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METHANETETRABORONIC AND METHANETRIBORONIC ESTERS*,**

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SUMMARY

Octamethyl methanetetraboronate, $[(MeO)_2B]_4C$, has been prepared in > 100 g batches by the reaction of dimethoxyboron chloride and carbon tetrachloride with lithium in tetrahydrofuran. Analogous reactions have yielded the methanetriboronic esters $[(MeO)_2B]_3CH$, $[(MeO)_2B]_3C{-}C_6H_5$, and $[(MeO)_2B]_3C{-}CH_3$. and the methanediboronic esters $[(MeO)_2B]_2CH_2$ and $[(MeO)_2B]_2CHC_6H_5$. A preliminary survey of the properties of these compounds has been made.

INTRODUCTION

Tetrasubstituted methanes not only have appealing symmetry, but often show greatly enhanced reactivity resulting from neighboring group interactions. One need but reflect briefly on the contrast between $C(NO_2)_4$ and CH_3NO_2 or between $C(OCH_3)_4$ and CH_3OCH_3 to appreciate our motivation for synthesizing $C[B(OCH_3)_2]_4$.

Few methods are available for attaching two or more metallic atoms to the same carbon. The oldest is Sakurai's conversion of CH_2I_2 to $CH_2(HgI)_2$ (ref. 2), from which we have made $CH_2[B(OH)_2]_2$ (ref. 3). Hydroboration of a vinylboronic ester has led to $CH_3CH[B(OH)_2]_2$ (refs. 4 and 5), and *gem*-bis(dialkylboryl)alkanes from the dihydroboration of acetylenes are well established as reaction intermediates[6-8]. Analogous *gem*-dialuminum compounds are known[9]. However, we have been unable to prepare any 1,1,1-triborylethane by hydroboration of dibutyl acetyleneboronate[10]. A third approach is provided by lithium reagents, which can be prepared with two lithium atoms on the same carbon[11,12] or generated from tri- or tetrahalomethanes in the presence of trimethylsilyl chloride[13]. This last approach, used by Merker and Scott to prepare $C(SiMe_3)_4$ and related compounds[13], served as a model for our synthesis of $C[B(OMe)_2]_4$.

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SYNTHESIS

Possible variables in the adaptation of the Merker and Scott synthesis[13] to boron compounds include the choice of metal (lithium or magnesium), carbon halide (chloride or bromide), solvent, source of boron, reaction temperature, order of mixing reagents, and method of isolating the product. In one early attempt, we added carbon tetrabromide slowly to $(Me_2N)_2BCl$ and magnesium in refluxing tetrahydrofuran. Subsequent experience has indicated that every one of these choices except the solvent was wrong, each sufficiently so to spoil the result by itself, and it is no wonder that intractable tar resulted. We began to make progress when we followed a lead provided by Gilman and Smith, who observed that lower temperatures improve the yields of $(Me_3Si)_4Si$ from Me_3SiCl, $SiCl_4$, and lithium[14]. Our problem was further simplified by choosing tetramethyl methanediboronate*, $[(MeO)_2B]_2CH_2$, as our initial synthetic goal, since methanediboronic acid[3] and related esters[5] had already been made and the conditions required for their survival were known.

Slow addition of methylene chloride to a stirred suspension of lithium dispersion (50% Li in hexane) in a mixture of trimethyl borate and tetrahydrofuran at 0° resulted in highly exothermic consumption of the lithium. The yield of distilled tetramethyl methanediboronate was only 8%, but increased to 28% when the reaction was carried out at −25°.

$$CH_2Cl_2 + 4\,Li + 4\,(MeO)_3B \xrightarrow{THF} [(MeO)_2B]_2CH_2 + 2\,LiCl + 2\,LiB(OMe)_4$$

The reaction is written as if the lithium methoxide produced complexes with excess methyl borate to form $LiB(OMe)_4$, but it might also form a nonvolatile salt with the methanediboronic ester. However, the yield was not improved by addition of aqueous acid, extraction with butanol, and distillation of the butyl ester.

Tetrahydrofuran was found to be essential to the reaction. The lithium did not react with methylene chloride in trimethyl borate alone or in diethyl ether, even at reflux.

The first step of the desired process is reaction of the lithium with methylene chloride, not methyl borate. After induction periods of a few minutes at reflux or hours at room temperature, trimethyl borate alone or in THF does react exothermically with lithium to produce an amorphous black precipitate which is inert toward methylene chloride and will react moderately vigorously with water. The nature of this material was not investigated.

The reaction of α,α-dichlorotoluene with methyl borate and lithium in THF yielded tetramethyl phenylmethanediboronate, $[(MeO)_2B]_2CHPh$, but attempts to extend this reaction to α,α,α-trichlorotoluene or carbon tetrachloride led only to undistillable tarry residues. It seemed likely that the lithium methoxide produced in the reaction might be catalyzing polymerization, and that a suitable Lewis acid could prevent this problem.

Dimethoxyboron chloride was the obvious choice, and it worked. In the procedure which has evolved from numerous trials, a mixture of carbon tetrachloride, dimethoxyboron chloride (~ 10% excess), and trimethyl borate is added dropwise to

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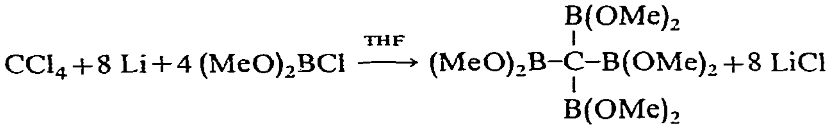
* According to rules recently proposed by an American Chemical Society committee on nomenclature, $[(MeO)_2B]_2CH_2$ is named bis(dimethoxyboryl)methane and $[(MeO)_2B]_4C$ is tetrakis(dimethoxyboryl)-methane.

a stirred suspension of lithium dispersion in tetrahydrofuran at about −30°. The reaction is highly exothermic at first, less so later, and is not completed until the mixture is warmed after the addition period. Distillation yields 50–60% of crystalline octamethyl methanetetraboronate, which on a scale convenient for laboratory preparations amounts to 120–150 g.



$$CCl_4 + 8\,Li + 4\,(MeO)_2BCl \xrightarrow{THF} (MeO)_2B\text{–}\underset{B(OMe)_2}{\overset{B(OMe)_2}{C}}\text{–}B(OMe)_2 + 8\,LiCl$$

Errors which we have encountered include the following. If there is even a slight deficiency of dimethoxyboron chloride, the product polymerizes during attempted distillation. Deficiency may arise if some hexane has evaporated from a previously opened jar of 50% lithium dispersion, resulting in inadvertent use of too much lithium. Alternatively, deficiency results if the dimethoxyboron chloride is distilled before use, which causes partial decomposition to trimethyl borate, methyl chloride, and perhaps other inert contaminants. The dimethoxyboron chloride should be freshly prepared merely by mixing the calculated amounts of boron trichloride and trimethyl borate below −40°.

Tetrahydrofuran cleavage, possibly in part by lithium reagent intermediates but probably mainly by dimethoxyboron chloride, is another problem. High-boiling boronic ester by-products result, and their NMR spectra reveal chlorobutoxy or related groups. It is probably important to avoid a large excess of dimethoxyboron chloride, and reactions have failed to yield methyl esters when this reagent was placed in the reaction flask with the lithium and THF prior to addition of methylene chloride, or when THF was used to dilute the dimethoxyboron chloride in the addition funnel. We tried reducing the amount of THF in the solvent, using trimethyl borate as a diluent instead, but this proved unsatisfactory. The reaction of the lithium tended to stop, with sudden temperature rises on resumption, sometimes an alarming 20–40° rise in 10–30 sec. In one instance, all the lithium appeared to have reacted and the mixture was left at room temperature, but a subsequent exothermic reaction led to vigorous refluxing, separation of a ground-joint connection, and spontaneous ignition of the mixture on contact with air. The problem of sudden exothermic outbursts is much reduced by the use of a large amount of THF. We also tried to reduce THF cleavage by introducing methanol after reaction of the lithium to destroy any excess dimethoxyboron chloride, a procedure which caused no harm in the preparation of $(MeO)_2BCH_2B(OMe)_2$ but caused deboronation of $[(MeO)_2B]_2CHPh$ to $(MeO)_2BCH_2Ph$ and was therefore abandoned.

Some THF cleavage may occur during the final reflux period because of the necessary small excess of dimethoxyboron chloride. However, results were erratic if the mixture was kept cold until after filtration of the LiCl and vacuum distillation of the solvents. Some exothermic reaction occurs when the mixture is warmed. Perhaps reaction of $[(MeO)_2B]_3CLi$ with $ClB(OMe)_2$, the last stage of the process, is relatively sluggish, and premature removal of the $ClB(OMe)_2$ may leave a surplus of base to catalyze polymerization of the product.

No lithium metal remains after a normal reaction. However, when we have encountered left-over lithium in exploratory reactions or as a result of miscalculation.

it has been pyrophoric. The potential hazard during filtration of the LiCl is reduced by blanketing the Büchner funnel with a stream of argon.

No methanediboronic ester was obtained when methylene bromide was used instead of methylene chloride, even though the lithium appeared to react normally. The use of dimethoxyboron chloride caused only a modest improvement in the yield of methanediboronic ester from methylene chloride.

The successful synthetic procedure converts chloroform to hexamethyl methanetriboronate, $[(MeO)_2B]_3CH$, in 35% yield. α,α,α-Trichlorotoluene has been converted to hexamethyl phenylmethanetriboronate, $[(MeO)_2B]_3CC_6H_5$. Side reactions evidently take a larger toll than in the tetraboronic ester preparation. The poorest yield, 12%, was obtained in the preparation of hexamethyl ethane-1,1,1-triboronate, $[(MeO)_2B]_3CCH_3$, from 1,1,1-trichloroethane, in which dehydrochlorination is another possible side reaction.

PROPERTIES

Typical acyclic boronic esters are liquids, but octamethyl methanetetraboronate, $[(MeO)_2B]_4C$, is a crystalline solid (m.p. 78°) as a consequence of its high symmetry. It is nonpolar and very soluble in hydrocarbons, and is most easily recrystallized from methanol, in which its solubility is about 20% at 25°. It will also crystallize from dimethyl sulfoxide. It can be transferred and weighed in air, provided the operations are done reasonably promptly. Atmospheric moisture does attack the crystal surfaces visibly after a few minutes exposure. The triboronic esters $[(MeO)_2B]_3CH$ and $[(MeO)_2B]_3CPh$ are lower-melting solids with generally similar properties, though they are attacked more rapidly by air.

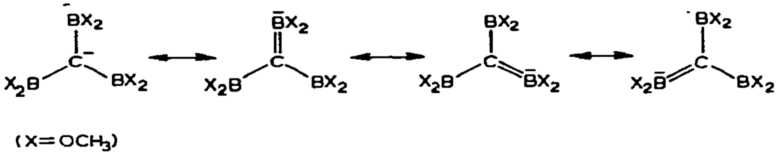
$[(MeO)_2B]_4C$ appears to be stable indefinitely in methanol, surviving an hour of refluxing with little if any loss. Exchange of methoxy groups with the solvent is surprisingly slow on the NMR time scale, the B-methoxy protons apprearing as a sharp singlet 0.13 ppm downfield from the solvent methoxy peak, even in the presence of 0.05 *M* sodium methoxide. However, the methoxide does catalyze deboronation to methanediboronic ester in a period of a few hours at 25°, easily followed by disappearance of the separate B-methoxy peak and the appearance of the broadened $B{-}CH_2{-}B$ peak near τ 10.0.

$$[(MeO)_2B]_4C + 2\,MeOH \xrightarrow{MeO^-} [(MeO)_2B]_2CH_2 + 2\,(MeO)_3B$$

Methanetriboronic ester, undoubtedly an intermediate, did not build up to an observable concentration.

Water does not dissolve $[(MeO)_2B]_4C$ as such, but gradually erodes the crystals by hydrolytic attack. A sample of 1–2 mm crystals required over a half hour to dissolve at 30°, and in this time degraded completely to methanol, boric acid, and methanediboronic acid, $CH_2[B(OH)_2]_2$, readily recognized by the NMR peak near τ 9.6. We have precipitated material having the approximate composition of methanetetraboronic acid, $C[B(OH)_2]_4$, from moist THF with methylene chloride, but we were unable to purify this hydrolytically unstable compound. The contrast between the stability of $[(MeO)_2B]_4C$ in methanol and the instability of $[(HO)_2B]_4C$ in water probably results from steric factors and the relative ionizing powers of the solvents.

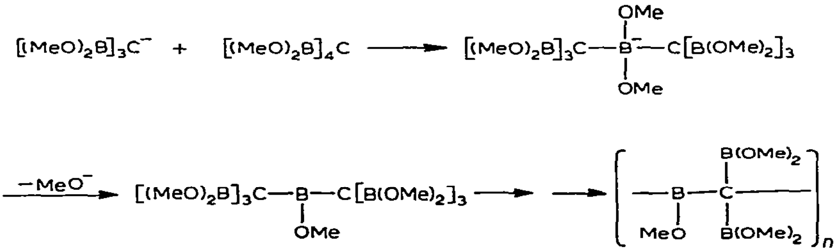
The interesting probable intermediate in the methoxide-catalyzed methanolysis of $[(MeO)_2B]_4C$ is the tris(dimethoxyboryl)methide ion, $[(MeO)_2B]_3C^-$, which could be formed by loss of $B(OMe)_3$ from $[(MeO)_2B]_3C{-}B(OMe)_3^-$.



Proton capture by the carbanion might be concerted with boron loss, as in the stereoselective deuterodeboronation of a benzylic boronic acid in $NaOD/D_2O$[15]. Even so, the transition state should have a high degree of carbanion character and considerable stabilization by delocalization of the electron pair from carbon to the boron atoms.

Proton capture by the carbanion $[(MeO)_2B]_3C^-$ in methanol is likely to be not only rapid but irreversible, that is, $[(MeO)_2B]_3CH$ is expected to lose a boron atom rather than a proton on attack by methoxide. We therefore attempted to prepare and trap triborylmethide and diborylmethide ions in aprotic media. $[(MeO)_2B]_4C$ was treated with one equivalent of methylmagnesium bromide in THF, then refluxed with benzyl bromide. Dibenzylation of a significant fraction occurred, even though some unchanged $[(MeO)_2B]_4C$ remained. Treatment of the high-boiling fraction and residue with hydrogen peroxide yielded 1% of phenylacetic acid, from $PhCH_2C[B(OMe)_2]_3$, and nearly 10% of dibenzyl ketone 2,4-dinitrophenylhydrazone, from $(PhCH_2)_2C[B(OMe)_2]_2$. This type of alkylation is currently being investigated in this laboratory, and further discussion of this exploratory trial is not warranted. We also tested the reaction of $[(MeO)_2B]_3CH$ with methylmagnesium bromide followed by benzaldehyde. Hydrolytic work-up yielded 8% of β-styreneboronic acid, $PhCH{=}CHB(OH)_2$. The reaction is analogous to the previously described condensation of 1,1-diborylalkanes with aldehydes[7]. We have recently found conditions for the condensation of methanetetraboronic ester with ketones or aldehydes to produce alkene-1,1-diboronic esters, $R_2C{=}C[B(OMe)_2]_2$, in moderately good yields[16].

In the absence of other electrophiles, or as a side reaction in their presence, the carbanion $[(MeO)_2B]_3C^-$ might attack one of the boron atoms of methanetetraboronic ester.



The resulting adduct might then lose methoxide, add another carbanion, and continue the process to form a polymer with a C–B–C–B... backbone. This polymer may be thought of as being derived from a carbon–boron double-bonded monomer, $[(MeO)_2B]_2C{=}B{-}OMe$, which would arise from methanetetraboronic ester by elimination of trimethyl borate, though it does not seem likely that this monomer is an actual intermediate in base-catalyzed polymerization.

Polymer is certainly a usual product of the treatment of either methanetetraboronic or triboronic ester with bases in aprotic media. Polymerization has frustrated our attempts to carry out a number of interesting reactions, for example, the exchange of hydride ligands for methoxy. When $[(MeO)_2B]_3CH$ was heated with an equimolar amount of (trimethylamine)borane, one mole of trimethyl borate distilled, followed by the unchanged amine-borane, and a polymeric residue having a broadened boronic ester-like IR spectrum remained. In the absence of the basic catalyst, methanetriboronic ester distilled without decomposition at atmospheric pressure.

Acid-catalyzed polymerization of methanetetraboronic ester derivatives also occurs. Treatment of the boronic ester with boron trichloride at 0° followed by attempted distillation has yielded only undistillable residue, even though $C(BCl_2)_4$ has been synthesized elsewhere by a different route and is fairly stable[17]. The polymer might contain B–C–B or B–O–B linkages or both and is probably cross-linked, being insoluble in inert solvents such as chloroform but soluble in water. The polymers from base catalysis have generally similar properties.

Distillable product was obtained when $[(MeO)_2B]_3CH$ was treated with BCl_3 at 0°, but there was considerable polymerization as well and complete replacement of the methoxy groups to form $HC(BCl_2)_3$ was not achieved.

Direct electrophilic displacement of the boron atoms from $[(MeO)_2B]_4C$ by mercuric acetate in refluxing ethanol has yielded $C(HgOAc)_4$. A carbanion is not a possible intermediate under these acidic conditions. Separation of the $C(HgOAc)_4$ from mercuric and mercurous acetates has been accomplished only recently and will be published elsewhere[18].

EXPERIMENTAL

Octamethyl methanetetraboronate

Dimethoxyboron chloride was prepared by adding 237 g of trimethyl borate* dropwise to 134 g of boron trichloride* stirred under argon at −70 to −30°. A 3-liter 3-neck flask was equipped with a pressure-equalized dropping funnel, an efficient Teflon-paddle stirrer, a reflux condenser having a low-temperature thermometer** suspended from a wire inside to reach the flask contents and having an argon supply connected to the top, and a large Dry Ice/acetone bath supported by a jack for rapid height adjustment. In the flask was placed 90 g (6.4 g-atoms) of 50% lithium dispersion in hexane*** and 1.5 l of tetrahydrofuran*. The dimethoxyboron chloride (3.4 moles) was mixed with 125 g (0.81 mole) of carbon tetrachloride* and 100 ml of trimethyl borate* and placed in the dropping funnel. The contents of the flask were stirred at −40 to −30° while the dimethoxyboron chloride solution was added dropwise over a period of 1.5–2 h. The very exothermic reaction began at once and was kept in the specified temperature range by adjusting the rate of addition and the height of the

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* Commercial reagent grade chemicals were used without further purification. The BCl_3 was taken from the cylinder as a gas and condensed. Redistilling the THF from $LiAlH_4$ did not improve the yield.

** The usual −100 to +50° thermometer withstands the final reflux at 65°.

*** Foote Mineral Co., low sodium, particle size 70–100 μm, shaken vigorously before use and weighed rapidly in air, lithium content assumed to be 45 g.

cooling bath. The reaction mixture turned brown and lithium salts precipitated. When the addition was completed, the thick slurry was warmed and refluxed 0.5 h with continued stirring. A sudden 5–10° temperature rise was usually observed between -10 and $+10°$ and a second more gradual exothermic stage occurred between 30° and reflux. The mixture was cooled in an ice bath and filtered rapidly through a 30 to 40-cm Büchner funnel blanketed with a stream of argon to reduce moisture contamination and fire hazard. The white or light gray lithium salts were rinsed with 200–400 ml of ether, and the combined filtrate was concentrated by rapid vacuum distillation. The lithium salts were disposed of promptly by spooning small portions into a large volume of running water. (*Caution*: If the filter cake contains dark gray unreacted lithium, which normally occurs only if an error has been made in weighing out the reagents, spontaneous ignition may be expected as soon as the solvent evaporates, 5–30 min.) The residue from concentration of the filtrate was a solid or a viscous liquid. It was distilled rapidly at 90–120° (0.1–1.0 mm) into a receiver designed not to be plugged by solid condensate (for example, a slightly curved tube 4 cm in diameter and 70 cm long). Some loss of vacuum and overheating occurred as a result of slight decomposition to trimethyl borate or other volatile by-products. (*Caution*: Distillation should be stopped as soon as the rate decreases sharply and the head temperature begins to fall. If strongly overheated, the residue decomposes semi-explosively, forcing ground-joint connections apart.) The collected solid $[(MeO)_2B]_4C$ was transferred by melting under argon, yield 125–147 g (50–60%), m.p. 70–74°, may be redistilled at 70–85° (0.1 mm) with negligible loss: IR* (CCl_4): 3.39 and 3.51 (C–H), 6.83, 6.93 (sh), 7.5–7.8, 8.0–8.1, and 8.6 (B–O), 9.92 (C–O), and weaker bands at 9.28, 12.03, 14.9, and 15.1 μm (unassigned); NMR (CCl_4): τ 6.55 (s, CH_3O). The analytical sample was recrystallized from methanol and sublimed, m.p. 76–78°. (Found**: C, 35.55; H, 8.11; B, 14.01. $C_9H_{24}B_4O_8$ calcd.: C, 35.61; H, 7.97; B, 14.25%.)

Hexamethyl methanetriboronate

The procedure described in the preceding paragraph was followed, substituting chloroform (95 g, 0.8 mole) for the carbon tetrachloride and using $\frac{3}{4}$ the quantities of the other reagents. The $[(MeO)_2B]_3CH$ distilled at 58–63° (0.1 mm) in 25–35% yield, m.p. ~45°. Liquid impurities were present which could be removed only by repeated distillation or sublimation, which gave long needles: m.p. 47–48°; IR (CCl_4): 3.39 and 3.50 (C–H), 6.75–6.8, 6.89, 7.3–8.0, and 8.5(B–O), 9.90(C–O), and weaker bands at 9.00, 9.43, 9.63, 10.2, and 15.5 μm (unassigned); NMR ($CDCl_3$): τ 6.48 (s, 18, CH_3O), 9.54 (broad singlet, 1, B_3CH). (Found: C, 36.45; H, 7.93; B, 13.91. $C_7H_{19}B_3O_6$ calcd.: C, 36.29; H, 8.27; B, 14.01%.)

Hexamethyl phenylmethanetriboronate

The standard procedure was followed with the calculated proportion of α,α,α-trichlorotoluene in place of carbon tetrachloride. The $[(MeO)_2B]_3CPh$ distilled at 85–87° (0.1 mm), yield 20%. One sample crystallized after cooling to $-78°$ and

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* IR curves of all new boronic esters reported here are reproduced in R. B. Castle's Ph.D. thesis, Washington State University, 1969, p. 58–65, available from University Microfilms, Ann Arbor, Mich. 48106. However, the $[(MeO)_2B]_3CH$ sample recorded there was grossly impure.

** Analyses by Galbraith Laboratories, Knoxville, Tenn.

warming, m.p. ~35°, but other batches remained viscous oils. IR (neat): 3.27 and 3.29 (Ph C–H), 3.40 and 3.51 (Me C–H), 6.31 (Ph C–C), 6.8–6.9, 7.3–8.1, and 8.6–8.7 (B–O), 9.97 (C–O), 13.50 and 14.33 (Ph C–H), and 9.43, 9.62, 11.1, 11.56, 12.0, 14.86, and 15.9 μm (weak, unassigned); NMR (CCl_4): τ 2.9 (s, 5, C_6H_5), 6.5 (s, 18, CH_3O). (Found: C, 51.03; H, 7.40; B, 10.25. $C_{13}H_{23}B_3O_6$ calcd.: C, 50.73; H, 7.54; B, 10.55%.)

Hexamethyl ethane-1,1,1-triboronate

1,1,1-Trichloroethane was used in the standard procedure and yielded 10–12% of $[(MeO)_2B]_3CCH_3$: b.p. 65–67° (0.1 mm); IR (neat): 3.39 and 3.50 (C–H), 6.82, 7.5–8.1, and 8.5–8.6 (B–O), 9.8 (C–O), and 9.08, 9.43, 10.51, 11.10, 12.45, 12.60, 14.83, and 15.6 μm (weak, unassigned): NMR (CCl_4): τ 6.53 (s, 18, CH_3O), 8.87 (s, 3, CH_3C). (Found: C, 39.36; H, 8.73; B, 13.17. $C_8H_{21}B_3O_6$ calcd.: C, 39.11; H, 8.62; B, 13.21%.)

Tetramethyl phenylmethanediboronate

α,α-Dichlorotoluene was used in the standard procedure and yielded 20% of $[(MeO)_2B]_2CHPh$: b.p. 58–59° (0.1 mm); IR (neat): 3.26, 3.28, 3.32, 3.40, and 3.51 (C–H), 6.31 (Ph C–C), 6.8, 6.97, 7.4–8.0, and 8.6 (B–O), 9.95 (C–O), 13.71 and 14.37 (Ph C–H), and 8.3, 9.09, 9.39, 9.6, 9.8, 11.10, 11.89, 12.5, 13.33, and 15.18 μm (weak, unassigned); NMR (CCl_4): τ 2.6 (s, 5, C_6H_5), 6.5 (s, 12, CH_3O), 7.7 (s, 1, PhB_2CH). (Found: C, 56.02; H, 7.63; B, 9.28. $C_{11}H_{18}B_2O_4$ calcd.: C, 56.01; H, 7.69; B, 9.17%.)

Tetramethyl methanediboronate

The usual procedure with methylene chloride yielded 35% of $(MeO)_2BCH_2B(OMe)_2$: b.p. 48–52° (15 mm); IR (neat) 3.39 and 3.50 (C–H), 6.8, 6.91, 7.3–7.9, and 8.55 (B–O), 9.82 (C–O), and 9.00, 9.33, and 12.8–12.9 μm (unassigned); NMR (CCl_4) τ 6.5 (s, 12, CH_3O), 9.9 (broad singlet, 2, B_2CH_2). (Found: C, 37.34; H, 8.69; B, 13.42. $C_5H_{14}B_2O_4$ calcd.: C, 37.58; H, 8.53; B, 13.54%.) This compound was also prepared in 28% yield from a solution of 21.2 g of methylene chloride, 100 ml of trimethyl borate, and 25 ml of tetrahydrofuran added dropwise to 16 g of 50% lithium dispersion, 100 ml of trimethyl borate, and 50 ml of tetrahydrofuran stirred at −30° and worked up in the usual manner.

Methanolysis of octamethyl methanetetraboronate

To a solution of 0.21 g of $[(MeO)_2B]_4C$ in 1.0 ml of methanol was added 3.3 mg of commercial sodium methoxide. The 60-MHz NMR spectrum of the solution showed a separate CH_3OB peak 8 Hz downfield from the methanol CH_3 peak both before and after addition of the methoxide. After 20 min at 25° a peak near τ 10.0 had appeared, with an intensity 1/230 that of the total methoxy protons. The relative intensity increased to 1/100 at 3.5 h, 1/80 at 6.5 h, and 1/77 at 24 h, and the separate CH_3OB peak gradually disappeared. The theoretical ratio for $[(MeO)_2B]_2CH_2$ is about 1/70 at complete conversion, and the crude data obtained correspond to a pseudo-first-order reaction with a half-life of 1–2 h. No substantial amount of $[(MeO)_2B]_3CH$ ever accumulated, since that would have shown a separate B_3CH peak about 0.3 ppm downfield from the B_2CH_2 peak. Because of the possibility of integration error, these data do not rigorously rule out $(MeO)_2BCH_3$ as the final product of methanolysis, though earlier data on ethane-1,1-diboronic acid in aqueous base[5] imply that the diboronic ester would not undergo rapid methanolysis.

Polymerization of hexamethyl methanetriboronate

Under nitrogen, 1.22 g of $[(MeO)_2B]_3CH$ and 1.26 g of trimethylamine borane were melted together and stirred in an oil bath at 165–175°. A low-boiling liquid, shown by IR to be trimethyl borate slightly contaminated with a B–H compound, distilled, 0.69 g. Vacuum sublimation yielded 1.03 g of unchanged trimethylamine borane. The polymeric residue showed a B–H band in the IR, presumably due to amine borane, and broad, almost undifferentiated absorption from 6.5–15 μm, strongest near 7 μm (B–O). In the absence of amine borane, $[(MeO)_2B]_3CH$ distilled ~180° without decomposition.

β-Styreneboronic acid

To a solution of 8.3 g of $[(MeO)_2B]_3CH$ in 25 ml of tetrahydrofuran stirred at 0° was added 12 ml of 3 *M* methylmagnesium bromide in 5 min. Then 5.5 ml of benzaldehyde was added and the solution was refluxed 12 h. The magnesium boronate salts which had precipitated were collected by filtration and treated with 25 ml of water and 3 ml of acetic acid. The boronic acid which crystallized was recrystallized from water: yield 0.43 g (8%); IR (KBr) 3.0 (O–H), 3.28, 3.31, 3.35, 3.46 (C–H), 6.30 (C=C), 7.3–7.6 (B–O), 13.35, 13.5 μm (Ph C–H), and other bands; m.p. 168–169°. (Found: C, 64.70; H, 6.03; B, 7.44. $C_8H_9BO_2$ calcd.: C, 64.93; H, 6.13; B, 7.31%.) Our m.p. differs considerably from the literature value[19], perhaps because of *cis–trans* isomerism. Another 2% of crude β-styreneboronic acid, m.p. 130–133°, was obtained when the filtrate from the reaction was distilled (30–80°, 0.1 mm) and hydrolyzed with water.

Reaction of hexamethyl methanetriboronate with boron trichloride

Approximately 20 ml of boron trichloride was condensed at −78° onto 5 g of $[(MeO)_2B]_3CH$ and the solution was allowed to stand 24 h at 0°. Distillation at 42–44° (0.1 mm) yielded 3.5 g of crude product, which was again treated with BCl_3 and redistilled, yield 2.3 g. The NMR spectrum showed that some methoxy groups remained. Reaction with water followed by titration with potassium hydroxide to the methyl red endpoint indicated 5.7 mmoles of HCl per 0.2831 g, which corresponds to replacement of about 80% of the methoxy groups by chloride.

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