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ALKENE-1,1-DIBORONIC ESTERS FROM THE CONDENSATION OF TRIBORYLMETHIDE ANIONS WITH KETONES OR ALDEHYDES*

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Summary

The triborylmethide ions, $[(RO)_2B]_3C^-$, from the reaction of methyllithium with the methyl ester of methanetetraboronic acid, $C[B(OMe)_2]_4$, or the pinacol ester, $C(BO_2C_2Me_4)_4$, condense readily with ketones, R'_2CO, to form alkene-1,1-diboronic esters, $R'_2C{=}C[B(OR)_2]_2$. The reaction is a general one and tolerates other functional groups, including α-chloro, carbethoxy, and tertiary amino substituents. Acetaldehyde and benzaldehyde also undergo the condensation. The alkene-1,1-diboronic esters are potentially useful synthetic intermediates. Their reactions include conversion to carboxylic acids by hydrogen peroxide, conversion to α-bromoalkeneboronic esters by bromine, and conversion to alkenyl-1,1-dimercuric chlorides by mercuric chloride and sodium acetate.

Introduction

The methyl ester of methanetetraboronic acid (Ia) serves as a source of the tris(dimethoxyboryl)methide anion (IIa) on reaction with butyllithium or other bases [2]. It was immediately apparent that the anion (IIa) might condense with aldehydes and ketones in a manner analogous to that of α-lithioboranes derived from 1,1-bis(dialkylboryl)alkanes [3]. We did succeed in obtaining a small yield of β-styreneboronic acid by way of the condensation of the analogous (bis)dimethoxyboryl)methide anion, $[(MeO)_2B]_2CH^-$, with benzaldehyde [2], and a high yield of *cis*- and *trans*-2-methyl-3-chloropropene-1-boronic ester from $[(MeO)_2B]_2CH^-$ and chloroacetone [4]. However, the instability of the alkene-1,1-diboronic ester function toward protolysis frustrated our earlier attempts to obtain these compounds from the tris(dimethoxyboryl)methide ion (IIa) [4].

We have now found that the methyl esters of alkene-1,1-diboronic acids can be isolated if proton sources are avoided in the work-up. Better yields are

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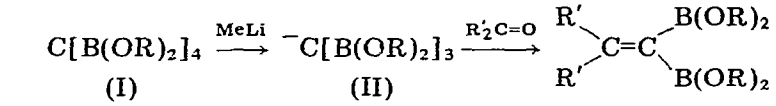
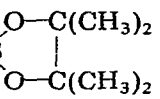
obtained by the use of the pinacol ester of methanetetraboronic acid (Ib) [5] and the corresponding tris(tetramethylethylenedioxyboryl)methide anion (IIb).



(a), $B(OR)_2 = B(OCH_3)_2$; (b), $B(OR)_2 =$



Nomenclature note

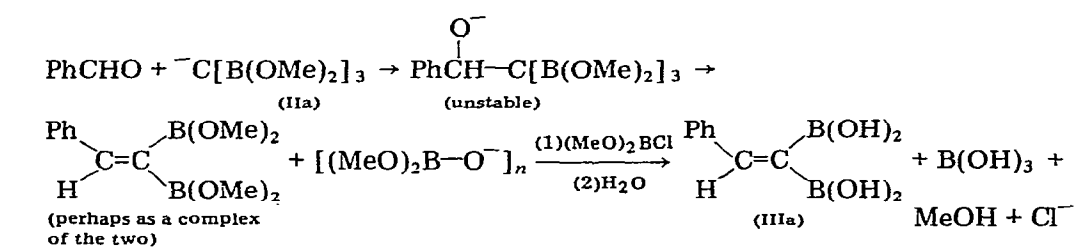
The Nomenclature Committee of the ACS Division of Inorganic Chemistry has suggested that the boronic acid nomenclature be abandoned in favor of naming the group $(RO)_2B$ as "dialkoxyboryl" [6]. We have followed this suggestion in recent papers [4, 5, 7, 8] but have abandoned it temporarily in the present one. The proposed systematic name for a cyclic ester such as "1,1-bis-(benzo-[*d*]-1,3,2-dioxaborol-3-yl)propene" is as intricate as the conjugation of a Basque verb. "The catechol ester of propene-1,1-diboronic acid" requires about the same space and reads like plain English.

We have resorted to the semi-systematic name "tris(tetramethylethylene-dioxyboryl)methide anion" for (IIb), which defies naming by the boronic acid approach, rather than the fully systematic "tris(4,4,5,5-tetramethyl-1,3,2-dioxaborol-3-yl)methide ion." We have found similar nomenclature suitable for other relatively simple cyclic boronic esters [5, 8].

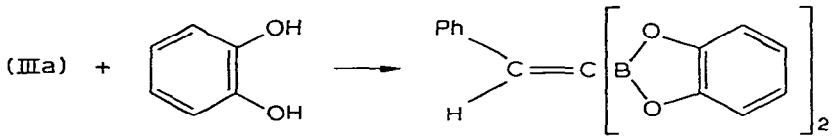
Results and discussion

Synthesis based on the methyl ester (Ia)

When we began this work, the only derivative of methanetetraboronic acid available was the methyl ester (Ia) [1, 2]. The reaction of the derived anion (IIa) with benzaldehyde must by stoichiometry yield some sort of basic borate by-product, which we neutralized by adding chlorodimethoxyborane. Methyl esters of boronic acids hydrolyze so rapidly that their isolation requires inconvenient precautions for the exclusion of moisture, and we therefore chose to isolate the product as 2-phenylethene-1,1-diboronic acid (IIIa) by crystallization from water. We were unable to obtain a pure sample of this boronic acid, perhaps because of the lability of the carbon—boron bond toward hydrolysis or air oxidation or because boronic acids are easily dehydrated to anhydrides. Conversion to the catechol ester (IIIb) led to an almost satisfactory analytical sample.



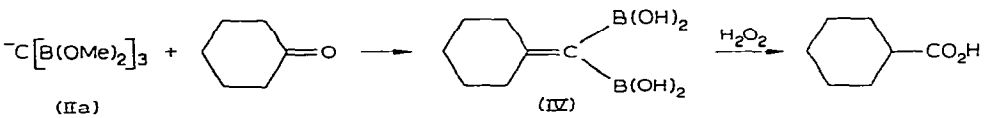
(perhaps as a complex of the two)



(IIIb)

Our basis for writing the elimination as occurring in basic solution is explained in the succeeding paper [9], and evidence for free tris(dialkoxyboryl)-methide ions such as (IIa) is described elsewhere [5, 8, 10]. The structure of the boronic acid product (IIIa) was also confirmed by oxidation with alkaline hydrogen peroxide to form phenylacetic acid (identity established by infrared).

Cyclohexanone and (IIa) under similar reaction conditions led to cyclohexylidenylmethanediboronic acid (IV), which fell a bit short of true analytical purity but yielded cyclohexanecarboxylic acid on oxidation with hydrogen peroxide.



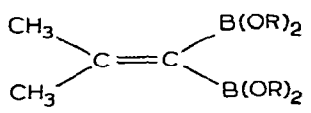
(IIa) (IV)

It is clear from the foregoing results that these reactions provide a method for the homologation $R_2C{=}O \rightarrow R_2CHCO_2H$. However, our immediate interest was in making boronic esters, and we have not yet developed the more general synthetic implications to the point of real practicality.

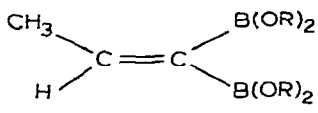
It appeared at this point that the hydrolytic work-up was creating more problems than it solved, and we therefore decided to attempt the isolation of the methyl esters directly by distillation.

The first problem encountered involved the use of butyllithium as the base for conversion of the methanetetraboronic ester (Ia) to the anion (IIa). The by-product methyl ester of butaneboronic acid, $BuB(OMe)_2$, has too close a boiling point to those of some of the desired products for easy separation by distillation. We therefore changed to methyllithium, which proved satisfactory, and used this base throughout the remainder of the work.

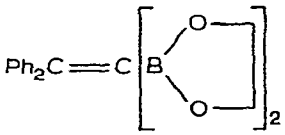
The reaction of the anion (IIa) with acetone gave fair yields of the methyl ester of 2-methylpropene-1,1-diboronic acid (Va), which was purified by distillation. Better yields of the ethylene glycol ester (Vb) were obtained by adding ethylene glycol to the crude methyl ester and crystallizing the product. The product from acetaldehyde, the methyl ester of propene-1,1-diboronic acid (VIa), resisted purification by distillation, and the ethylene glycol ester failed to crystallize, but we obtained a pure sample of the catechol ester (VIb). The product from benzophenone was isolated as the crystalline ethylene glycol ester (VIII).



(V)

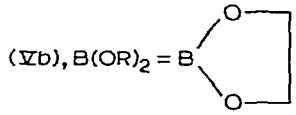


(VI)



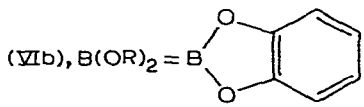
(VII)

(Va), $B(OR)_2 = B(OCH_3)_2$;



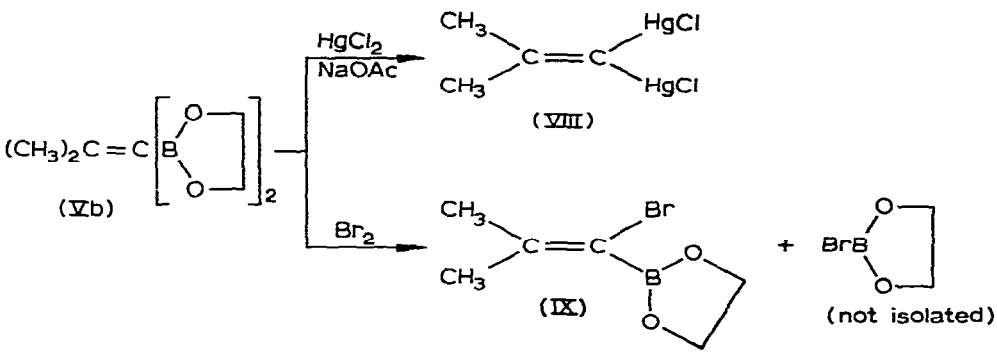
(Vb), $B(OR)_2 = B$

(VIa), $B(OR)_2 = B(OCH_3)_2$;



(VIb), $B(OR)_2 = B$

Since the ethylene glycol ester of 2-methylpropene-1,1-diboronic acid (Vb) was easily prepared, we made a brief investigation of its chemistry. Reaction with mercuric chloride and sodium acetate rapidly yielded 2-methylpropene-1,1-dimercuric chloride (VIII). Bromination of (Vb) gave the ethylene glycol ester of 1-bromo-2-methylpropene-1-boronic acid (IX). Although it is conceivable that (IX) might be formed by a direct electrophilic displacement on (Vb), from our earlier work on β-bromoalkaneboronic esters [11] it appears more likely that an addition-elimination mechanism is operating. The alkene-1,1-diboronic acid function is highly labile to direct electrophilic displacement, as illustrated by the conversion of $(CH_3)_2C{=}C[B(OH)_2]_2$ to $(CH_3)_2C{=}CHB(OH)_2$ (based on NMR evidence) on recrystallization from hot water.



(Vb)

(VIII)

(IX)

(not isolated)

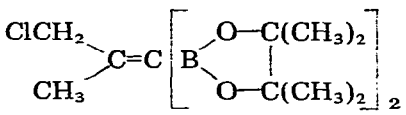
The vinyl CH proton of propene-1,1-diboronic esters (VI) appears remarkably far downfield at δ 7.40 ppm in the NMR. This signal is hidden under the aromatic proton signals in the catechol ester (VIb), and the corresponding vinyl proton signal in 2-phenylethene-1,1-diboronic acid (IIIa) is similarly hidden. This chemical shift is unexpected, inasmuch as the pair of boronic ester groups β to these vinyl protons seems unlikely to be a particularly strong electron-withdrawing function, and there is no readily apparent simple explanation for these results.

Synthesis based on pinacol esters

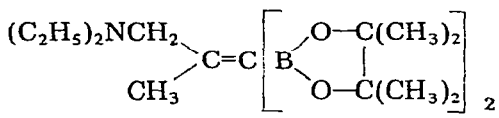
In a separate investigation, we found that the reaction of the tris(dimethoxyboryl)methide ion (IIa) with chloroacetone occurs at the carbonyl group rather than the alkyl halide function, but on conversion to the ethylene glycol ester

one boronic ester function was lost and only the *cis* and *trans* isomers of the 2-methyl-3-chloropropene-1-boronic ester could be isolated [4]. The need for avoiding all proton sources during work-up in order to isolate some of the more interesting functionally substituted alkene-1,1-diboronic esters was thus apparent. The ethylene glycol ester of methanetetraboronic acid had been made, but proved too insoluble for convenient synthetic use [4, 8].

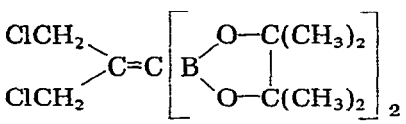
The synthesis of the pinacol ester of methanetetraboronic acid (Ib) for another project [5] provided an attractive starting material for the present work. As anticipated, the reaction products could generally be crystallized directly after acidification of the reaction mixture with chlorodimethoxyborane and removal of the volatile by-products, or purified by column chromatography. New boronic esters synthesized from the corresponding ketones in this way included structures (X) through (XIII).



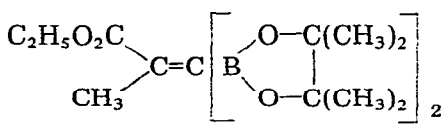
(X)



(XIa), Free base;
(XIb), Hydrochloride

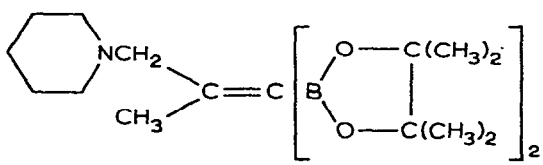


(XII)



(XIII)

The diethylamino compound (XI) was also prepared by reaction of the corresponding chloro compound (X) with diethylamine. The related piperidino compound (XIV) was prepared from piperidine and the chloro compound (X).



(XIV)

In spite of the facility of these displacements with amines, we were unable to find conditions for the displacement of the two chloro groups fo the dichloro compound (XII) by ammonia or sodamide, though we did not try ammonia under pressure at elevated temperatures.

We also attempted the reaction of the triborylmethide anion (IIb) with ethyl bromopyruvate, but were unable to obtain any alkene-1,1-diboronic ester. Some pinacol ester of methanetriboronic acid was recovered, suggesting that the α-hydrogens of the bromopyruvate ester are acidic and react in preference to the carbonyl group with the triborylmethide anion (IIb).

Experimental

Tris(dialkoxyboryl)methide ions (IIa) and (IIb)

Solutions of the tris(dimethoxyboryl)methide anion (IIa) were generally prepared by the dropwise addition of 20 ml of 1.6 *M* methyllithium in 15 min to 6.0 g (0.02 mole) of the methyl ester of methanetetraboronic acid (Ia) in 30 ml of anhydrous tetrahydrofuran stirred at 0° under argon. The tris(tetramethylethylenedioxyboryl)methide anion (IIb), which precipitates as the lithium salt, was similarly prepared by the addition of 14 ml of 1.6 *M* methyllithium to 10.4 g (0.02 mole) of the pinacol ester of methanetetraboronic acid (Ib) in 60 ml of anhydrous ether and was used directly as a suspension.

Methyl ester of 2-methylpropene-1,1-diboronic acid (Va)

Addition of 1.1 g of acetone to a solution of 0.02 mole of the tris(dimethoxyboryl)methide anion (IIa) at 0° resulted in an exothermic reaction and decolorization of the yellow solution. The solution was then refluxed 0.5 h, cooled to 0°, treated with 2 ml of chlorodimethoxyborane (which had been prepared by mixing the theoretical proportions of trimethyl borate and boron trichloride), again refluxed 0.5 h, chilled to 0°, and filtered to remove lithium chloride. The solvents were distilled under vacuum. The viscous residue was distilled through a spinning-band column, b.p. 30°/5 mmHg; yield 28%. NMR (CCl_4): δ 3.52 (s, 12, OCH_3) and 1.71 ppm (s, 6, $C(CH_3)_2$). (Found: C, 48.23; H, 9.04; B, 11.09. $C_8H_{18}B_2O_4$ calcd.: C, 48.2; H, 9.03; B, 10.63%.)

Ethylene glycol ester of 2-methylpropene-1,1-diboronic acid (Vb)

The methyl ester (Va) was prepared as described, except that the compound was not distilled after removal of the solvents but was treated with a small excess of ethylene glycol. The resulting (Vb) was crystallized at 20—25° overnight, and recrystallized from carbon tetrachloride, yield 52%; m.p. 101°. NMR (CCl_4): δ 4.15 (s, 8, OCH_2CH_2O) and 1.96 ppm [s, 6, $C(CH_3)_2$]. IR ($CHCl_3$): 1598 cm^{-1} (C=C). (Found: C, 48.87; H, 6.93; B, 11.33. $C_8H_{14}B_2O_4$ calcd.: C, 48.97; H, 7.14; B, 11.22%.)

Methyl and catechol esters of propene-1,1-diboronic acid (VIa) and (VIb)

One ml of acetaldehyde was added dropwise to a solution of 0.02 mole of the tris(dimethoxyboryl)methide ion (IIa) stirred at 0° under argon and the same procedure used for the analogous reaction of acetone to form (Va) was followed. Fractionation yielded 32% of impure methyl ester of propene-1,1-diboronic acid (VIa), b.p. 70°/15 mmHg. NMR (CCl_4): δ 7.40 (quartet, *J* 6 Hz, 1, C=C<u>H</u>CH), 3.45 (s, 12, OCH_3), and 1.96 ppm (d, *J* 6 Hz, 3, $CHC\underline{H}_3$). IR ($CHCl_3$): 1598 cm^{-1} (C=C). This methyl ester was refluxed in benzene with an equivalent amount of catechol. On cooling the catechol ester (VIb) crystallized; recrystallized from benzene, m.p. 138°. NMR ($CDCl_3$): δ 6.92—7.42 [(m, 9, $(C_6H_4O_2B)_2$ + C=C<u>H</u>CH_3] and 2.35 ppm (d, *J* 6 Hz, 3, $CHC\underline{H}_3$). (Found: C, 63.99; H, 4.73; B, 8.04. $C_{15}H_{12}B_2O_4$ calcd.: C, 64.7; H, 4.3; B, 7.9%.)

Catechol ester of 2-phenylethene-1,1-diboronic acid (IIIb)

Addition of 1.2 g of benzaldehyde to 0.01 mole of the tris(dimethoxyboryl)-

methide ion (IIa) (prepared from butyllithium in this case) was followed by the same procedure described for preparation of (Va) to the point of evaporation of the solvents. The residue was then treated with water and the solution was concentrated under vacuum to crystallize 2-phenylethene-1,1-diboronic acid (IIIa), which we were unable to purify satisfactorily. Refluxing with catechol in benzene followed by crystallization yielded the catechol ester (IIIb), m.p. 149°. The NMR spectrum showed only a multiplet in the aromatic region, the lone vinyl CH absorbing so far downfield it was hidden. (Found: C, 69.5; H, 4.24; B, 6.24. $C_{24}H_{14}B_2O_4$ calcd.: C, 70.6; H, 4.1; B, 6.46%).

Cyclohexylidenylmethanediboronic acid (IV)

Cyclohexanone (1.6 g) was used in place of acetone in the procedure already described for the preparation of the methyl ester of 2-methylpropene-1,1-diboronic acid (Va). However, in this case the methyl ester was not distilled but treated with water to yield the boronic acid (IV), recrystallized from water, yield 22%; m.p. 146° (dec.). (Found: C, 44.43; H, 7.14; B, 12.40. $C_7H_{14}B_2O_4$ calcd.: C, 45.6; H, 7.6; B, 11.9%.) Oxidation of this boronic acid with dilute alkaline hydrogen peroxide yielded cyclohexanecarboxylic acid, compared with an authentic sample by IR.

Ethylene glycol ester of 2,2-diphenylethene-1,1-diboronic acid (VII)

The procedure followed was the same as that described for the preparation of the ethylene glycol ester of 2-methylpropene-1,1-diboronic acid (Vb), with 0.02 mole of benzophenone in place of acetone. Since the initial reaction was not exothermic, the reflux period was extended to 6 h. The product (VII) was crystallized from chloroform, yield 48%; m.p. 162°. (Found: C, 67.79; H, 5.74; B, 6.52. $C_{18}H_{18}B_2O_4$ calcd.: C, 67.56; H, 5.66; B, 6.76%.)

Ethylene glycol ester of 1-bromo-2-methylpropene-1-boronic acid (IX)

A solution of 0.8 g of bromine in 5 ml of carbon tetrachloride was added dropwise in 15 min to a stirred solution of 1.3 g of the ethylene glycol ester of 2-methylpropene-1,1-diboronic acid (Vb) in 10 ml of carbon tetrachloride at −20°. The mixture was stirred an additional 0.5 h until the bromine color was discharged. The product (IX) was fractionated, b.p. 55—56°/0.5 mmHg; yield 70%. NMR (neat): δ 3.82 (s, 8, OCH_2CH_2O), 2.03 (s, 3, CCH_3), and 1.95 ppm (s, 3, the other CCH_3). IR ($CHCl_3$): 1597 cm^{-1} (C=C). (Found: C, 34.33; H, 4.7; B, 5.15; Br, 38.1. $C_6H_{10}BBrO_2$ calcd.: C, 35.1; H, 4.8; B, 5.3; Br, 39.0%.)

2-Methylpropene-1,1-dimercuric chloride (VIII)

A solution of 2.8 g of mercuric chloride and 0.4 g of sodium acetate in 10 ml of 50% aqueous methanol was added to a solution of 1.3 g of the ethylene glycol ester of 2-methylpropene-1,1-diboronic acid (Vb) in 20 ml of 100% methanol. The dense white precipitate which formed was filtered and washed several times with methanol, yield 90%; did not melt below 250°. NMR (DMSO-d_6): δ 2.02 ppm [s, with ^{199}Hg satellites J 36 Hz, $C(CH_3)_2$]. (Found: C, 8.92; H, 1.11; Cl, 13.02; Hg, 76.51. $C_4H_6Cl_2Hg_2$ calcd.: C, 9.14; H, 1.14; Cl, 13.3; Hg, 76.38%.)

Pinacol ester of 2-methyl-3-chloropropene-1,1-diboronic acid (X)

4 ml of freshly distilled chloroacetone was added to 0.02 mole of the tris-(tetramethylethylenedioxyboryl)methide ion (IIb) in ether under argon. An exothermic reaction occurred. After stirring 2 h at 25° the mixture was treated with 2 ml of chlorodimethoxyborane, the lithium chloride was removed by filtration, and the solution was concentrated under vacuum. The by-product 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was distilled at ≈ 27°/1 mmHg, identified by its NMR and mass spectra. Failure to remove this by-product at this point caused subsequent difficulties in purification of the desired product. The residue was cooled with a −10° bath, washed quickly with two 10 ml portions of distilled water, and dissolved in 40 ml of ether, discarding the ether-insoluble material. The ether solution was dried over sodium sulfate, concentrated under vacuum to 10 ml, and chilled to −15° to crystallize. The product (X) was recrystallized from chloroform, yield 48%; m.p. 93°. NMR (CCl_4): δ 4.16 (s, 2, CH_2Cl), 1.96 (s, 3, $=CCH_3$), 1.16 ppm [s, 24, $OC(CH_3)_2C(CH_3)_2O$]. IR (CCl_4): 1640 cm^{-1} (C=C). (Found: C, 56.11; H, 8.33; B, 6.17; Cl, 10.41. $C_{16}H_{29}B_2ClO_4$ calcd.: C, 56.11; H, 8.53; B, 6.31; Cl, 10.35%.)

Pinacol ester of 2-methyl-3-(diethylamino)propene-1,1-diboronic acid hydrochloride (XIb) from diethylaminoacetone and (IIb)

A small excess of diethylaminoacetone was added to 0.02 mole of the tris-(tetramethylethylenedioxyboryl)methide ion (IIb) in ether under argon. The mixture was refluxed 1 h, treated with 2 ml of chlorodimethoxyborane, filtered to remove lithium chloride, and concentrated under vacuum. The dark, viscous residue was treated with ether and the ether-soluble portion was decolorized with charcoal. Bubbling anhydrous hydrogen chloride through the solution precipitated the product as white flakes; recrystallized from methylene chloride; yield 38%; m.p. 162° (dec.). NMR (D_2O): δ 3.86 (s, 2, $C=CCH_2N$), 3.16 [quartet, 4, $N(C\underline{H}_2CH_3)_2$], 1.96 (s, 3, $C=CCH_3$), 1.25 [s, 24, $OC(CH_3)_2C(CH_3)_2O$, perhaps hydrolyzed to free *O*-deuteropinacol], and 1.10 ppm [t, 6, $N(CH_2C\underline{H}_3)_2$]. (Found: C, 57.47; H, 10.07; B, 5.33; Cl, 8.30; N, 3.10. $C_{20}H_{40}B_2ClNO_4$ calcd.: C, 57.80; H, 9.69; B, 5.21; Cl, 8.50; N, 3.37%.)

Pinacol ester of 2-methyl-3-(diethylamino)propene-1,1-diboronic acid (XIa) from diethylamine and (X)

A solution of 3.4 g of the pinacol ester of 2-methyl-3-chloropropene-1,1-diboronic acid (X), and 1.4 g of diethylamine in ≈ 10 ml of acetone was refluxed 12 h, cooled to crystallize the diethylamine hydrochloride, concentrated under vacuum, treated with ether to precipitate more diethylamine hydrochloride, filtered, and concentrated to crystallize the product (XIa), m.p. 128°. NMR (CCl_4): δ 2.90 (s, 2, $=CCH_2N$), 2.51 [quartet, 4, $N(C\underline{H}_2CH_3)_2$], 1.83 (s, 3, $=CCH_3$), 1.19 [s, 12, $OC(CH_3)_2C(CH_3)_2O$], 1.13 [s, 12, the other $OC(CH_3)_2C(CH_3)_2O$], and 0.80 ppm [t, 6, $N(CH_2C\underline{H}_3)_2$]. This compound gave the same NMR spectrum as its hydrochloride (XIb) in acidic D_2O.

Pinacol ester of 2-methyl-3-N-piperidinopropene-1,1-diboronic acid (XVI) and its hydrochloride salt

Piperidine was substituted for diethylamine in the procedure described in

the preceding paragraph for the reaction with the pinacol ester of 2-methyl-3-chloropropene-1,1-diboronic acid (X). The free base (XIV) was crystallized from a mixture of ether and hexane, yield 80%; m.p. 101°. NMR (CCl_4): δ 3.27 (s, 2, $=CCH_2N$), 2.83 (m, 4, $NC\underline{H}_2CH_2$), 1.90 (s, 3, $=CCH_3$), 1.61 [m, 6, $(CH_2)_3$), 1.28 [s, 12, $OC(CH_3)_2C(CH_3)_2O$], and 1.22 ppm [s, 12, and other $OC(CH_3)_2$-$C(CH_3)_2O$]. (Found: C, 64.33; H, 10.14; B, 5.80; N, 3.44. $C_{21}H_{39}B_2NO_4$ calcd.: C, 64.48; H, 10.04; B, 5.52; N, 3.58%.) The hydrochloride was prepared by bubbling hydrogen chloride through an ethereal solution of the base, m.p. 162°. NMR (D_2O): δ 3.97 (s, 2, $=CCH_2N$), 3.5 (m, 4, $NC\underline{H}_2CH_2$), 2.10 (s, 3, $=CCH_3$), 1.83 (m, 6, $(CH_2)_3$), and 1.40 ppm [s, 24, $OC(C\underline{H}_3)_2C(C\underline{H}_3)_2O$]. (Found: C, 59.12; H, 9.77; B, 5.23; Cl, 8.60; N, 3.13. $C_{21}H_{40}B_2ClNO_4$ calcd.: C, 58.94; H, 9.42; B, 5.05; Cl, 8.28; N, 3.27%.)

Pinacol ester of 2-chloromethyl-3-chloropropene-1,1-diboronic acid (XII)

A solution of 2.5 g of 1,3-dichloroacetone in 20 ml of ether was added to 0.02 mole of the tris(tetramethylethylenedioxyboryl)methide anion (IIb) in 60 ml of ether under argon. The reaction was exothermic and the precipitate dissolved. After stirring 15 min, 2.1 ml of chlorodimethoxyborane was added, stirring was continued 10 min, the lithium chloride was removed by filtration, and the solvent and by-product 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were removed under vacuum, and the residue was chromatographed on acid-washed alumina with hexane as the eluant and the middle fraction recrystallized from hexane, yield of (XII) 35%; m.p. 112°. NMR (CCl_4): δ4.36 (s, 4, CH_2Cl) and 1.21 ppm (s, 24, CH_3). IR (CCl_4): 1620 cm^{-1} (C=C). (Found: C, 51.25; H, 7.64; B, 5.92; Cl, 18.43. $C_{16}H_{28}B_2Cl_2O_4$ calcd.: C, 50.98; H, 7.49; B, 5.74; Cl, 18.81%.)

Pinacol ester of 2-carbethoxypropene-1,1-diboronic acid (XIII)

The addition of 1.8 g of freshly distilled ethyl pyruvate to 0.02 mole of the tris(tetramethylethylenedioxyboryl)methide ion was followed by 0.5 h reflux, the addition of chlorodimethoxyborane, and the work-up procedure described in the preceding paragraph for the preparation of (XII), except that diethyl ether was used as the eluant, yield 50%. Some pinacol ester of methanetetraboronic acid (Ib) remained as a contaminant and was removed from the analytical sample by gas chromatography on 20% SF 86 on Chromosorb at 210°, the desired product (XIII) having about twice the retention time; m.p. 89°. NMR (CCl_4): δ 4.13 (quartet, 2, $OC\underline{H}_2CH_3$), 2.04 (s, 3, $=CCH_3$), and 1.16 ppm (s + t, 27, $OC(C\underline{H}_3)_2C(C\underline{H}_3)_2O + OCH_2C\underline{H}_3$). (Found: C, 59.26; H, 8.87; B, 5.19. $C_{18}H_{32}B_2O_6$ calcd.: C, 59.05; H, 8.84; B, 5.11%.)

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References

1 D.S. Matteson and P.B. Tripathy, J. Organometal. Chem., 21 (1970) P6.
2 R.B. Castle and D.S. Matteson, J. Amer. Chem. Soc., 90 (1968) 2194; J. Organometal. Chem., 20 (1969) 19.
3 G. Cainelli, G. Dal Bello and G. Zubiani, Tetrahedron Lett., (1965) 3429; (1966) 4315.
4 D.S. Matteson and J.R. Thomas, J. Organometal. Chem., 24 (1970) 263.
5 D.S. Matteson, R.A. Davis and L.A. Hagelee, J. Organometal. Chem., 69 (1974) 45.
6 J. Carter, R.M. Adams, and K.L. Loening, Inorg. Chem., 7 (1968) 1945.
7 D.S. Matteson and G.L. Larson, J. Organometal. Chem., 57 (1973) 225.
8 D.S. Matteson and R.J. Wilcsek, J. Organometal. Chem., 57 (1973) 231.
9 D.S. Matteson and M. Furue, J. Organometal. Chem., 69 (1974) 63.
10 D.S. Matteson, L.A. Hagelee and R.J. Wilcsek, J. Amer. Chem. Soc., 95 (1973) 5096.
11 D.S. Matteson and J.D. Liedtke, J. Amer. Chem. Soc., 87 (1965) 1526.