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LITHIUM BIS(ETHYLENEDIOXYBORYL)METHIDE AND ITS REACTIONS WITH CARBONYL COMPOUNDS AND WITH THE CHLOROTRIPHENYL DERIVATIVES OF GERMANIUM, TIN AND LEAD

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Summary

Transesterification of tris(dimethoxyboryl)methane, $HC[B(OCH_3)_2]_3$, with ethylene glycol yielded tris(ethylenedioxyboryl)methane (I), $HC(BO_2C_2H_4)_3$ which with methyllithium in THF at —70°C precipitated lithium bis(ethylenedioxyboryl)methide (II), $Li^+ HC(BO_2C_2H_4)_2^-$. Reaction of II with Ph_3MCl, where M = Ge, Sn, or Pb, gave $Ph_3MCH(BO_2C_2H_4)_2$. The analogous 1,3-propanediol ester, $Li^+HC(BO_2C_3H_6)_2^-$, yielded $Ph_3MCH(BO_2C_3H_6)_2$. Treatment of $Ph_3SnCH(BO_2C_2H_4)_2$ with MeLi followed by Ph_3SnCl gave $(Ph_3Sn)_2CHBO_2C_2H_4$, showing that one B and one Sn atom are sufficient to stabilize a carbanion. Reaction of II with aldehydes gave high yields of 1-alkene-1-boronic esters, $RCH{=}CHBO_2C_2H_4$, with unexpectedly high stereoselectivity, 90—100% *trans* by NMR analysis. Aqueous work-up of these boronic esters yielded the boronic acids, $RCH{=}CHB(OH)_2$, which crystallized as the pure *trans* isomers. Ketones react with II in an analogous manner. The reaction with acetophenone was not stereospecific. Functional group compatibility has been demonstrated in condensations of II with 1,3-dichloroacetone, cinnamaldehyde, *p*-nitrobenzaldehyde, and *p*-dimethylaminobenzaldehyde. The *trans* geometry of the major isomer of $CH_3CH{=}CHBO_2C_2H_4$ was proved by *B*-butylation with butyllithium followed by rearrangement with iodine and base to form *cis*-2-heptene, a sequence of known stereochemistry, and analogous structure proofs were carried out with *cis*-$CH_3CH{=}CHBO_2C_2H_4$ and *trans*-$C_6H_5CH{=}CHBO_2C_2H_4$.

Introduction

Boron-substituted carbanions show great promise as synthetic intermediates. We have previously found that tris(dialkoxyboryl)methide ions, $[(RO)_2B]_3C^-$, react readily with R'_3MCl, where M = Sn, Pb, Ge, or Si, to form $[(RO)_2B]_3CMR'_3$ [1—3], or with aldehydes or ketones, R'COR", to form alkene-1,1-diboronic esters, $[(RO)_2B]_2C{=}CR'R''$ [4,5]. Cyclic boronic esters generally give better

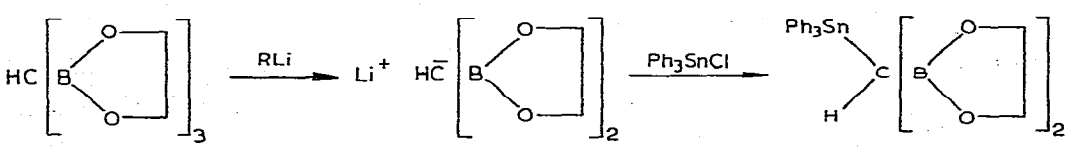
yields of more easily purified products than acyclic boronic esters [2,3,5], and the use of a cyclic ester has permitted the isolation of the lithium salt of a boron-substituted carbanion, lithium tris(trimethylenedioxyboryl)methide [5,6].

Two boronic ester groups have been shown to provide sufficient stabilization of a carbanion to permit its formation. Tris(dimethoxyboryl)methane has been converted to bis(dimethoxyboryl)methide ion, $[(CH_3O)_2B]_2CH^-$, and condensed with benzaldehyde to form the β-styreneboronic ester in low yield [7], or alkylated with various alkyl halides, RX, to form $[(CH_3O)_2B]_2CHR$ in yields up to 42% [8]. We undertook the present investigation in the hope that the use of cyclic boronic esters and other recent improvements in our techniques would result in much improved yields and real synthetic utility.

A preliminary account of part of this work, together with its extension to the homologation of aldehydes, has been published elsewhere [9]. Another objective of the present work was to find a route to a 2-phenylethane-1,1-diboronic ester for subsequent conversion to boron compounds of possible biological interest. This has been accomplished by alkylation of a diborylmethide ion with benzyl bromide, but the reasons for choosing this route are complex and the details will be published separately [10].

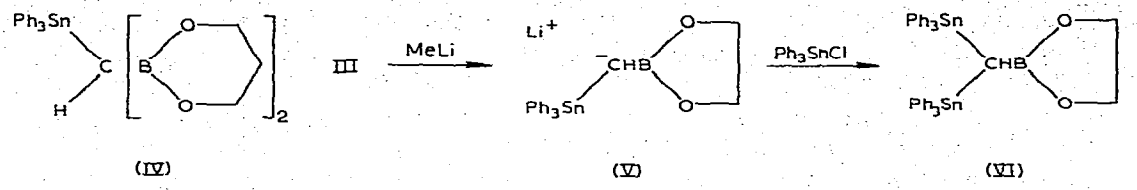
Results

Transesterification of tris(dimethoxyboryl)methane [7,11], $HC[B(OCH_3)_2]_3$, with ethylene glycol in tetrahydrofuran yielded tris(ethylenedioxyboryl)methane (I). Treatment of a suspension of I in THF, in which I is slightly soluble, with methyllithium or butyllithium at −75° C resulted in immediate precipitation of lithium bis(ethylenedioxyboryl)methide (II). Since the reaction of the analogous lithium tris(trimethylenedioxyboryl)methide with triphenyltin chloride gives a good yield of easily crystallized product [2], we used the reaction of II with triphenyltin chloride to check the efficiency of formation of II. The yield of triphenylstannylbis(ethylenedioxyboryl)methane (III) was 77%.



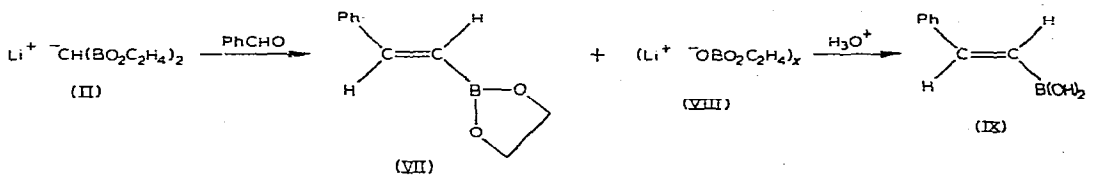
(I) (II) (III)

The propanediol ester analog of I, tris(trimethylenedioxyboryl)methane [5], was similarly converted to lithium bis(trimethylenedioxyboryl)methide and reacted with triphenyltin chloride to form the analogous derivative IV in 68% yield. Triphenylgermanium and triphenyllead chloride were also reacted with both lithium salts to form derivatives analogous to III and IV. These were formed in lower yields than the tin compounds, but series III was consistently favored over series IV. A further extension of this type of chemistry was the successful conversion of the tin compound III to the carbanion stabilized by one boron and one tin atom (V) and finally to bis(triphenylstannyl)ethylenedioxyborylmethane (VI).



(IV) (V) (VI)

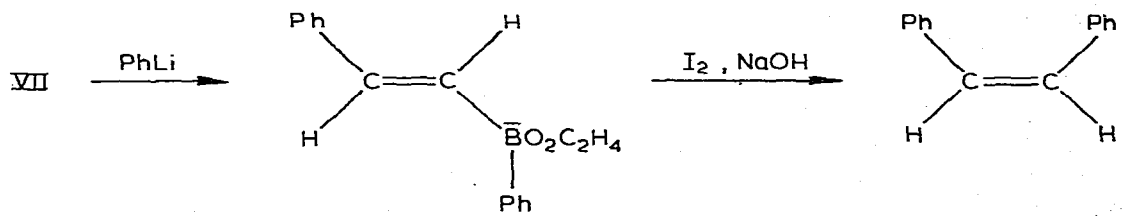
The reaction of lithium bis(ethylenedioxyboryl)methide (II) with carbonyl compounds was first examined with benzaldehyde. The boronic ester product, *trans*-1-ethylenedioxyboryl-2-phenylethene (VII), was separated from the by-product lithium salt (VIII) by extraction with diethyl ether, in which VII is readily soluble and VIII is insoluble. The boronic acid product, β-styreneboronic acid or *trans*-2-phenylethene-1-boronic acid (IX), was obtained by treating the reaction mixture with aqueous acid and extracting with ether.



(II) (VII) (VIII) (IX)

Evidence that the β-styreneboronic ester (VII) is the *trans* isomer was provided by the NMR spectrum. The doublet due to the proton α to boron appeared at δ 6.12 ppm, J 18 Hz. (The β-proton absorption is partially hidden by the phenyl group.) The doublet at δ 5.53 ppm, J 16 Hz, which Pasto and coworkers assigned to the *cis* isomer [12], was absent. A crude sample of the bronic acid IX which had not been recrystallized similarly showed only the α-proton doublet at δ 6.11 ppm, J 18 Hz, due to the *trans* isomer. If as much as 1—2% of the *cis* isomer had been present, it should have been detected. We have also prepared a mixture of the *cis* and *trans* isomers of dimethyl β-styreneboronate, $PhCH{=}CHB(OCH_3)_2$, as part of another investigation [10], and observed the α-proton doublets of the *cis* at δ 5.50 and the *trans* at δ 6.10 ppm.

The *trans* geometry of the β-styreneboronic ester VII was further proved by its reaction with phenyllithium followed by rearrangement of the *B*-phenyl intermediate with iodine and alkali, which gave *cis*-stilbene in up to 65% yield.



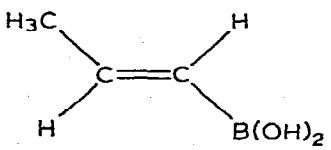
Zweifel and coworkers have carried out analogous rearrangements on *trans*-alkenylboranes from hydroboration of acetylenes and have shown that the products are stereospecifically the *cis*-alkenes, and they have provided a reasonable mechanistic interpretation [13,14].

Other aromatic aldehydes which were condensed with the lithium salt II included furfural, *p*-dimethylaminobenzaldehyde, cinnamaldehyde, and *p*-nitrobenzaldehyde. Yields of $ArCH{=}CHBO_2C_2H_4$ or $ArCH{=}CHB(OH)_2$ were generally about 40%, though Moody has repeated the reaction with furfural and ob-

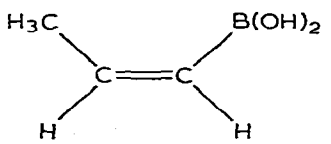
tained a high yield [15]. The reaction with *p*-nitrobenzaldehyde (34%) gave a lot of dark, insoluble by-product. The NMR spectra of all of the arylethene-boronic esters were consistent with *trans* geometry.

The aromatic ketones benzophenone and acetophenone both gave good yields of condensation products with II. The NMR spectrum indicated that the boronic acid from acetophenone, $PhC(CH_3)=CHB(OH)_2$, consisted of a *cis—trans* mixture. No attempt was made to separate the isomers.

Aliphatic aldehydes also condensed with II to give good yields of the alkene-1-boronic acids, $RCH=CHB(OH)_2$, where R is n-C_3H_7 to n-C_7H_{15}. Again, the NMR spectra indicated that the products were mainly *trans*. Small peaks due to the downfield half of the α-proton multiplet of the *cis* isomer were generally visible near 320 Hz (60 MHz spectra) in samples of the liquid ethylene glycol esters, $RCH=CHBO_2C_2H_4$, indicating the *cis* isomer content to be about 5—10%, but no evidence for *cis* isomer was seen in crystalline samples of the boronic acids. The assignment of the NMR absorption is based on the 1-propene-1-boronic acids X and XI and their ethylene glycol esters, which were chosen for detailed stereochemical study because of their structural simplicity.



(X)



(XI)

A mixture of both isomers X and XI was obtained from the reaction of 1-propenylmagnesium bromide with trimethyl borate [16] followed by aqueous work-up and extraction with ether. The less soluble *trans*-1-propene-1-boronic acid X was separated by fractional crystallization from ether, and the more soluble *cis* isomer XI concentrated to a proportion of about 80% in the mother liquors.

The α-proton of the *trans* isomer X was observed as a doublet of quartets in the NMR, δ 5.44 ppm, J 18 and 1.5 Hz. The α-proton of the *cis* isomer appeared at δ 5.34 ppm, J 14 and 1.5 Hz (in deuteroacetone). The downfield halves of these multiplets provided the best separated peaks for analyzing mixtures, though all of the protons showed significant differences. Even the $B(OH)_2$ peaks are separated in deuteroacetone, indicating that hydroxyl group exchange between boronic acid groups is slow on the NMR time scale, unless a few per cent of D_2O are added, which leads to a single DOH peak. The ethylene glycol esters of X and XI showed the expected analogies to the free boronic acids in their NMR spectra.

The crude boronic acid derived from the reaction of acetaldehyde with II was found to contain 7% *cis* isomer XI by NMR analysis. A sample of the ethylene glycol ester isolated directly from the reaction of acetaldehyde and II showed a *cis* content of about 5%.

Chemical proof of the *trans* geometry of X was provided by treatment of its ethylene glycol ester with butyllithium followed by rearrangement with iodine and alkali, which gave a mixture of products including about a 30% yield of *cis*-2-heptene, identified by comparison of its NMR spectrum in the vinylic proton

region with that of an authentic sample [17]. Other products appeared to include 1-iodopropene and were not separable by small-scale simple distillation. Similar treatment of 80% *cis* isomer XI ethylene glycol ester yielded a mixture containing 2-heptene which was predominantly *trans*. These results, like the conversion of *trans*-β-styreneboronic ester to *cis*-stilbene described in an earlier paragraph, are in accord with the observations of Zweifel and coworkers [13,14].

Aliphatic ketones condensed with II included acetone, cyclohexanone, and 1,3-dichloroacetone. The boronic acids from the latter two ketones were not obtained in pure condition by recrystallization from ether. Moist chloroform proved to be effective. This observation was made after most of the rest of this study had been completed. Several alkeneboronic acids were found to be only moderately soluble in chloroform, suggesting that this solvent may be generally useful for the recrystallization of the boronic acids.

Discussion

Two features of the condensation of the diborylmethide anion II with carbonyl compounds have considerable potential synthetic utility. These are, first, the high selectivity of II for aldehydes and ketones even in the presence of other groups that are sensitive to nucleophiles and, second, the high stereoselectivity in the conversion of aldehydes to *trans*-1-alkene-1-boronic esters.

The selectivity of the diborylmethide anion II is tested particularly severely by *p*-nitrobenzaldehyde. The 34% yield of *p*-nitro-β-styreneboronic acid implies some selectivity in favor of the aldehyde group, inasmuch as a purely statistical attack on the aldehyde and nitro groups would approach a 25% yield as an upper limit if attack on the second group of the molecule is as rapid as on the first.

The selectivity of II is tested in a synthetically more useful fashion by 1,3-dichloroacetone. In spite of the reactive α-chloroketone function, which might undergo displacement, enolization by proton loss, or enolization by chlorine loss, and in spite of the reactive allylic chlorines in the product, the crude yield of $(ClCH_2)_2C{=}CHB(OH)_2$ was 65%, and the NMR spectrum indicated that this was the major constituent, even though considerable loss was suffered on crystallization. Other reactions of boron-substituted carbanions with α-haloketones have also yielded carbonyl group condensation products [4,8].

In other work, we have established that boron-substituted carbanions will react selectively with ketones or aldehydes in the presence of esters or carbon—carbon double bonds [4,5,9]. The rather mediocre yield of $PhCH{=}CHCH{=}CHB(OH)_2$ from the reaction of II with cinnamaldehyde suggests that α,β-unsaturation may cause problems, though mesityl oxide worked well [9], and further exploration will be required in order to determine the limitations. We anticipate no difficulty with functional groups that are normally compatible with carbanions, though we have not yet tested ketals, silyl ethers, and other common protected functions.

The stereoselectivity of the condensation of II with aldehydes makes this reaction a useful alternative to hydroboration for making *trans*-1-alkene-1-boronic acids, which have already been shown to undergo stereospecific conversions to *trans*-1-iodoalkenes [18] and *cis*-1-bromoalkenes [19]. Zweifel and coworkers have shown that *trans*-alkenyldialkylboranes react with iodine and alkali to form

cis-alkenes [13,14], and we have described the conversion of *trans*-1-alkene-1-boronic esters to *B*-alkyl derivatives followed by rearrangement (see Results). Our yields in the migrations of *n*-butyl groups were not good. This is consistent with the finding by Zweifel and Fisher that the migratory aptitude of a methyl group in these reactions is very low [20], and secondary alkyl groups migrate preferentially. Since secondary alkyl groups do migrate in good yields [13,14] and the *B*-alkylation of boronic esters by Grignard and other organometallic reagents is generally applicable [21], it is clear that *trans*-1-alkene-1-boronic acids are potentially useful sources of some types of *cis*-alkenes, RCH=CHR′, at least where R′ is secondary or, from our present synthesis of *cis*-stilbene, aryl. However, much development work remains in order to find general and optimum conditions for this *cis*-alkene synthesis.

The choice between hydroboration and the condensation of an aldehyde with II as routes to *trans*-1-alkene-1-boronic acids will depend on several factors. For simple structures that can be derived from readily available acetylenes, hydroboration is most economical. However, condensations with II become advantageous if there is unsaturation elsewhere in the molecule or if a one-carbon chain extension of a structurally complex carbonyl compound is needed. The condensation of II with ketones yields alkeneboronic acids of the general formula $R_2C{=}CHB(OH)_2$. These cannot be made by hydroboration, though in some simple cases they can be made from $R_2C{=}CHBr$ by the Grignard route. The condensation of II with unsymmetrical ketones is not stereoselective. Acetophenone yielded about a 3 : 2 mixture of isomers, a smaller ratio than might have been expected from the relative stereoselectivities of the reactions of II with benzaldehyde and acetaldehyde. The sterically favored isomer should be the one with phenyl *trans* to the boronic acid group, and this assignment is consistent with the trends in the NMR chemical shifts (see Experimental), but the isomers were not separated and this structure assignment is tentative.

Our most careful estimate based on NMR data for the *cis* content of crude 1-propene-1-boronic acid from acetaldehyde and II was 7%, but a more conservative upper limit would be about 10%. For synthetic purposes, boronic acids usually crystallize easily and the *cis* isomer disappears in one recrystallization. We had no problems with air sensitivity as long as the boronic acids were kept slightly moist to avoid anhydride formation.

The work on the germanium, tin and lead compounds reported here is a straightforward extension of our previous work [1,2], but the carbanion V stabilized by only one boronic ester group and one triphenyltin group represents a new minimum of stabilizing substituents for this series. One boronic ester group and two triphenyltin groups have been shown to be sufficient to stabilize a carbanion [2], but we were unable to make the tris(triphenylstannyl)methide ion, $(Ph_3Sn)_3C^-$, by a deboronation route. Carbanions or perhaps covalently bonded alkyllithium compounds are known to be stabilized by a single dialkylboryl group, R_2B—[22—24], which may provide stronger carbon—carbon π bonding than the boronic ester group.

Experimental

Tris(dimethoxyboryl)methane

Tris(dimethoxyboryl)methane [7] was prepared by the improved procedure

previously described [11] with the following additional improvements. For distillation of the crude product, the distillation apparatus was constructed with no constrictions smaller than a 24/40 joint in the path of the distillate, and with less than 1 m of wide-bore tubing connecting the receiver via a Dry Ice trap to the pump. The crude product contains by-products which cause decomposition with evolution of volatile material which does not condense at —78°C and interferes with the distillation, sometimes resulting in total decomposition of the product, if these precautions are not taken. Use of a liquid nitrogen trap on one occasion yielded 10—20 ml of condensate, which on removal of the trap liquefied and boiled away under vacuum, without noticeable odor from the pump vented into the room. It was found best to distil the crude tris(dimethoxyboryl)-methane rapidly, then redistil moderately rapidly, b.p. 60—85°C (0.1 mm Hg), 25—30% yield.

Tris(ethylenedioxyboryl)methane (I)

A solution of 79.3 g (0.34 mol) of tris(dimethoxyboryl)methane in 150 ml of anhydrous tetrahydrofuran was stirred under argon at 0°C and 63.7 g (1.03 mol) of ethylene glycol was added. The product began to crystallize within a few min. The mixture was stirred 20—30 min, concentrated under vacuum, and heated to about 100°C to distil ethylene glycol and volatile by-products. After cooling, the solid residue was stirred with 150 ml of anhydrous ether, filtered, washed with 100 ml of ether, and sublimed at 150—170°C (0.02 mm Hg), yield 60.7 g (79%), m.p. 170—172°C, NMR ($CDCl_3$): δ 0.73 ppm (s, 1, $\underline{H}CB_3$), 4.21 (s, 12, $OC\underline{H}_2C\underline{H}_2O$). (Found: C, 37.44; H, 5.81; B, 14.59. $C_7H_{13}B_3O_6$ calcd: C, 37.27; H, 5.81; B, 14.38%.) The use of a highly purified sample of tris(dimethoxyboryl)methane led to an 85% yield of I.

Lithium bis(ethylenedioxyboryl)methide (II)

Procedure A. A solution of 11.3 g (50 mmol) of tris(ethylenedioxyboryl)-methane (I) in 250 ml of anhydrous tetrahydrofuran under argon was cooled with a Dry Ice/acetone bath, which caused crystallization of the I, and was stirred during the dropwise addition of 31.5 ml (50 mmol) of 1.6 *M* butyllithium in hexane, which resulted in formation of a slurry of precipitated lithium bis(ethylenedioxyboryl)methide (II). The slurry was stirred 10 min at —78°C before use.

Procedure B. A suspension of 4.52 g (20 mmol) of I in 25 ml of tetrahydrofuran was treated with 13 ml of 1.6 *M* methyllithium in ether under the same conditions as described for Procedure A.

Procedure C. An 11.5 mmol sample of I was dissolved in 10 ml of dichloromethane, 10 ml of tetrahydrofuran was added, and the mixture was treated with 12 mmol of 1.6 *M* methyllithium as described for procedure A, except that the slurry was stirred 0.5—2.5 h at —78°C before use.

Triphenylstannylbis(ethylene- and trimethylene-dioxyboryl)methane (III and IV) and their germanium and lead analogs

Lithium bis(ethylenedioxyboryl)methide (II), Procedure A, was stirred with 19.3 g (50 mmol) of triphenyltin chloride and allowed to warm to 25°C. After stirring overnight, the solvent was distilled under vacuum, the residue was stirred

with 100 ml of ether and filtered under argon, and the solid was stirred with 100 ml of chloroform and filtered to remove lithium salts. The filtrate was concentrated to 25 ml and 100 ml of ether was added to precipitate III, which was cooled to 0°C before filtration. The analytical sample was recrystallized from chloroform/ether. The use of tris(trimethylenedioxyboryl)methane [5] in place of I led to IV. The germanium and lead analogs were similarly prepared. Yields and other data are given in Table 1.

Bis(triphenylstannyl)ethylenedioxyborylmethane (VI)

Procedure A for the preparation of II was modified by using 5.0 g of triphenylstannylbis(ethylenedioxyboryl)methane (III) in place of I, 100 ml of tetrahydrofuran, and 6 ml of 1.6 *M* methyllithium to form the lithium salt V. Reaction with triphenyltin chloride under the conditions described for the preparation of III followed by recrystallization of the product from chloroform/methanol yielded 47% of VI, m.p. 121—123°C, NMR ($CDCl_3$): δ (ppm) 1.10 (s, 1, $Sn_2C\underline{H}B$), 3.70 (s, 4, $OC\underline{H}_2C\underline{H}_2O$), 7.20 (m, 30, $C_6\underline{H}_5$). (Found: C, 59.49; H, 4.66; B, 1.50; Sn, 30.18. $C_{39}H_{35}BO_2Sn_2$ calcd.: C, 59.75; H, 4.47; B, 1.38; Sn, 30.31%.)

1-Alkene-1-boronic acids

A 20 mmol portion of the aldehyde or ketone was added to 20 mmol of lithium bis(ethylenedioxyboryl)methide II prepared by Procedure B (or 10 mmol of aldehyde or ketone was added to 11.5 mmol of II prepared by Procedure C in more recent work). The mixture was allowed to warm to 25°C and stirred under argon 2—4 h. The solvent was distilled (vacuum) and the residue was stirred with water (50 ml) or dilute phosphoric acid (no difference in results was noted) and the solution was extracted with ether. Concentration of the

TABLE 1

TRIPHENYLMETALBIS(DI- AND TRI-METHYLENEDIOXYBORYL)METHANES, $Ph_3MCH[BO_2(CH_2)_n]_2$

M of Ph_3M	*n* of $BO_2(CH_2)_n$	Yield (%)	M.p. (°C)	NMR, δ [a] (ppm) $MC\underline{H}B_2$	Analysis found (calcd.) (%) C	H	B	M
Ge	2	42	128—129	1.18	59.99 (60.23)	5.41 (5.24)	4.77 (4.72)	15.71 (15.84)
Sn	2	77	140—141	0.98	54.68 (54.73)	4.87 (4.76)	4.24 (4.28)	23.48 (23.54)
Pb	2	72	144—145	1.40	46.67 (46.56)	4.10 (4.05)	3.87 (3.64)	34.70 (34.96)
Ge	3	36	93—94	0.80	61.47 (61.60)	5.72 (5.76)	4.56 (4.44)	14.80 (14.93)
Sn	3	68	126—128	0.68	56.41 (56.36)	5.41 (5.26)	4.06 (4.06)	22.46 (22.30)
Pb	3	62	115—116	1.15	48.24 (48.32)	4.46 (4.51)	3.79 (3.48)	33.10 (33.38)

[a] External tetramethylsilane reference; $CDCl_3$. All six compounds showed phenyl at δ 7.30 ppm. The ethylene glycol esters showed a singlet at δ 3.75, the 1,3-propanediol esters a triplet at δ 3.60 and a quintet at δ 1.35 ppm.

ether phase under vacuum yielded a crystalline residue of the boronic acid, which was dried to constant weight under a slow stream of argon. Crude yields of 60% and above in Table 2 are generally based on this isolation procedure, which generally yielded fairly pure boronic acids based on NMR analysis. The yield of product from cyclohexanone was duplicated when the boronic acid was crystallized from methanol/water, and the good yield of product from acetophenone is also from methanol/water. Yields of 50% and below (Table 2) are based on material crystallized from ether with considerable loss. Analytical samples were recrystallized from ether, but several failures to obtain pure samples were encountered. On reinvestigation, cyclohexylidenemethaneboronic acid and 3-chloro-2-(chloromethyl)propene-1-boronic acid were successfully recrystallized from chloroform moistened with a drop of water. 2-Phenylpropene-1-boronic acid was recrystallized from dichloromethane/2,2,4-trimethylpentane. Analytical samples were dried very briefly, usually a few min under vacuum, except that $(ClCH_2)_2C{=}CHB(OH)_2$ dehydrated too easily to survive even that mild treatment and was successfully dried in air 20—30 min (25°C). Crude yields, melting points of purified samples, and NMR data are summarized in Table 2, and elemental analyses are listed in Table 4.

1-(Ethylenedioxyboryl)-1-alkenes (Ethylene glycol esters of alkeneboronic acids)

The reaction of the aldehyde or ketone with II was carried out as described in the preceding paragraph, but after the solvent was distilled the residue was

TABLE 2

ALKENEBORONIC ACIDS RR'C=CHB(OH)$_2$ FROM CARBONYL COMPOUNDS RCOR' AND LiCH(BO$_2$C$_2$H$_4$)$_2$ (II)

R (*trans* to B)	R'	Yield (%)	M.p. (°C)	NMR (CD_3SOCD_3): δ (ppm), splitting, (*J* (Hz)) [a]		
				=CHB [b]	R' [b]	R
CH_3	H	50—67	72—75	5.34	6.46	1.77d of d's (6, 1.5)
$CH_3(CH_2)_2$	H	68	79—81	5.32	6.45	0.88m, 1.38m, 2.05m
$CH_3(CH_2)_4$	H	81	88—90	5.30	6.46	0.88m, 1.3m, 2.0m
$CH_3(CH_2)_6$	H	82	67—68	5.30	6.44	0.85m, 1.27m, 2.05m
α-Furyl	H	43	133—135	5.93	7.12	6.53m, 7.67m (unresolved)
C_6H_5	H	87	165—166 [c]	6.11	7.28	7.4m
p-$O_2NC_6H_4$	H	34	223—225	6.37	7.40	7.74d, 8.23d (9)
$C_6H_5CH{=}CH$	H	41	131—135 (dec.)	5.88	see R	7.0—7.6m
CH_3	CH_3	65	81—82 [d]	5.05	1.88s	1.77d(1)
$ClCH_2$	$ClCH_2$	60	70—72.5	5.77	4.63s	4.35s
$-CH_2CH_2CH_2CH_2CH_2-$		84	92—94 (dec.)	4.93	see R	1.49m, 2.10m, 2.44m
C_6H_5	CH_3 } [e]	80	111—118 (dec.)	6.05	7.6m	2.63s } [e]
CH_3	C_6H_5 }			5.80	2.42s	7.6m }

[a] Internal reference provided by CD_3SOCD_2H, δ 2.52 ppm [25]. The $B(OH)_2$ peaks were generally observed as broad singlets between δ 6.2 and 7.8 ppm, subject to broadening and shifting by water. [b] Where R' = H, the *trans*-vinyl proton *J* 18 ± 1 Hz. Smaller splittings by R were often superimposed. [c] Lit. m.p. 168—169°C [7], 163—164°C [26]. [d] Lit. m.p. 84—86°C [27]. [e] Mixture of *cis—trans* isomers, approx. ratio 3 : 2, first set of NMR peaks listed is the more abundant, structure assignment uncertain. NMR solvent $CDCl_3$, $B(OH)_2$ broad and unobserved.

TABLE 3

1-(ETHYLENEDIOXYBORYL)-1-ALKENES $RR'C{=}CHBO_2C_2H_4$ FROM RCOR' AND $LiCH(BO_2C_2H_4)_2$ (II)

R (*trans* to B)	R'	Yield (%)	M.p. (°C)	NMR ($CDCl_3$ or CCl_4): δ (ppm), splitting, (*J* (Jz))			
				=CHB [a]	R' [a]	R	OCH_2
CH_3	H	15	liquid	5.36	6.60	1.90 (6.5, 1.5)	4.29
$CH_3(CH_2)_4$	H		oil	5.31	6.55	0.88, 1.30, 2.15m's	4.10
α-Furyl	H	27	69	5.86	7.04	6.27, 7.28m's, 2H:1H	4.07
C_6H_5	H	67	44	6.12	7.4	7.3m	4.11
p-$O_2NC_6H_4$	H	11	175—176	6.34	7.48	7.63, 8.24d's (9)	4.34
p-$(CH_3)_2NC_6H_4$	H	38	146—147	5.95	7.41	6.69, 7.45d's (9); Me_2N, 3.00	4.28
$C_6H_5CH{=}CH$	H	37	115—117	5.64	see R	6.8—7.3m	4.22
C_6H_5	C_6H_5	72	56—58	5.85	7.13	7.13	3.86
$-CH_2CH_2CH_2CH_2CH_2-$			oil	5.00	see R	1.53, 2.2, 2.5m's	4.15

[a] Where R' = H, the *trans*-vinyl proton coupling constant *J* 18 ± 1 Hz, and smaller splittings by R were seen where expected.

treated with ether to extract the ethylene glycol boronic ester from the insoluble lithium borate salt VIII. The solution was filtered under argon, concentrated, and cooled with Dry Ice and/or treated with pentane to initiate crystallization. Only aryl-substituted boronic esters crystallized, and distillation of alkyl-substituted boronic esters failed to remove impurities, probably including substantial amounts of unchanged tris(ethylenedioxyboryl)methane (I) based on the NMR spectrum of a distilled sample of 1-(ethylenedioxyboryl)-1-heptene. Yield, m.p., and NMR data are listed in Table 3 and elemental analyses of those esters successfully purified are included in Table 4.

cis- and trans-1-Propene-1-boronic acids from the Grignard reagent

1-Propenylmagnesium bromide was reacted with trimethyl borate as previously described [16], but instead of extracting with butanol to make the butyl ester [16], ether was used to extract the boronic acids. Partial concentration of the ether solution, which was kept saturated with water, led to crystallization of *trans*-1-propene-1-boronic acid (X), shown by NMR to be the same as X prepared from acetaldehyde and II. The progress of the separation was monitored by NMR. Attempts to crystallize the *cis* isomer preferentially from water or 2-propanol/water yielded crystals that were relatively rich in *trans* isomer. Combined residues from mother liquors estimated to be 80% *cis* were recrystallized from water without significant change in the isomer ratio, and this was used for the analytical sample (Table 4). The m.p. of this mixture was not determined but appeared to be considerably lower than that of the *trans* isomer (75°C). The NMR spectra of both isomers were taken in deuteroacetone with CD_3COCD_2H at δ 2.06 ppm [25] as the internal reference: *trans*-X, δ (ppm) 1.77 (doublet of doublets, J 6.2 and 1.5 Hz, 3, $C\underline{H}_3$), 5.44 (d of quartets, J 18 and 1.5 Hz, 1, $=C\underline{H}B$), 6.60 (d of quartets, J 18 and 6.0 Hz, 1, $CH_3C\underline{H}=$), 6.66 (broad s, 2, $B(OH)_2$); *cis*-XI, δ (ppm) 1.89 (d of d's, J 6.7 and 1.5 Hz, 3, $C\underline{H}_3$), 5.34 (d of quartets, J 14 and 1.5 Hz, 1, $=C\underline{H}B$), 6.41 ± 0.1 (m of broadened and overlapping peaks, J 7 and, presumably, 14, 1, $CH_3C\underline{H}=$), 6.77 (broad s, 2, $B(O\underline{H})_2$). The NMR spectrum of the *trans* isomer in deuterodimethyl sulfoxide is included in Table 2.

cis- and trans-1-(Ethylenedioxyboryl)propene (Ethylene glycol esters of X and XI)

A 0.86 g portion of *trans*-1-propene-1-boronic acid (X) was stirred with 1 ml of ethylene glycol and 15 ml of ether. The ether phase was decanted, the ethylene glycol phase was extracted with additional ether, the combined ether phase was treated with a second portion of ethylene glycol, the ether phase was concentrated, and the residue was treated with pentane and filtered to remove the remaining ethylene glycol. The pentane was evaporated and the residue (0.62 g) appeared to be pure *trans*-1-(ethylenedioxyboryl)propene on NMR examination. The *cis*-isomer was similarly prepared on a larger scale from 80% *cis*-1-propene-1-boronic acid and distilled through a packed column, b.p. 132—135°C, without separation of the *trans* isomer. The elemental analysis is included in Table 4. The NMR spectra of both isomers were taken on neat samples with external tetramethylsilane as the reference: *trans*, δ ppm 1.47 (d of d's, J 6.5 and 1.7 Hz, 3, $C\underline{H}_3$), 3.80 (s, 4, $OC\underline{H}_2$), 5.09 (d of quartets, J 18 and 1.5 Hz, 1, $=C\underline{H}B$), 6.34 (d of quartets, J 18 and 6 Hz, 1, $CH_3C\underline{H}=$); *cis*, δ ppm 1.60 (d of d's,

TABLE 4

ELEMENTAL ANALYSES OF ALKENEBORONIC ACIDS $RR'C{=}CB(OH)_2$ AND ETHYLENE GLYCOL ESTERS $RR'C{=}CHBO_2C_2H_4$

R	R′	Acid (A) or Ester (E)	Found [a] (calcd.) (%)			
			C	H	B	other
trans-CH_3	H	A	42.09 (41.95)	8.14 (8.21)	12.36 (12.59)	
cis-CH_3	H [b]	A	42.09 (41.95)	8.15 (8.21)	12.69 (12.59)	
cis-CH_3	H	E	53.48 (53.65)	7.98 (8.10)	9.47 (9.66)	
$CH_3(CH_2)_2$	H [b]	A	53.00 (52.72)	9.90 (9.67)	9.21 (9.49)	
$CH_3(CH_2)_4$	H	A	59.09 (59.24)	10.46 (10.58)	7.39 (7.61)	
$CH_3(CH_2)_6$	H	A	63.43 (63.60)	11.19 (11.20)	6.16 (6.36)	
$ClCH_2$	$ClCH_2$	A	28.30 (28.46)	4.26 (4.18)	6.64 (6.40)	Cl 41.73 (42.00)
$-(CH_2)_5-$		A	60.17 (60.06)	9.41 (9.36)	7.69 (7.72)	
α-C_4H_3O (furyl)	H	A	52.05 (52.25)	5.07 (5.08)	7.71 (7.84)	
α-C_4H_3O (furyl)	H	E	58.66 (58.61)	5.43 (5.49)	6.80 (6.59)	
C_6H_5	H	E	68.92 (69.04)	6.38 (6.32)	6.37 (6.21)	
p-$O_2NC_6H_4$	H	E	54.75 (54.84)	4.64 (4.56)	4.72 (4.94)	N 6.38 (6.40)
p-$(CH_3)_2NC_6H_4$	H	E	66.24 (66.42)	7.34 (7.38)	5.09 (4.98)	N 6.23 (6.43)
$C_6H_5CH{=}CH$	H	A	68.90 (69.04)	6.10 (6.32)	6.20 (6.21)	
$C_6H_5CH{=}CH$	H	E	72.13 (72.13)	6.55 (6.50)	5.25 (5.40)	
C_6H_5	C_6H_5	E	76.78 (76.86)	6.14 (6.00)	4.39 (4.32)	
C_6H_5	CH_3	A	66.50 (66.73)	6.72 (6.84)	6.60 (6.67)	

[a] Galbraith Laboratories, Knoxville, Tenn. [b] All R′ = H compounds are *trans* except where *cis* is specified. The *cis*-$CH_3CH{=}CHB(OH)_2$ and its ester are 80% *cis*.

J 6.8 and 1.5 Hz, 3, $C\underline{H}_3$), 3.82 (s, 4, $OC\underline{H}_2$), 5.01 (d of quartets, J 13.5 and 1.5 Hz, 1, $=C\underline{H}B$), 6.13 (broad, unresolved m, peaks approx. 6 Hz apart, 1, $CH_3C\underline{H}=$). The NMR spectrum of the *trans* isomer in $CDCl_3$ is included in Table 3.

cis- and trans-2-Heptene; cis-stilbene

A 10 mmol sample of *trans*-1-(ethylenedioxyboryl)propene in 10 ml of ether was stirred at −78°C under argon and 11.5 ml of 2 *M* butyllithium in hexane was added dropwise. The solvent was removed under vacuum and the residue was treated with iodine and sodium hydroxide in aqueous tetrahydrofuran as described by Zweifel and coworkers [13,14]. The hydrocarbon product was extracted with pentane, concentrated, and analyzed by NMR comparison with an authentic sample [17]. Estimation of the alkene content relative to iodoalkene and residual pentane was based on integrals of NMR peaks, yield 30 ± 10% of *cis*-2-heptene. A sample of 80% *cis*-1-(ethylenedioxyboryl)propene was similarly converted to predominantly *trans*-2-heptene. Similar treatment of *trans*-1-(ethylenedioxyboryl)-2-phenylethene with phenyllithium followed by rearrangement with iodine and alkali gave *cis*-stilbene (65%), purified by distillation, b.p. 65—75°C (0.5 mmHg), identified by its characteristic NMR spectrum [25].

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