; propanediol 1-phenyloctane-3,3-diboronate, 63035-44-9; heptanal, 111-71-7; cyclohexanone, 108-94-1; octanal, 124-13-0; cyclohexanecarboxaldehyde, 2043-61-0; C_6H_5CHO, 100-52-7; $C_6H_5CO_2CH_3$, 93-58-3; C_6H_5COCl, 98-88-4; $CH_3CO_2C_2H_5$, 141-78-6; $CH_3(CH_2)_2CO_2CH_3$, 623-42-7; $C_6H_5CH_2CO(CH_2)_4CH_3$, 6683-94-9; $C_6H_5CO(CH_2)_5CH_3$, 1671-75-6; $C_6H_5CO(CH_2)_5CH_3$ 2,4-DNP, 66591-15-9; $CH_3CO(CH_2)_5CH_3$, 111-13-7; $CH_3(CH_2)_2CO(CH_2)_5CH_3$, 624-16-8; $(HO)_2BCH_2^-$, 78782-28-2; $[(HO)_2B]_2CH^-$, 78782-29-3; $[(HO)_2B]_3C^-$, 78782-30-6; $(HO)_2BCH_2\cdot$, 78782-31-7; $[(HO)_2B]_2CH\cdot$, 78782-32-8; $[(HO)_2B]_3C\cdot$, 78782-33-9; 1,2-ethanediol, 107-21-1; 1,3-propanediol, 504-63-2; 2,3-dimethyl-2,3-butanediol, 76-09-5; 2,2-dimethyl-1,3-propanediol, 126-30-7; 1,2-benzenediol, 120-80-9; bis(dimethoxyboryl)methane, 17936-82-2; bis(dimethoxyboryl)phenylmethane, 17936-83-3; 1-phenyloctane-3,3-diboronic acid, 78782-34-0; propanediol 2-phenylethene-1,1-diboronate, 56998-81-3; propanediol 2-phenyl-1-propene-1,1-diboronate, 56998-82-4; propanediol cyclohexylidenemethane-1,1-diboronate, 56998-80-2; methaneboronic anhydride, pyridine complex, 78782-35-1; dimethyl benzylboronate, 25292-03-9; *β*-styreneboronic acid, 4363-35-3.

Organoboranes. 26. ^{11}B NMR Investigation of Reactions of 2,3-Dimethyl-2-butene with Monochloroborane Complexes. Preparation and Hydroboration Characteristics of Thexylchloroborane Reagents

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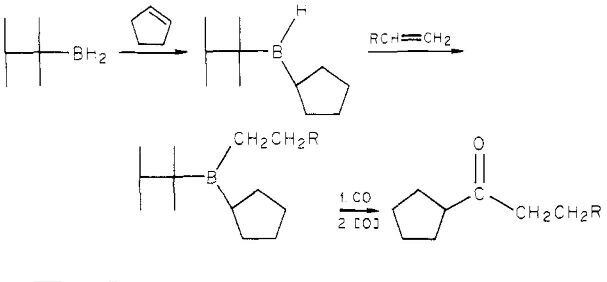
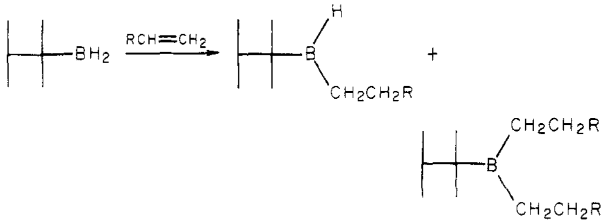
Under selected conditions, the hydroboration of 2,3-dimethyl-2-butene with 1 equiv of monochloroborane proceeds cleanly to give the monohydroboration product, thexylchloroborane (ThxBHCl). This reaction was examined with several monochloroborane complexes, including $BH_2Cl{\cdot}THF$, $BH_2Cl{\cdot}OEt_2$, and $BH_2Cl{\cdot}SMe_2$. The resulting thexylchloroboranes were fully characterized by IR and ^{11}B NMR spectroscopy. Monomeric ThxBHCl·THF was obtained cleanly from $BH_2Cl{\cdot}THF$. Similarly, monomeric $ThxBHCl{\cdot}SMe_2$ was obtained cleanly from $BH_2Cl{\cdot}SMe_2$. On the other hand, the product resulting from hydroboration of 2,3-dimethyl-2-butene with $BH_2Cl{\cdot}OEt_2$ was demonstrated to be a complex, equilibrating mixture of thexylborane (dimeric), thexylchloroborane, and thexyldichloroborane. The hydroboration properties of each of these reagents were also examined. Hydroboration of terminal alkenes with the ThxBHCl·THF and $ThxBHCl/Et_2O$ reagents led to complex mixtures containing trialkylborane, dialkylchloroborane, and alkyldichloroborane species. However, hydroboration of terminal alkenes with $ThxBHCl{\cdot}SMe_2$ in CH_2Cl_2 proceeded cleanly to the desired dialkylchloroborane product. Subsequent oxidation produced the desired primary alcohols in nearly quantitative yields with high regioselectivity.

Thexylborane is a particularly valuable reagent for the preparation of unsymmetrical trialkylboranes via sequential hydroboration. Subsequent carbonylation or cyanidation produces the corresponding unsymmetrical ketones in high yield[2] (eq 1).



(1)

In this procedure, it is important that the first alkene introduced be a relatively hindered one, such as cyclopentene or 2-methyl-1-butene. Treatment of thexylborane with an unhindered terminal alkene cannot be controlled to give exclusively monohydroboration[3] (eq 2). Consequently, this synthesis fails when one attempts to stitch together two different primary alkyl groups.



(2)

It occurred to us that this problem might be solved by employing a thexylchloroborane (ThxBHCl) derivative (eq

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[1] Graduate research assistant on Grant GP 41169X from the National Science Foundation. Taken in part from the M.S. Thesis of J. A. Sikorski, Purdue University, West Lafayette, IN, 1976.

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