CHARACTERIZATION OF A BORON-STABILIZED CARBANION, TRIS-(TRIMETHYLENEDIOXYBORYL)METHIDE ION, AND ITS REACTIONS WITH CARBONYL COMPOUNDS*

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Summary

Addition of butyllithium to tetrakis(trimethylenedioxyboryl)methane, $C[BO_2(CH_2)_3]_4$ (I), in tetrahydrofuran at −70°C precipitates lithium tris-(trimethylenedioxyboryl)methide, Li^+ $^-C[BO_2(CH_2)_3]_3$ (II), which has been isolated and characterized. The ^{11}B NMR spectrum of II in hexamethylphosphoramide consists of one peak 1.05 ppm downfield from boron trifluoride etherate. The ^1H NMR spectrum of II after solvolysis in protic solvents shows that the *B*-butyl group has been cleaved off to the extent of 90-100%, presembly as the butaneboronic ester III. The identity of II has been further checked by its conversion to the known triphenyltin derivative VI and to the bromo derivative XI, which was difficult to purify if II was not isolated before reaction with bromine. For condensation with aldehydes and ketones, II was most conveniently generated from I with methyllithium and not isolated, and alkene-1,1-diboronic esters XII and XIV were obtained in good yields. The condensation product from paraformaldehyde (XII, R = H) underwent Diels-Alder reactions with cyclopentadiene and perchlorocyclopentadiene, and the chemistry of the benzaldehyde derivative XII (R = Ph) was investigated briefly.

Introduction

Boron-substituted carbanions have been postulated as intermediates in a number of synthetically useful reactions. Most noteworthy are syntheses of carbon—carbon double bonds from carbonyl compounds and carbanions derived from base-induced deboronation of *gem*-diboryl compounds [2,3] or

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methanetetraboronic and methanetriboronic esters [4,5]. Alkylation [6] and substitution by Group IV metals [7,8] have also been carried out. Boron-substituted carbanions have also been generated by deprotonation of a suitable borane by a sterically hindered base [9,10].

In all of these cases the boron-substituted carbanion has been postulated as a synthetic intermediate but not isolated as a salt and characterized. In most cases [2-8] the synthetic results can be just as well accounted for by assuming that the reactive intermediate is a tetrasubstituted boron anion of the general formula $X_2BCY_2BX_3^-$, which may readily transfer the carbanion unit $X_2BCY_2^-$ directly from the electrofuge BX_3 to the attacking electrophile in a displacement reaction, or may release a small equilibrium concentration of the reactive species $X_2BCY_2^-$. It is difficult to account for all of the results reported by Rathke and Kow [9] on the basis of such assumptions, though the failure to achieve more than about three-quarter replacement of the α-hydrogen might be regarded as evidence for end-capped oligomeric structures such as $X_2BCH_2\overline{B}X_2\text{-}CH_2BX_3^-$. Where both allylic and boron activation are present [10], it becomes hard to argue for anything but a boron-substituted allyl anion structure, but allyl anions do not need boron stabilization in order to exist.

It may also be noted that covalent α-lithioborane structures are possible alternatives to carbanion or boron anion structures in the examples cited.

The aromatic B-phenylborabenzene anion has been characterized by Ashe and Shu [11], but this interesting structure must owe a great part of its stability to its aromaticity, and it therefore casts little light on the foregoing structure questions. For completeness, the existence of a variety of carborane anions may be noted [12], but these represent a different class altogether.

The yields in our previous condensations of aldehydes and ketones with anions from methanetetraboronic esters left room for improvement [5], and we have found considerably better reaction conditions for this synthesis.

Results and discussion

### Characterization of lithium tris(trimethylenedioxyboryl)methide (II)

Wilcsek observed that the lithium salt II precipitates when butyllithium is added to a tetrahydrofuran solution of tetrakis(trimethylenedioxyboryl)methane (I), and he was also able to show that the precipitated material contained little or no B-butyl protons after dissolving it in D_2O [1,13].
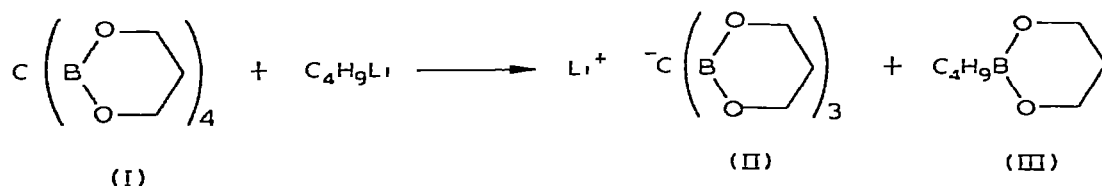
The precipitated salt II is extremely moisture-sensitive and is pyrophoric, therefore in the present work we used a Schlenk apparatus to obtain reproducible results. In order to obtain an easily filterable precipitate and avoid gum formation, we found it necessary to use a considerable excess of the tet-

raborylmethane (I), though for simple synthetic processes where II was not isolated a 1/1 ratio with alkyllithium was used successfully.

Dissolving the salt II in D_2O should, on the basis of known chemistry [4], result in hydrolysis to 1,3-propanediol-$\underline{O},\underline{O}'$-$d_2$, $B(OD)_3$, and $CD_2[B(OD)_2]_2$. NMR spectra of D_2O solutions of II showed only the expected 1,3-propanediol C—H peaks. Integration revealed a small amount of absorption near δ 1 ppm corresponding to 4 mole % of the B-butyl compound IV or half as much of the expected byproduct dibutylborinate anion V, which would arise from reaction of the butaneboronic ester III formed in the primary reaction with butyllithium, in competition with the reaction of butyllithium with I.
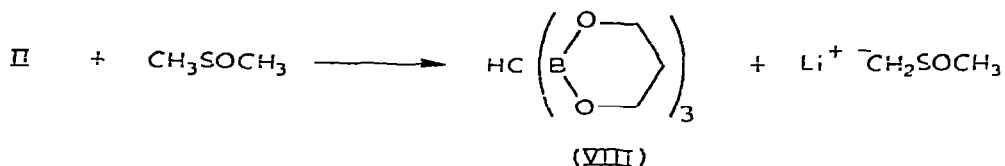

(IV)   (V)
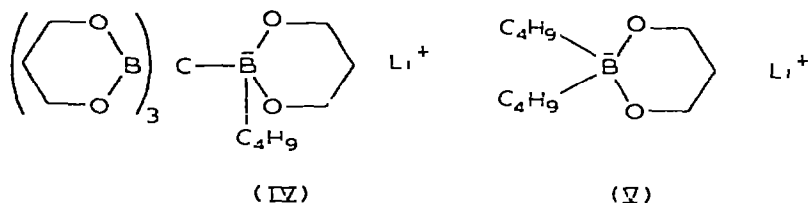
The D_2O solutions of II appeared cloudy, and we therefore checked these results by using methanol-d_4 as the solvent. Some increase in the butyl group content was noted, up to 9.6 mole % calculated as IV, but it seems most likely that this water-insoluble by product is related to V, perhaps a polymer of V or perhaps $LiB(C_4H_9)_4$.

Having proved the absence of any major amount of B-butyl groups, it was then necessary to prove the presence of the triborylmethide group. This was done by collecting the precipitated salt II and reacting it with triphenyltin chloride, which yielded 70% crude, 57% recrystallized, of the known [8] triphenyltin derivative VI. This experiment eliminates the possibility that a major component of the precipitate might be the spiro borate salt VII instead of II. Although the likelihood of obtaining VII might seem small, it could conceivably arise by way of a protonation and/or disproportionation process, and in early experiments using ethylene glycol esters, Wilcsek isolated the ethylene glycol ester analog of VII, lithium bis(dimethylenedioxy)borate [13].

(VI)   (VII)
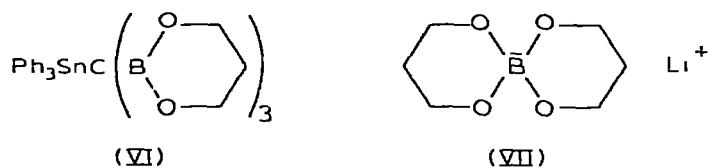
A better structure proof would be provided by an NMR spectrum of the lithium salt II itself. The problem was to find a suitable solvent. Dimethyl sulfoxide-d_6 was found to dissolve the salt II readily, and on addition of triphenyltin chloride the triphenyltin derivative VI precipitated in 50% yield. However, with undeuterated dimethyl sulfoxide ("silylation grade"), the yield of VI was only 4% and the NMR spectrum of the solution showed the characteristic B_3CH proton near δ O ppm. When II was kept 16 h in dimethyl sulfoxide, tris(trimethylenedioxyboryl)methane (VIII) was obtained in 32% yield.

(An authentic sample of VIII was prepared from the corresponding methyl ester [4] and 1,3-propanediol.) Thus, the anion II is basic enough to abstract a proton from dimethyl sulfoxide:

$$\text{II} \quad + \quad CH_3SOCH_3 \quad \longrightarrow \quad HC\left(\begin{array}{c} O \\ B \\ O \end{array}\right)_3 \quad + \quad Li^+ \ ^-CH_2SOCH_3$$

(VIII)

Other common solvents also proved unsuitable, the salt II being insoluble in dichloromethane, triglyme, or 1,2-bis(dimethylamino)ethane and reactive toward chloroform, dimethylformamide, or the crown ether tetramer of 1,2-epoxypropane.

The ^{11}B NMR spectrum of the salt II was obtained in hexamethylphosphoramide, which was found to dissolve a moderate amount of III without destroying it. A single peak approximately 100 Hz wide at half-height was observed at 1.05 ppm downfield from boron trifluoride etherate sealed in a capillary placed in the NMR tube. For comparison, ^{11}B chemical shifts of tris- and tetrakis-(trimethylenedioxyboryl)methane (I and VIII) (in deuterochloroform, since they are insufficiently soluble in hexamethylphosphoramide) and several compounds from the literature [14] are listed in Table 1.

From Table 1 it can be seen that the observed ^{11}B chemical shift of II suggests some degree of negative charge on the boron atoms. This supports the assigned carbanion structure, since the carbanion would donate π-electron density to the vacant p-orbitals of the boron atoms. We have previously suggested resonance structures describing this electron donation and rationalized the stability of the anion II and related species on that basis [4].

Another alternative structure to be considered is IX, which is merely the addition product of I and II. The ^{11}B spectrum would require that IX be undergoing rapid dissociation to I and II and recombination to make all seven boron atoms equivalent. Borohydride anion would seem to provide an upper limit for the chemical shift of the anionic boron atom in IX and the others should resemble ordinary boronic esters. The weighted average chemical shift should be near —20 ppm, which is inconsistent with the observed value. Other evidence against IX is provided by the reaction with triphenyltin chloride, which yields consider-

TABLE 1

^{11}B CHEMICAL SHIFTS RELATIVE TO BORON TRIFLUORIDE ETHERATE

Compound	Chemical shift δ(ppm)	Ref.
BH_4^-	38.0	[14]
$LiBEt_4$	17.48	[14]
$LiC[BO_2(CH_2)_3]_3$ (II)	—1.05	This work
$CH_3B(OCH_3)_2$	—29.5	[14]
$HC[BO_2(CH_2)_3]_3$ (VIII)	—30.7	This work
$C[BO_2(CH_2)_3]_4$ (I)	—33.6	This work
$(CH_3)_2BOCH_3$	—53.0	[14]
$(CH_3)_3B$	—86.0	[14]

ably more of the purified derivative VI than is theoretically possible from IX. The elemental analyses of II deviate less than 1% from the theoretical values in the directions expected for the inevitable degradation by air and water and do not support IX.
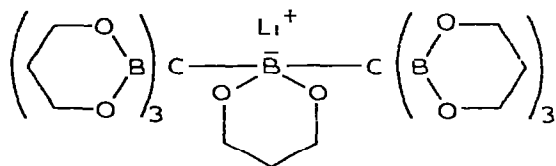
(IX)

To further prove the structure of II in hexamethylphosphoramide solution, we tried to make the triphenyltin derivative VI, but instead isolated the disproportionation products I (insoluble in hexamethylphosphoramide) and the ditin compound, $(Ph_3Sn)_2C[BO_2(CH_2)_3]_2$ (X). Disproportionation of this sort has been observed before in the dimethoxyboryl series [7]. Some of our data suggest that a considerable amount of the monotin compound VI may also have been among the products, but it was lost during the purification of I and X.

A final question regarding the structure of II is whether the compound is a salt or a covalent lithium compound. The only evidence available is the solubility properties. A covalent alkyllithium should be highly soluble in ethereal solvents such as tetrahydrofuran, more soluble than the symmetrical boronic ester I used as starting material. The insolubility of II in nonpolar solvents and its solubility in dimethyl sulfoxide and hexamethylphosphoramide strongly suggest ionic character. The oxygen atoms of the boronic ester groups in II provide likely coordination sites to stabilize the lithium cation in the crystal lattice.

Bromotris(trimethylenedioxyboryl)methane (XI)

When lithium tris(trimethylenedioxyboryl)methide (II) was prepared as described previously [8] and the unfiltered tetrahydrofuran suspension was treated with excess bromine at $-75°C$, the crude monobromo compound, $BrC[BO_2(CH_2)_3]_3$ (XI), was easily isolated, but all attempts to recrystallize or sublime XI resulted in gradual decomposition to a brown oil. However, when the lithium salt II was prepared and filtered as described in the preceding section, then treated with bromine in dichloromethane, the crude bromo compound XI survived recrystallization from chloroform/ether and was readily purified, though XI is sensitive to air and moisture.

Condensation of II with aldehydes and ketones

In previous work we have described the condensation of the pinacol boronic ester analog of II, lithium tris(tetramethylethylenedioxyboryl)methide, with aldehydes and ketones [5]. The reaction was found to provide a useful general synthesis of alkene-1,1-diboronic esters, but the yields were generally only fair to good, and we failed to purify some of the compounds we attempted to make.

Our initial attempts to condense II with acetaldehyde failed to yield a crystalline product. We then found that the use of dimethoxyboron chloride, $(CH_3O)_2BCl$, as previously described to neutralize the basic byproduct [5] is unnecessary, at least with the propanediol ester series. The lithium salt II may be reacted with the aldehyde in tetrahydrofuran, the solvents removed under vacuum, and the residue treated with diethyl ether to dissolve the alkene-1,1-diboronic ester (XII) and leave the byproduct lithium salt XIII (which may be polymeric) as an insoluble residue. Since XIII is basic and might complex with XII or exchange the basic oxide moiety with XII, we were concerned that XII might be lost with the precipitate, but our results indicated no significant loss by this route.
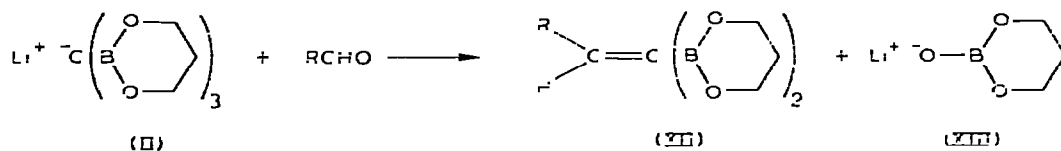
In further refining the preparative procedure, we found that there is no advantage in filtering the lithium salt II before reacting it with the aldehyde. However, best results are obtained if II is prepared from methyllithium rather than butyllithium with I, since the byproduct methaneboronic ester, CH_3BO_2-$(CH_2)_3$, is volatile and easily separated from the desired product XII. Crystallization of the products XII was generally achieved by dissolving them in ether, cooling in Dry Ice/acetone, and adding pentane while scratching the mixture. The products from butyraldehyde and hexaldehyde proved to be liquids and were purified by distillation.

Formaldehyde was found to react with II to give the expected product XII (R = H). At first we tried depolymerizing paraformaldehyde and passing the gas into a suspension of II, but it was found easier, and at least equally effective, merely to reflux a suspension of II in tetrahydrofuran with paraformaldehyde. This product XII (R = H) polymerizes readily, but is stabilized by the radical inhibitor galvinoxyl. The other aldehyde tried successfully was benzaldehyde. The yields of XII ranged from 66% (formaldehyde) to about 90%.

We were unable to purify the condensation product of cinnamaldehyde with II. The NMR evidence indicated that the major product was the expected one XII (R = PhCH=CH—) but there may have been some conjugate addition product interfering with the purification. Attempted chromatography on silica gel failed to purify the compound, and distillation led to decomposition.

Ketones, RCOR', react with II in the same manner as aldehydes to yield 70-90% of $RR'C=C[BO_2(CH_2)_3]_2$ (XIV). The relatively unreactive ketones, benzophenone and cyclohexanone, worked as well as acetone and acetophenone. 1,3-Dichloroacetone gave only 40% of XIV, about the same yield as with the the pinacol boronic ester used previously [5]. Attempts to react benzil or cyclohexane-1,2-dione with II failed to yield any condensation product, and workup of the benzil reaction mixture yielded VIII, the product of protonation of II by the chloroform or solvent impurities during the workup.

Reactions of alkene-1,1-diboronic esters (XII) and (XIV)

The ethene-1,1-diboronic ester (XII, R = H) was found to undergo Diels-Alder reaction with cyclopentadiene to yield the adduct XV, and to react similarly with perchlorocyclopentadiene. Attempts to carry out Diels-Alder reactions with 1,3-cyclohexadiene or sulfolene (as a source of butadiene) at atmospheric pressure failed, but higher pressures were not tried.
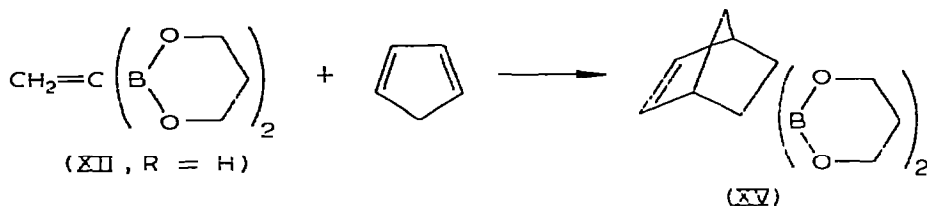
Oxidation of an alkene-1,1-diboronic ester with alkaline hydrogen peroxide should lead to the corresponding carboxylic acid, and this was previously demonstrated in one case [5]. We tried a direct conversion of benzaldehyde to phenylacetic acid, oxidizing the crude reaction mixture of benzaldehyde and II, and isolated pure phenylacetic acid in 60% yield. With further work, it appears that this conversion of RCHO to RCH_2CO_2H could be made a useful synthetic procedure.

Zweifel and coworkers have shown that alkenylboranes, $RCH=CHBR'_2$, can be rearranged to alkenes, $RCH=CHR'$, by treatment with iodine and alkali [15,16]. We started with 2-phenyl-1,1-bis(trimethylenedioxyboryl)ethene (XII, R = Ph), treated it with methyllithium, and then treated the product in situ with iodine and alkali followed by oxidation with hydrogen peroxide and obtained phenylacetone in 30% yield, as shown by gas chromatography. No exploration for optimum conditions was attempted.
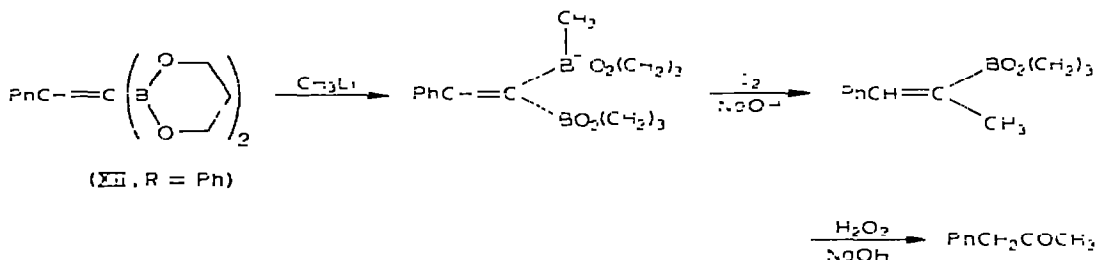
Experimental

Lithium tris(trimethylenedioxyboryl)methide (II)

A Schlenk apparatus was constructed with a medium fritted filter near one end of a bent connecting tube having two rubber-septum-capped entry ports at the bend. 2.0 g (5.6 mmol) of tetrakis(trimethylenedioxyboryl)methane (I) and a magnetic stirring bar were placed in the reaction vessel and the assembled apparatus was evacuated and filled with argon three times via one of the entry ports. 80 ml of anhydrous (from $LiAlH_4$) tetrahydrofuran was

injected, in which the solid (I) was partially soluble, and the suspension was stirred and cooled to −70°C with Dry Ice/acetone bath. 2 ml (3.2 mmol) of 1.6 M butyllithium in hexane was added dropwise in a few min from a syringe. With stirring continued, the mixture was kept at −70°C for 15 min and then allowed to warm to −10 to 0°C. For filtration, the apparatus was rotated appropriately (90°C) and vacuum was applied to the receiver flask while the argon pressure was maintained on the reaction vessel. The apparatus was kept cold with the aid of a Dry Ice/acetone soaked towel in order to prevent gum formation during the filtration. The collected white solid was washed with 10 ml of cold (∼0°C) tetrahydrofuran and dried at 0.1 Torr, 25°C, for 2 h, yield 0.87 g (99% based on butyllithium). A portion of the pyrophoric white powder II was transferred in a glove bag under argon and sealed in an evacuated ampoule for analysis. (Found: C, 43.15; H, 7.53; B, 10.95; Li, 1.90. $C_{10}H_{18}B_3LiO_6$ calcd.: C, 43.90; H, 6.63; B, 11.85; Li, 2.54%.) Another portion of the analyzed sample was dissolved in D_2O under argon. The NMR spectrum showed the peaks characteristic of 1,3-propanediol-O-d_2 at δ 3.67 (t, 4.08, OCH_2CH$_2$) and 1.77 (quintet, 2.00, CH$_2$C$\underline{H}_2$CH$_2$) with a small amount of contaminant at δ 1.0 ppm (m, 0.077, BC$_4$H$_9$) (actual curve recorded in the Ph. D. thesis of L.A.H.). If the contaminant were the B-butyl tetrakis(trimethylenedioxyboryl)methane anion (IV) it would amount to 3.4 mole %. Because the D_2O solution was cloudy, another sample of II was dissolved in methanol-d_4 to yield a clear solution and found to contain 9.6 mole % of the B-butyl contaminant calculated as IV, while in D_2O the apparent figure was 4.0 mole %.

^{11}B NMR of lithium tris(trimethylenedioxyboryl)methide (II)

A 1.01 g sample of II was stirred with 9.5 ml of anhydrous (from CaH$_2$) hexamethylphosphoramide for 2 h, yielding a light yellow solution with no visible undissolved solid. A portion of the solution was transferred by syringe to an argon-purged NMR tube containing a capillary of boron trifluoride etherate and the tube was evacuated and sealed. The ^{11}B NMR spectrum at 32.1 MHz consisted of a single broad peak 1.08 ppm downfield from the BF$_3$ etherate, and no other peaks were detected within 50 ppm to either side. (This spectral curve is recorded in the Ph. D. thesis of L.A.H.) Since the sample and reference peaks overlap, the spectrum of II was also taken without an internal reference to verify that it consists of a single peak.

Triphenyltin chloride and lithium tris(trimethylenedioxyboryl)methide (II)

In tetrahydrofuran. A 0.54 g (2 mmol) portion of the lithium salt II was stirred with 10 ml of tetrahydrofuran at 0°C, 0.76 g (2 mmol) of triphenyltin chloride was added, and the mixture was stirred at 25°C overnight. Workup as previously described [8] yielded 0.67 g of crude, 0.51 g (57%) of purified tris-(trimethylenedioxyboryl)triphenylstannylmethane (VI), identity confirmed by IR and NMR.

In hexamethylphosphoramide. 3.6 mmol of the lithium salt II was stirred 1 h with 18 ml of hexamethylphosphoramide. Approximately half the solid dissolved. The solution was added to 0.69 g (1.8 mmol) of triphenyltin chloride in 5 ml of tetrahydrofuran at 0°C and stirred overnight at 25°C. Distillation of the solvents followed by addition of ether precipitated 0.32 g (0.9 mmol) of

crude tetrakis(trimethylenedioxyboryl)methane (I). Concentration of the filtrate yielded an oil which crystallized on standing. After washing with methanol, the yield of crude bis(trimethylenedioxyboryl)bis(triphenylstannyl)methane (X) was 0.54 g (0.6 mmol), recrystallized from methanol/chloroform, 0.10 g. The identities of the products were confirmed by NMR and IR.

In dimethylsulfoxide-d_6. A 2.27 mmol portion of the lithium salt II was dissolved in 5 ml of DMSO-d_6, 0.85 g (2.27 mmol) of triphenyltin chloride was added, and the product precipitated immediately. After recrystallization from chloroform/ether, the yield of triphenylstannyltris(trimethylenedioxyboryl)-methane (VI) 0.68 g (50%). When undeuterated DMSO was used as solvent, only 4% of the tin derivative VI was obtained. When the lithium salt II was stirred 16 h in DMSO and then treated with triphenyltin chloride, a 32% yield of tris-(trimethylenedioxyboryl)methane (VIII) slightly contaminated with the triphenyltin compound VI was isolated.

Tris(trimethylenedioxyboryl)methane (VIII)

A solution of 9.0 g of tris(dimethoxyboryl)methane, $HC[B(OCH_3)_2]_3$ [4], in 30 ml of tetrahydrofuran was treated with 9 ml of 1,3-propanediol and 1 ml of boron trifluoride etherate and stirred 16 h. Removal of most of the solvent under vacuum precipitated 8.0 g (77%) of VIII, which was sublimed under vacuum, m.p. 146-148°C. NMR (CDCl$_3$): δ 0.25 (s, 1, HCB$_3$), 1.87 (quintuplet, 6, CH$_2$CH$_2$CH$_2$), 3.95 (t, 12, OCH$_2$CH$_2$) (external TMS ref.); ^{11}B NMR, see Table 1. (Found: C, 44.86; H, 7.19; B, 11.75. C$_{10}$H$_{19}$B$_3$O$_6$ calcd.: C, 44.87; H, 7.15; B, 12.11%.)

Bromotris(trimethylenedioxyboryl)methane (XI)

3.6 mmol of the lithium salt II was isolated in the usual way, transferred to a Schlenk flask, and stirred with 10 ml of methylene chloride at −75°C while a solution of 0.2 ml (3.8 mmol) of bromine in 10 ml of methylene chloride was added over a period of 0.5 h. The mixture was warmed to 25°C and most of the solvent was removed under vacuum. The residue was treated with ether, which precipitated a light yellow air-sensitive solid. The solid was collected, dissolved in a small amount of chloroform, and recrystallized by adding ether, yield of XI 0.52 g (42%); sublimed at 180°C (0.1 Torr); m.p. 124-138°C (sealed capillary). NMR (CDCl$_3$): δ 1.93 (quintuplet, 6, CH$_2$CH$_2$CH$_2$), 4.05 (t, 12, -OCH$_2$); m/e 347 (C$_{10}$H$_{18}$^{11}B$_3$^{81}BrO$_6$$^+$) with isotopic satellites, strongest peak m/e 290. (Found: C, 33.99; H, 5.48; B, 8.86; Br, 23.01. C$_{10}$H$_{18}$B$_3$BrO$_6$ calcd.: C, 34.65; H, 5.23; B, 9.36; Br, 23.06%.)

Alkene-1,1-diboronic esters (XII) or (XIV)

2.0 g (5.6 mmol) of tetrakis(trimethylenedioxyboryl)methane (I) and 40 ml of anhydrous tetrahydrofuran were stirred under argon and cooled with a Dry Ice/acetone bath during the dropwise addition of 3.5 ml (5.6 mmol) of 1.6 *M* methyllithium in ether. Stirring was continued while the mixture was kept at −70°C for 15 min, warmed to between −10 and 0°C, and cooled below −60°C. A 5.6 mmol portion of the selected aldehyde or ketone in 10 ml of tetrahydrofuran was added and the mixture was stirred 0.5 h at −70°C and overnight at 25°C. (When the aldehyde was paraformaldehyde, the solid was added neat,

TABLE 2

ANALYTICAL DATA OF ALKENE-1,1-DIBORONIC ESTERS (XII) AND (XIV)

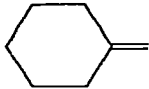| Aldehyde or Ketone	Crude Product		Analytical Sample	Analysis found (calcd.) (%)		
	Yield (%)	Purity (%)	m.p. or (b.p.) (°C)	C	H	B
Formaldehyde	66	98	68-70	48.95 (49.07)	7.35 (7.21)	10.90 (11.04)
Acetaldehyde	74	90	65-67	51.58 (51.51)	7.71 (7.69)	10.40 (10.30)
Acetone	84	97	98-99	53.88 (53.65)	7.79 (8.10)	9.53 (9.66)
Dichloroacetone	41		98-99.5	41.08 (41.03)	5.43 (5.51)	7.48[a] (7.39)
Butyraldehyde	82		(116/0.1 mm)	55 50 (55.54)	8.28 (8.47)	8 64 (9.09)
Hexaldehyde	93		(131/0.2 mm)	58.58 (58.71)	8.89 (9.10)	8.19 (8.13)
Cyclohexanone	90	97	108-109	59.34 (59.16)	8.32 (8.40)	8.16 (8.19)
Benzaldehyde	89	96	120-121.5	62.00 (61.84)	6.68 (6.67)	8.18 (7.95)
Acetophenone	72	96	75-76	63.00 (63.01)	7.00 (7.05)	7.64 (7.56)
Benzophenone	75	94	164-166	69.01 (69.03)	6.36 (6.37)	6.37 (6.21)

[a] Found: Cl, 24.09. Calcd.: 24.23.

the mixture was stirred and refluxed 2 h, stirred at 25°C overnight, and then treated with a few mg of galvinoxyl to inhibit polymerization during workup.) The solvent was removed under vacuum and the residue was treated with 10 ml of chloroform and 30 ml of ether, which caused precipitation of the white solid byproduct XIII. The solid was removed by filtration and the filtrate was concentrated under vacuum. The residue of XII or XIV was crystallized (if possible) by dissolving it in ether and adding pentane at −70°C with vigorous scratching of the flask. If this failed, the product was distilled under vacuum. The purity of the product was estimated in several cases by examining the ratio of the NMR integrals of the $OCH_2CH_2CH_2O$ group to those of other protons, and it was assumed that any excess of the former was due to impurities such as XIII. Yields, purities, melting or boiling points, and microanalyses of the products XII or XIV are listed in Table 2, and proton NMR spectra with tetramethylsilane as an internal reference are listed in Table 3. IR spectra generally showed a C=C absorption near 1600 cm^{-1}. (Selected NMR and IR curves are recorded in the Ph. D. thesis of L.A.H.)

5,5-Bis(trimethylenedioxyboryl)bicyclo[2.2.1]hept-2-ene (XV)

A solution of 2.21 g (11.1 mmol) of 1,1-bis(trimethylenedioxyboryl)ethene (XII, R = H) and 1.03 ml (12.8 mmol) of freshly distilled cyclopentadiene in 20 ml of chloroform was refluxed 16 h and concentrated under vacuum. The residue was crystallized from ether/pentane at −75°C and recrystallized from ether/ pentane to yield 0.92 g (31%) of the adduct XV; m.p. 78-80°C. NMR (CDCl₃); δ 5.70 (m, 2, CH=CH), 3.76 (m, 8, OCH₂), 1.77 (m, 5, CH₂CH₂CH₂ and one

TABLE 3

60 MHz ^{1}H NMR SPECTRA OF ALKENE-1,1-DIBORONIC ESTERS (XII) AND (XIV)

RR'C=	OCH$_2$CH$_2$CH$_2$O δ(ppm)		—CH=C of (XII)^c δ(ppm)	R protons δ(ppm)
	OCH$_2$^{a}	CCH$_2$C^b		
H$_2$C=	4.08	1.97	6.46 (s)^d	
CH$_3$CH=	4.04	1.9	6.85 (m)	1.87 (d, J ~ 6 Hz)
(CH$_3$)$_2$C=	4.00	1.9		near 1.9 (s)
(ClCH$_2$)$_2$C=	4.05	1.98		4.40 (s)
CH$_3$CH$_2$CH$_2$CH=	4.04	2.0	6.70 (t)	1.36 (m), 0.90 (m)
CH$_3$(CH$_2$)$_4$CH=	4.03	2.0	6.95 (t, J = 7 Hz)	1.33 (m), 0.92 (m)
⬡=	4.10	1.97		2.36 (m), 1.60 (m)
PhCH=	3.80, 4.08	1.72, 1.98	(7.34)^e	7.34
Ph(CH$_3$)C=	4.00	1.90		7.30, 2.30 (s)
Ph$_2$C=	3.84	1.80		7.24 (s)

^{a} Triplet, J 6 Hz, except that unsymmetrical RR'C= usually leads to two overlapping triplets. ^{b} Quintet, or overlapping quintets. ^{c} s = singlet, d = doublet, t = triplet, m = multiplet (unresolved). ^{d} ~ 8 Hz wide at half-height. ^{e} The vinyl peak is coincident with the phenyl.

bicycloheptyl CH), and multiplets due to bicycloheptyl protons at 2.84 (1), 2.64 (1), 1.33 (1), and 1.13 (2). (Found: C, 59.37; H, 7.76; B, 8.44. C$_{13}$H$_{20}$B$_2$O$_4$ calcd.: C, 59.61; H, 7.70; B, 8.26%.)

5,5-Bis(trimethylenedioxyboryl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene

A solution of 4.01 g of 1,1-bis(trimethylenedioxyboryl)methane (XII, R = H), 5.8 ml of perchlorocyclopentadiene, and 5 ml of toluene was refluxed 16 h and concentrated under vacuum. The product (7.4 g) was recrystallized from ether/chloroform and sublimed; m.p. 193-194°C. NMR (CDCl$_3$): δ 4.05 (2 overlapping triplets, 8, OCH$_2$), 2.58 (pair of doublets, 2, bicycloheptyl CH$_2$), 1.92 (quintuplet, 4, CH$_2$CH$_2$CH$_2$). (Found: C, 33.45; H, 3.02; B, 4.51; Cl, 45.49. C$_{13}$H$_{14}$B$_2$O$_6$Cl$_6$ calcd.: C, 33.32; H, 3.01; B, 4.61; Cl, 45.39%.)

Phenylacetic acid from 1,1-bis(trimethylenedioxyboryl)-2-phenylethene (XII, R = Ph)

The standard preparation of alkene-1,1-diboronic esters (XII) was followed on a 5.6 mmol scale using benzaldehyde, except that instead of concentrating the solution and isolating the product, the mixture was treated with 5 ml of 3M aqueous sodium hydroxide and 5 ml of 30% hydrogen peroxide at 25°C, refluxed for 1 h, cooled, and treated with aqueous hydrochloric acid. The organic phase which formed was separated, the aqueous phase was extracted with ether, the combined organic phase was dried over magnesium sulfate, and the solution was concentrated to yield 0.69 g of a mixture containing phenylacetic acid and propanediol in a molar ratio of 1 to 0.3 by NMR analysis. After extraction from ether into 15 ml of 5% aqueous sodium bicarbonate and acidification with hydrochloric acid, 0.45 g (60%) of phenylacetic acid crystallized at 0°C, and its identity was checked by IR.

Phenylacetone from 1,1-bis(trimethylenedioxyboryl)-2-phenylethene (XII, R = Ph)

A 1.0 g (3.67 mmol) sample of 1,1-bis(trimethylenedioxyboryl)-2-phenyl-ethene (XII, R = Ph) in 20 ml of anhydrous tetrahydrofuran at 5 °C was stirred under argon during the addition of 4.6 ml (7.3 mmol) of 1.6M methyllithium in ether. The mixture was stirred 1 h at 5°C and 0.93 g (3.67 mmol) of iodine in 10 ml of tetrahydrofuran was added dropwise. About half of the iodine reacted immediately during the addition. After stirring for an additional 1 h, 10 ml of 3M sodium hydroxide was added, followed by 10 ml of 30% hydrogen peroxide, which caused an exothermic reaction. Addition of a measured amount of bicyclohexyl as an internal standard followed by gas chromatography indicated a 30.6% yield of phenylacetone, which had the same retention time as an authentic sample.

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