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C-ALKYLATION OF METHANETETRABORONIC AND METHANETRIBORONIC ESTERS*

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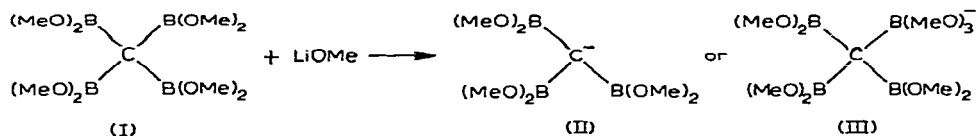*Department of Chemistry, Washington State University Pullman, Washington 99163 (U.S.A.)*

(Received March 25th, 1970)

SUMMARY

Tetrakis(dimethoxyboryl)methane, $[(MeO)_2B]_4C$, and lithium methoxide in tetrahydrofuran behave as a source of $[(MeO)_2B]_3C^-$, which displaces halide ion from alkyl halides (RX) to yield mixtures of $[(MeO)_2B]_3C-R$ and $[(MeO)_2B]_2CR_2$. The latter must result from transfer of a dimethoxyboryl group from $[(MeO)_2B]_3CR$ to $[(MeO)_2B]_3C^-$ to form $[(MeO)_2B]_4C$ and $[(MeO)_2B]_2CR^-$, which then reacts with a second mole of RX. The products from methyl iodide and $[(MeO)_2B]_3C^-$ were converted to the more stable ethylene glycol esters and isolated by gas chromatography. Tris(dimethoxyboryl)methane, $[(MeO)_2B]_3CH$, reacts with one equivalent of alkyl halide and lithium ethoxide to yield $[(MeO)_2B]_2CHR$, best isolated by conversion to the ethylene glycol ester and distillation. Alkyl groups R include CH_3, C_4H_9, $CH_2=CHCH_2$, $HC\equiv CCH_2$, and $CH_3O_2CCH_2$. Chloroacetone reacted at the carbonyl group with $[(MeO)_2B]_2CH^-$, and the product isolated after ethylene glycol treatment was $C_2H_4O_2BCH=C(CH_3)CH_2Cl$. Incidental compounds prepared include the pinacol triboronic ester $HC(BO_2C_2Me_4)_3$ and the methoxymethanediboronic ester $CH_3OCH[B(OMe)_2]_2$.

RESULTS AND DISCUSSION

Tetrakis(dimethoxyboryl)methane (I) (also named octamethyl methanetetraboronate) is easily prepared from carbon tetrachloride, lithium dispersion, and dimethoxyboron chloride[1]. Treatment with bases such as methyllithium or lithium methoxide leads to the tris(dimethoxyboryl)methide ion (II) or perhaps its methyl borate complex (III), which readily transfers (II) to other electrophiles[1-3].

The tris(dimethoxyboryl)methide ion (II) is analogous to the bis(ethoxycarbonyl)methide ion from malonic ester and ought to react with alkyl halides. We have previously shown that reaction with benzyl bromide does occur, but the yield was low and the boronic ester products were not isolated[1]. In the present investigation, methyl iodide was chosed for systematic study of the reaction conditions. After a few trials, it became apparent that direct formation of a single distillable product was not going to be the outcome. Gas chromatography of the methyl esters was tried but it failed, probably because traces of moisture in the reaction mixture or free hydroxyl groups on the column rapidly replace the methoxy groups on boron to form random B–O–B linkages and hence products having high molecular weight. Treatment of the product methyl ester solutions with ethylene glycol yielded the cyclic ethylene glycol esters (named as 1,3,2-dioxaborol-2-ylalkanes), which proved stable and suitable for gas chromatography.

Both monomethylation and dimethylation products were always formed. Evidently the tris(dimethoxyboryl)methide ion (II) abstracts a dimethoxyboryl group from the monomethylation product (IV) to form 1,1-bis(dimethoxyboryl)ethide ion (V), which reacts with methyl iodide to form 2,2-bis(dimethoxyboryl)propane (VI). The products isolated after treatment with ethylene glycol are 1,1,1-tris(1,3,2-dioxaborol-2-yl)ethane (VII) and 2,2-bis(1,3,2-dioxaborol-2-yl) propane (VIII).

Tetrahydrofuran was found to be convenient solvent. Butyllithium could be used as the base, but it leads to $C_4H_9B(OR)_2$ by-products which are sometimes difficult to separate from the desired products. Lithium methoxide works equally well or better, yielding no troublesome side product. It is slightly soluble in tetrahydrofuran; moderately soluble in the presence of boronic ester.

Approximately equimolar mixtures of mono- and dimethylation products (VII) and (VIII) were obtained in about 50 % total yield (70 % based on available $LiOCH_3$) when one mole of methyl iodide was added dropwise to a refluxing solution of one

mole of tetrakis(dimethoxyboryl)methane (I) and one mole of lithium methoxide in tetrahydrofuran. The same results were obtained when the last two reagents were added to the first. Halving the amount of lithium methoxide increased the proportion of monomethylation product (VII) to 70%, and doubling the lithium methoxide increased the fraction of dimethylated product (VIII) to 70%, but total yields based on [(MeO)$_2$B]$_4$C (I) were reduced. Detailed results are summarized in Table 1 in the *Experimental Section*. These results suggest that the equilibration between (II)+(IV) and (I)+(V) is much faster than the competing reactions of the anions (II) and (V) with methyl iodide.

Some unreacted methoxide remained after the mixture had refluxed a few minutes. This was neutralized with dimethoxyboron chloride to prevent loss of product to salt formation and to the known base-catalyzed polymerization[1]. Prolonged refluxing appeared to increase the amount of polymerization, which is always a major side reaction under any conditions.

Since the triborylmethide ion (II) readily captures a proton irreversibly from hydroxylic solvents, degrading ultimately to [(RO)$_2$B]$_2$CH$_2$[1], it is obvious that the alkylation of (II) can only be carried out in aprotic solvents. We tried methanol anyway, and were surprised to obtain the methylation products (VII) and (VIII), though the yields were naturally low. Even in tetrahydrofuran, some protolytic deboronation by stray moisture occurs, and bis(1,3,2-dioxaborol-2-yl)methane (IX), (C$_2$H$_4$O$_2$B)$_2$-CH$_2$, could often be isolated in 5% yield by gas chromatography.

Other alkyl halides led to more problems than did methyl iodide in reactions with methanetetraboronic ester (I). Benzyl bromide yielded mainly the dibenzylation product, 2,2-bis(1,3,2-dioxaborol-2-yl)-1,3-diphenylpropane (X), (C$_2$H$_4$O$_2$B)$_2$C(CH$_2$-C$_6$H$_5$)$_2$, but separation from monobenzylation product was incomplete even by gas chromatography. Allyl bromide also yielded a mixture, and neither the ethylene glycol nor the pinacol esters could be separated by gas chromatography. From ethyl iodide we were able to obtain pure 3,3-bis(1,3,2-dioxaborol-2-yl)pentane (XI), (C$_2$H$_4$-O$_2$B)$_2$C(C$_2$H$_5$)$_2$, but the monoethylation product could not be purified, even though it appeared as a separate peak on gas chromatography. In all cases, the nature of the products was verified by NMR spectra, and products which gave poor analyses also gave poor NMR integrals.
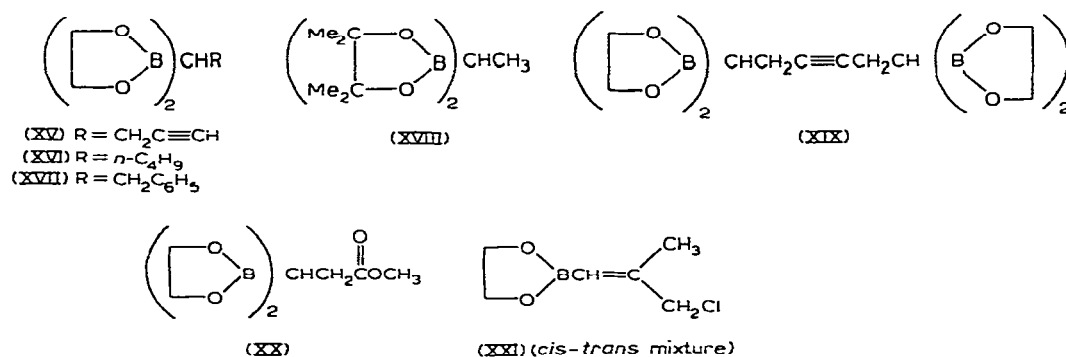
Much better results were obtained in the alkylation of tris(dimethoxyboryl)-methane (XII). It should be emphasized that bases remove a dimethoxyboryl cation, not a proton, from this compound and yield the bis(dimethoxyboryl)methide ion (XIII) or its borate ester complex. The reaction with allyl bromide leads smoothly to 4,4-bis(1,3,2-dioxaborol-2-yl)-1-butene (XIV).
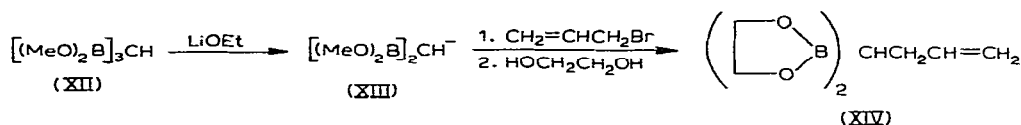
There is no detectable disproportionation to mono(dimethoxyboryl)alkide anion, (MeO)$_2$BCHR$^-$, and the product (XIV) can be purified adequately by simple distillation. Lithium ethoxide appeared to be slightly more soluble than lithium methoxide in tetrahydrofuran. Better yields (~40%) were obtained when the lithium alkoxide (as a solution with some suspended solid) was added to a mixture of triboronic ester

(XII) and allyl bromide in tetrahydrofuran than those ($\sim$25%) obtained when the triboronic ester (XII) and lithium alkoxide were mixed first and then treated with allyl bromide. Polymerization of the boronic ester (XII) appears to be the major side reaction.

Other alkyl halides used with tris(dimethoxyboryl)methane (XII) and the products isolated are as follows: propargyl bromide, (XV); butyl iodide, (XVI); benzyl bromide, (XVII); methyl iodide, (XVIII); 1,4-dibromo-2-butyne, (XIX); methyl bromoacetate, (XX); and chloroacetone, (XXI).

(XV) R = CH$_2$C≡CH
(XVI) R = n-C$_4$H$_9$
(XVII) R = CH$_2$C$_6$H$_5$

(XVIII)

(XIX)

(XX)

(XXI) (cis-trans mixture)

The product from methyl iodide (XVIII) was obtained as the pinacol ester because the ethylene glycol ester proved difficult to purify by gas chromatography. The benzyl bromide product (XVII) was not prepared from the methyl ester (XII) but from the ethylene glycol ester, $(C_2H_4O_2B)_3CH$, and was isolated without exposure to hydroxylic solvents. Thus, the possibility that these products, $(C_2H_4O_2B)_2CHR$, might have arisen from protolytic cleavage of $(C_2H_4O_2B)_3CR$ is ruled out*.

Saturated diboryl compounds related or identical to (XVI)[4], (XVII)[5], and (XVIII)[6] are available by hydroboration reactions and therefore are not the primary synthetic objectives of this investigation. Unsaturated products (XIV), (XV), and (XIX) or the carboxylic ester (XX) would be difficult or impossible to make by previously known methods. We also investigated the possibility of reacting the diborylmethide anion (XIII) with cis- and trans-1,4-dichloro-2-butene but always obtained inseparable mixtures, which appeared from their NMR spectra to contain isomers resulting from allylic S_N2' displacement as well as simple S_N2 displacement. Chloroacetonitrile failed to alkylate the anion (XIII) and yielded about 50% of $(C_2H_4O_2B)_2CH_2$ (IX) instead, as if the protons of $ClCH_2CN$ are so acidic that the displacement process cannot compete.

The product (XXI) from the reaction of chloroacetone with the bis(dimethoxyboryl)methide ion (XIII) clearly arises from a typical condensation at the ketone group[2]. The yield (78%) is surprisingly high. However, attempts to condense chloroacetone with $[(MeO)_2B]_3C^-$ (II) led only to the same monoboronic ester (XXI) obtained from $[(MeO)_2B]_2CH^-$ (XIII). To be sure the problem was not one of

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* Cleavage of $[(MeO)_2B]_3CSnPh_3$ by ethylene glycol to form $(C_2H_4O_2B)_2CHSnPh_3$ has been observed[3], though the present contrast between the products from alkylation of $[(MeO)_2B]_4C$ (I) and $[(MeO)_2B]_3CH$ (XII) seems sufficient by itself to rule out proton abstraction from $[(MeO)_2B]_3CH$ to form $[(MeO)_2B]_3C^-$ (II) as a major pathway.

experimental technique, we duplicated the reported[2] preparation of $(C_2H_4O_2B)_2$-$C=C(CH_3)_2$. Evidently $(C_2H_4O_2B)_2C=C(CH_3)CH_2Cl$ is much more labile to protolytic deboronation by ethylene glycol than are the previously prepared alkenediboronic esters. An obvious solution to this problem would be to start with tetrakis-(1,3,2-dioxaborol-2-yl)methane, $(C_2H_4O_2B)_4C$, which is easily prepared from the methyl ester (I) and ethylene glycol[7], but this compound is so insoluble in tetrahydrofuran and other possible solvents that we have been unable to carry out any useful reactions with it. Other glycol esters derived from $[(MeO)_2]_4C$ (I) are under current investigation.

An alternative approach to the C-alkylation of methanetetraboronic or triboronic esters (I) and (XII) was tried without success, but two incidental new compounds were obtained. If a halogenated boronic ester such as $BrC[B(OMe)_2]_3$ or $BrCH[B(OMe)_2]_2$ could be made, reaction with carbanions should form a carbon–carbon bond, as found[8] with $ICH_2B(OBu)_2$. We made a number of unsuccessful attempts to brominate $[(MeO)_2B]_2CH^-$ (XIII) and $[(MeO)_2B]_3C^-$ (II). Bromine was consumed, but the recovered boronic ester fractions generally consisted of starting material, and some polymer was often formed. The pinacol ester $HC(BO_2C_2Me_4)_3$ (XXII) was prepared from the methyl ester (XII), but attempted chlorination of (XXII) with tert-butyl hypochlorite resulted in little reaction, and reaction with chlorine resulted in attack on the pinacol ester carbons. Bis(dimethoxyboryl)methoxymethane (XXIII), $[(MeO)_2B]_2CHOCH_3$, was prepared from Cl_2CHOCH_3, Li, and ClB-$(OMe)_2$ in the hope that the C-methoxy group might be cleaved by hydrogen bromide or iodide, but several attempts to cleave the ether were unsuccessful.

EXPERIMENTAL

Most of the NMR spectra are referred to external tetramethylsilane (because an internal reference might be confused with a B_2CH peak). Reactions of air-sensitive boron compounds were run under nitrogen.

1,1,1-Tris(1,3,2-dioxaborol-2-yl)ethane (VII) and 2,2-bis(1,3,2-dioxaborol-2-yl)propane (VIII)

A solution of 5.5 g of tetrakis(dimethoxyboryl)methane (I) in 20 ml of anhydrous tetrahydrofuran was heated to reflux under nitrogen, and 0.704 g of lithium methoxide powder (prepared by dissolving lithium in methanol and removing the methanol under vacuum) was added in several portions. The reaction was exothermic and the mixture darkened. The solution was refluxed 15 min and was then added dropwise from a syringe to a refluxing solution of 7.7 g of methyl iodide in 10 ml of tetrahydrofuran. After refluxing 40 min, the solution was cooled, a second 0.7-g portion of lithium methoxide was added, and refluxing was resumed for 1 h. The solvent was removed under vacuum and the residue was treated with 5 g of ethylene glycol and 10 ml of tetrahydrofuran. The solution was acidified by addition of 0.9 ml of dimethoxyboron chloride and concentrated under vacuum. The organoboron compounds were extracted from the residual salts into ether (three 15-ml portions) and distilled, b.p. 82–90° (1 mm), yield 1.6 g of mixture. The products were separated by gas chromatography at 140° on a column of 20% XF 1150 methyl(cyanoethyl)-siloxane polymer on Chromosorb P. The $(CH_3)_2C(BO_2C_2H_4)_2$ has the shorter reten-

tion time; NMR (CCl_4): τ 5.91 (s, 8, OCH_2) and τ 9.01 (s, 6, CCH_3). The analytical sample was redistilled. (Found: C, 45.61; H, 7.51; B, 11.49. $C_7H_{14}B_2O_6$ calcd.: C, 45.73; H, 7.67; B, 11.77%.) The $CH_3C(BO_2C_2H_4)_3$ has the longer retention time; NMR (CCl_4): τ 5.97 (s, 12, OCH_2) and τ 9.10 (broadened s, 3, CCH_3). (Found: C, 39.80; H, 6.47; B, 13.10. $C_8H_{15}B_3O_6$ calcd.: C, 40.09; H, 6.31; B, 13.54%.)

Exploration of conditions for reaction of tetrakis(dimethoxyboryl)methane (I) with methyl iodide.

Samples of 0.8–1.5 g of tetrakis(dimethoxyboryl)methane (I) in 10–15 ml of the selected solvent were treated with 1 or 2 equivalents of base as listed in Table 1. The solution was heated briefly (except where methanol was the solvent), resulting in formation of an amber color. Either the methyl iodide (or sulfate) was added dropwise in a few min to the tetraborylmethane (I) solution (method A), or the latter was added to the former (method B). The solution was stirred 15 min, then treated with small portions of dimethoxyboron chloride until a drop of solution was acidic to moistened pH paper. The solvent was distilled at 1 mm, the residue was stirred overnight with 3 ml of ethylene glycol and 10 ml of tetrahydrofuran, the solvent was again removed under vacuum, and the organoboron products were extracted from the residue into ether (3 × 15 ml). The ether solution was concentrated to about half its original volume and allowed to stand over calcium chloride to remove ethylene glycol, then filtered. A measured amount of dimethylformamide was added to serve as a reference. Small portions of this solution were analyzed by gas chromatography. Yields were calculated from comparison of peak area ratios with those from mixtures of known composition. The results are summarized in Table 1.

TABLE 1

REACTIONS OF TETRAKIS(DIMETHOXYBORYL)METHANE, BASE, AND METHYL IODIDE

Solvent	Base	CH_3I (moles)	Temp.	Mode of addition	Total yield (%)	Mole ratio mono/di-Me[a]
THF	1 LiOMe	1	60°	A	48	57/43
THF	1 LiOMe	1	65°	B	47	56/44
THF	2 BuLi	5	−50°	B	40	31/69
THF	2 LiOMe	5	65°	B	39	30/70
$(MeOCH_2)_2$	2 LiOMe	5	89°	B	22	35/65
THF	1 LiOMe	5	65°[b]	A	23	67/33
THF	1 LiOMe	0.5	65°	B	33[c]	69/31
THF	1 LiOMe	1[d]	60°	A	27	66/34
MeOH	1 LiOMe	5	0°	A	6	63/37
MeOH	1 LiOMe	5	65°	A	4	67/33

[a] "Mono" is $CH_3C(BO_2C_2H_4)_3$, (VII), "di" is $(CH_3)_2C(BO_2C_2H_4)_2$, (VIII). [b] Refluxed 6 h (instead of 15 min). [c] 66% based on actual limiting reagent, MeI. [d] Me_2SO_4 used in place of MeI.

Bis(1,3,2-dioxaborol-2-yl)methane (IX)

This was obtained as a by-product of the reaction of ethyl iodide and tetrakis-(dimethoxyboryl)methane and was separated by gas chromatography, b.p. 58–61° (0.3 mm); NMR (CCl_4): τ 5.9 (s, 8, OCH_2) and τ 9.7 (broad s, 2, B_2CH_2). (Found: C, 38.30; H, 6.48; B, 13.60. $C_5H_{10}B_2O_4$ calcd.: C, 38.55; H, 6.47; B, 13.89%.)

2,2-Bis(1,3,2-dioxaborol-2-yl)-1,3-diphenylpropane (X)

This compound was prepared by the method described for $CH_3C(BO_2-C_2H_4)_3$ (VII) and $(CH_3)_2C(BO_2C_2H_4)_2$ (VIII), with benzyl bromide (1 mole) instead of methyl iodide as a reactant. Gas chromatography of the product (X) was carried out at 190° with a column of 20% DC 710 dimethylsiloxane/phenylmethylsiloxane copolymer on firebrick. The yield was 17%, b.p. 170–190° (1 mm); NMR (CCl_4): τ 2.6 (s, 10, C_6H_5), τ 6.1 (s, 8, OCH_2), and τ 7.1 (s, 1.6, CCH_2). The NMR integral values and elemental analyses imply contamination with a moderate amount of monobenzylated product, $PhCH_2C(BO_2C_2H_4)_3$. (Found: C, 65.81; H, 6.68; B, 6.36. $C_{19}H_{22}B_2O_4$ calcd.: C, 67.92; H, 6.60; B, 6.44%.)

3,3-Bis(1,3,2-dioxaborol-2-yl)pentane (XI)

Ethyl iodide was used in place of methyl iodide in the usual procedure, method A. Gas chromatography at 170° with a column of 20% SF 96 poly(dimethylsiloxane) on firebrick separated the product, yield 25%; NMR (CCl_4): τ 5.9 (s, 8, OCH_2), 8.4 (q, 4, CH_2), and 9.3 (t, 6, CH_3). (Found: C, 50.79; H, 8.45; B, 10.44. $C_7H_{18}B_2O_4$ calcd.: C, 51.02; H, 8.56; B, 10.21%.) The other expected product, 1,1,1-tris(1,3,2-dioxaborol-2-yl)propane, was not completely purified by gaschromatography but appeared to be present in 12% yield, 50% concentration, mixed with (XI) or a related compound, in a peak preceding that of (XI).

4,4-Bis(1,3,2-dioxaborol-2-yl)-1-butene (XIV)

A suspension of 1.08 g (0.02 mole) of ethanol-free lithium ethoxide in 32 ml of tetrahydrofuran was added in 10 min from a dropping funnel to a warm ($\sim$50°), stirred solution of 4.8 g (0.02 mole) of tris(dimethoxyboryl)methane and 2.51 g (0.02 mole) of freshly distilled allyl bromide in 30 ml of tetrahydrofuran. The exothermic reaction caused refluxing of the solution during the addition. The solution was refluxed 10 min longer, then treated with 0.7 ml of dimethoxyboron chloride. The solvent was removed under vacuum, the residue was treated with 4 ml of ethylene glycol and 20 ml of tetrahydrofuran and stirred 3 h, the solvent was again distilled under vacuum, and the residue was extracted with three 15-ml portions of ether, which were easily decanted from the syrupy phase. The ether extract was concentrated and distilled to yield 1.7 g (42%) of product (XIV), b.p. 80–90° (0.2 mm); IR (CCl_4): 1613 cm^{-1} (C=C), 1190–1370 (B–O bands); NMR (CCl_4): τ 4.3 (m, 1, =CH), 5.0–5.3 (m, 2, CH_2=), 5.9 (s, 8, OCH_2), 7.8 (m, 2, –CH_2–), and 9.2 (m, 1, CHB_2). (Found: C, 48.95; H, 7.26; B, 10.91. $C_8H_{14}B_2O_4$ calcd.: C, 49.06; H, 7.21; B, 11.05%.) Similar results were obtained when lithium methoxide instead of ethoxide was used as the base. When the lithium methoxide was added to the boronic ester first, followed by introduction of the allyl bromide, the yield was only 25%. An attempt was also made to isolate the methyl ester, 4,4-bis(dimethoxyboryl)-1-butene, by omitting the ethylene glycol treatment, but the yield of material boiling at 70–90° (0.5 mm) was only 12% and complete characterization was not attempted.

4,4-Bis(1,3,2-dioxaborol-2-yl)-1-butyne (XV)

Propargyl bromide was used in place of allyl bromide in the procedure described for the preparation of (XIV). The product (XV) was distilled, b.p. 98–103° (0.2 mm), yield 39%; NMR (CCl_4): τ 5.83 (s, 8, OCH_2), 7.67 (pair of doublets, J 2.5

and 7.5 Hz, 2, C≡CCH$_2$), 8.29 (t, $J=2.5$, HC≡C), and 9.00 (broadened t, $J=7.5$, 1, CHB$_2$). (Found: C, 49.62; H, 6.35; B, 11.12. C$_8$H$_{12}$B$_2$O$_4$ calcd.: C, 49.57; H, 6.24; B, 11.16%.)

1,1-Bis(1,3,2-dioxaborol-2-yl)pentane (XVI)

Butyl iodide was used in place of allyl bromide in the procedure described for (XIV). The prcduct (XVI) was obtained in 25% yield, b.p. 90–130° (0.3 mm), and was purified by gas chromatography at 225° on 20% DC 710 on firebrick. The analytical sample crystallized on cooling, m.p. 24–25°; NMR (CCl$_4$): τ 5.9 (s, 8, OCH$_2$), 8.3–9.8 (m, 10, C$_4$H$_9$CHB$_2$). (Found: C, 51.23; H, 8.33; B, 10.41. C$_9$H$_{18}$B$_2$O$_4$ calcd.: C, 51.02; H, 8.56; B, 10.21%.)

1,1-Bis(1,3,2-dioxaborol-2-yl)-2-phenylethane (XVII)

Tris(1,3,2-dioxaborol-2-yl)methane, 4.8 g, m.p. 170–172°, prepared from tris-(dimethoxyboryl)methane and ethylene glycol in tetrahydrofuran[7], was dissolved in the minimum amount of tetrahydrofuran, cooled to 0°, and stirred while 13.4 ml of 1.6 M methyllithium in ether was added dropwise. Benzyl bromide, 3.7 g, was added dropwise in 5 min at 0°, and the mixture was then stirred ∼3 h at room temperature. Distillation yielded 2.2 g (40%) of the product (XVII), b.p. 90–120° (0.1 mm), NMR identical to that previously reported[5].

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)ethane (XVIII)

Tris(dimethoxyboryl)methane (XII) was substituted for the tetraborylmethane (I) in the usual procedure (method A) for reaction with methyl iodide. Instead of the ethylene glycol ester, the methyl ester was distilled in 5% yield, then treated with anhydrous pinacol to form the product (XVIII), which was purified by gas chromatography at 210° on 20% SF 96 on firebrick. (Found: C, 59.40; H, 10.28; B, 7.51. C$_{14}$H$_{28}$B$_2$O$_4$ calcd.: C, 59.62; H, 10.01; B, 7.67%.)

1,1,6,6-Tetrakis(1,3,2-dioxaborol-2-yl)-3-hexyne (XIX)

1,4-Dibromo-2-butyne was used in place of allyl bromide in the procedure described for the preparation of (XIV). The crude product was obtained as an oil in 10% yield by distillation, b.p. 140–160° (0.1 mm). Crystallization from tetrahydrofuran and recrystallization from carbon tetrachloride gave 3% of pure (XIX), m.p. 148–151°; NMR (CDCl$_3$): τ 5.85 (s, 16, OCH$_2$), 7.7 (broadened d, 4, C≡CCH$_2$), and 9.0 (broadened t, 2, CHB$_2$). (Found: C, 46.53; H, 6.14; B, 11.72. C$_{14}$H$_{22}$B$_4$O$_6$ calcd.: C, 46.50; H, 6.13; B, 11.97%.)

Methyl 3,3-bis(1,3,2-dioxaborol-2-yl)propanoate (XX)

Methyl bromoacetate was used in place of allyl bromide in the procedure described for preparation of (XIV). The product (XX) crystallized when the ether solution was concentrated, yield 35%; NMR (CCl$_4$): τ 5.80 (s, 8, OCH$_2$), 6.34 (s, 3, OCH$_3$), 7.37 (d, 2, CH$_2$CO$_2$), and 8.75 (broadened t, 1, CHB$_2$). The analytical sample was recrystallized from carbon tetrachloride, m.p. 99.5–100.5°. (Found: C, 42.23; H, 6.26; B, 9.33. C$_8$H$_{14}$B$_2$O$_6$ calcd.: C, 42.17; H, 6.19; B, 9.50%.)

1-(1,3,2-Dioxaborol-2-yl)-2-methyl-3-chloropropene (XXI)

A suspension of 1.37 g of ethanol-free lithium ethoxide in 20 ml of tetrahydro-

furan was added in several portions to a stirred solution of 2.44 g of chloroacetone and 6.1 g of tris(dimethoxyboryl)methane in 30 ml of tetrahydrofuran at $\sim 40°$. The resulting solution was stirred at reflux 20 min, then acidified with 1.9 ml of dimethoxy-boron chloride. The solvent was distilled at 1 mm and the residue was treated with 4.5 ml of ethylene glycol and 20 ml of tetrahydrofuran. The mixture was stirred 3 h, the solvents were removed under vacuum, the residue was extracted with four 15-ml portions of ether, and the ether extract was concentrated and distilled to yield 3.3 g (78 %) of a $\sim 50/50$ mixture of cis- and trans-isomers of (XXI), b.p. 47–50° (0.2 mm); NMR (CCl_4): τ 4.61 and 4.73 (d, $J \sim 1$ Hz, 1, C=CH), 5.40 and 6.05 (s, 2, $ClCH_2$), 5.64 (s, 4, OCH_2), and 8.03 and 8.05 (d, $J \sim 1$, 3, CCH_3). Gas chromatography on 20% DC 710 on firebrick at 190° failed to separate the isomers but yielded an analytical sample of the mixture. (Found: C, 44.71; H, 6.44; B, 6.81; Cl, 21.83. Calcd. for $C_6H_{10}BClO_2$: C, 44.92; H, 6.34; B, 6.74; Cl, 22.10%.)

Tris(4.4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)methane (XXII)

A slight excess of pinacol (anhydrous) was added to a solution of tris(di-methoxyboryl)methane (XII). The mixture was stirred a few hours and concentrated under vacuum. The excess pinacol was removed by sublimation at 48° (0.1 mm) and the product (XXII) was sublimed at 100–110° (0.1 mm), m.p. 176–178°; NMR (CCl_4): τ 8.8 (s, 36, CCH_3) and 9.7 broad s, 1, B_3CH). (Found: C, 57.77; H, 9.27; B, 8.03. $C_{19}H_{37}B_3O_6$ calcd.: C, 57.93; H, 9.47; B, 8.23%.)

Bis(dimethoxyboryl)methoxymethane (XXIII)

The general procedure described previously for the preparation of octamethyl methanetetraboronate[1] (I) was followed with 50.4 g of (0.49 mole) dichloromethyl methyl ether, 1.76 g-atom of lithium, 0.92 mole of dimethoxyboron chloride, 500 ml of tetrahydrofuran, and 230 ml of trimethyl borate. The yield of (XXIII) was 4.7 g (6%), b.p. 36–40° (0.1 mm); NMR (neat): τ 6.5 (s, 12, $BOCH_3$), 6.8 (s, 3, $COCH_3$), and 8.5 (broad s, 1, CH). (Found: C, 38.07; H, 8.23; B, 11.28. $C_6H_{16}B_2O_5$ calcd.: C, 37.96; H, 8.50; B, 11.40%.)

REFERENCES

1 R. B. CASTLE AND D. S. MATTESON, J. Amer. Chem. Soc., 90 (1968) 2194; J. Organometal. Chem., 20 (1969) 19.
2 D. S. MATTESON AND P. B. TRIPATHY, J. Organometal. Chem., 21 (1970) P6.
3 D. S. MATTESON AND G. L. LARSON, J. Amer. Chem. Soc., 91 (1969) 6541.
4 G. ZWEIFEL AND H. ARZOUMANIAN, J. Amer. Chem. Soc., 89 (1967) 291.
5 D. J. PASTO, J. CHOW AND S. K. ARORA, Tetrahedron Lett., (1967) 723; Tetrahedron, 25 (1969) 1557.
6 D. S. MATTESON AND J. G. SHDO, J. Org. Chem., 29 (1964) 2742.
7 D. S. MATTESON AND R. J. WILCSEK, unpublished results.
8 D. S. MATTESON AND T. C. CHENG, J. Organometal. Chem., 6 (1969) 100; J. Org. Chem., 33 (1968) 3055.