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# TETRAMETALLOMETHANES CONTAINING ONE, TWO, OR THREE GROUP IV METAL ATOMS AND BORON*

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## SUMMARY

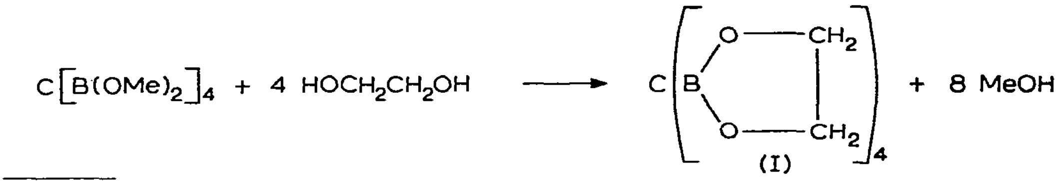
The propanediol methanetetraboronic ester, $C(BO_2C_3H_6)_4$, provides much better properties than the previously used methyl ester, $C[B(OMe)_2]_4$, for the synthesis of new tetrametallomethanes. Treatment with butyllithium yields the lithium salt $LiC(BO_2C_3H_6)_3$, which reacts with $Ph_3MCl$ to form $Ph_3MC(BO_2C_3H_6)_3$, where M is Ge, Sn, or Pb. Repetition of these processes leads to $(Ph_3M)_2C(BO_2C_3H_6)_2$, where the Group IV metals M may be the same or different. The series was extended to $(Ph_3Sn)_3CBO_2C_3H_6$, but the last boron atom resisted removal. Iodination of the appropriate lithium salt intermediates yielded $Ph_3SnCI(BO_2C_3H_6)_2$ and $(Ph_3Sn)_2CIBO_2C_3H_6$.

## INTRODUCTION

The synthesis of tin and lead derivatives of tetrakis(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, has been described in the preceding paper of this series, and the previous literature on tetrametallomethanes has been cited there[1]. In the present work, we have used a cyclic boronic ester function in the hope of getting better control over the reactions as well as more stable and easily crystallized products. These hopes have been realized and a considerable variety of tetrametallomethanes and trimetallohalomethanes can now be described.

## CYCLIC BORONIC ESTERS

We began by preparing the ethylene glycol ester, tetrakis(ethylenedioxyboryl)methane (I), from tetrakis(dimethoxyboryl)methane. The transesterification proceeded



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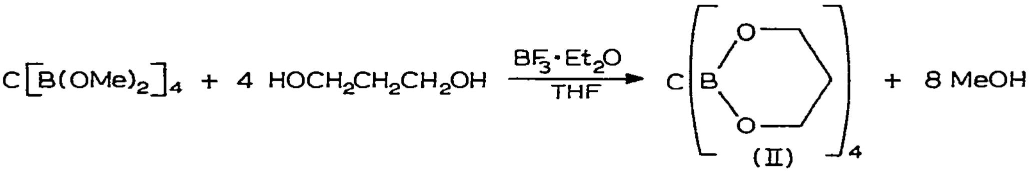
readily but the ethylene glycol ester (I) was practically insoluble in common ethereal solvents and consequently very difficult to use in reactions. The insolubility may be rationalized as a consequence of molecular rigidity and shape and the lack of any significant dipole moment that could interact with the solvent. (The methyl ester $C[B(OMe)_2]_4$ has a substantial dipole moment, 1.73 D, because the $B(OMe)_2$ groups have random orientations of the C–O bonds[2].)

We then decided to try a six-membered ring. Boronic esters of 2-methyl-2,4-pentanediol, $CH_3CHOHCH_2C(CH_3)_2OH$, have been reported to be stable and relatively inert[3], perhaps too inert for our purposes. 1,3-Propanediol boronic esters[4] seemed likely to have desirable properties, and we therefore transesterified $C[B(OMe)_2]_4$ with 1,3-propanediol and obtained tetrakis(trimethylenedioxyboryl)methane (II).



Fortunately, the first samples of $C[B(OMe)_2]_4$ used contained some impurity, probably a boron halide persisting from the synthetic process, and the transesterification proceeded smoothly. Later it was found that pure $C[B(OMe)_2]_4$ does not undergo transesterification with 1,3-propanediol but is degraded slowly to the protodeboronation products, $HC[B(OR)_2]_3$ and $H_2C[B(OR)_2]_2$ (as revealed by the NMR peaks near $\delta$ 0). An acid catalyst such as boron trifluoride etherate must be added in order to achieve transesterification*. Exchange of ligands on boronic esters is normally rapid[5], and this slow reaction in the tetraborylmethane series must result from severe steric hindrance. The mechanism of action of the acid catalyst is not known.

The propanediol ester (II) proved to be easily crystallized but soluble enough in tetrahydrofuran to permit further reactions, which was the desirable combination of properties sought.

## MONOSUBSTITUTION PRODUCTS

The first problem was to find an efficient way to convert the tetraborylmethane (II) to the corresponding lithium triborylmethide (IV). Butyllithium turned out to be convenient and effective. Our evidence suggests but does not prove that a *B*-butylated tetraborylmethane salt (III) may be an intermediate. We have recently obtained strong evidence that the species which reacts with electrophiles is the triborylmethide (IV)[6].

The test reaction for the success of formation of the triborylmethide salt (IV) was the conversion to the triphenylstannyl derivative (V) on treatment with triphenyltin chloride.

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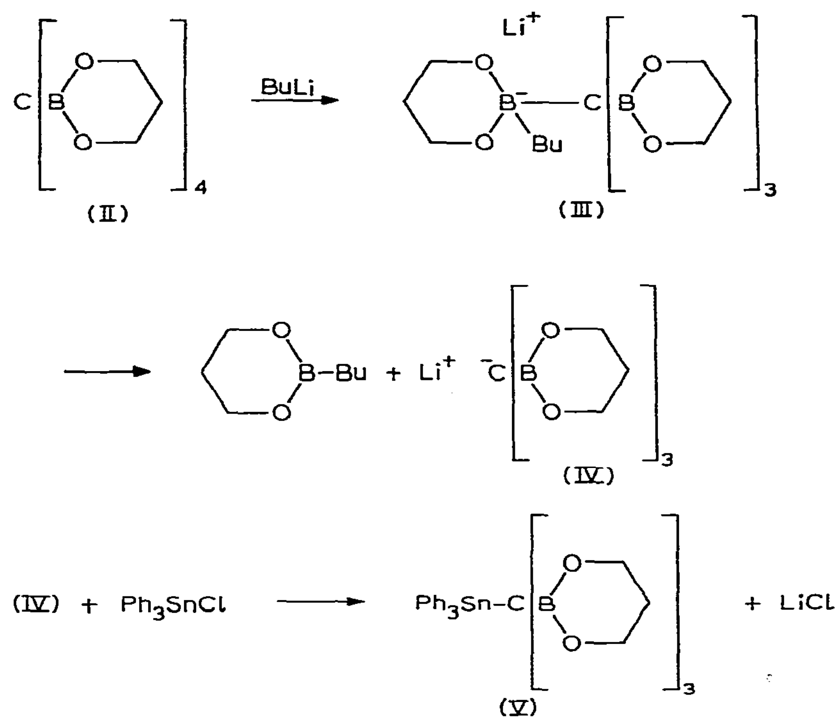
* We are indebted to Karl Arne and Leon Hagelee for this discovery.



(II) (III) (IV) (V)

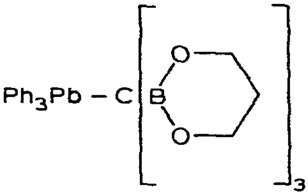
The procedure which gave the best yields of $Ph_3SnC(BO_2C_3H_6)_3$ (V) began with the addition of one equivalent of butyllithium to a suspension of $C(BO_2C_3H_6)_4$ (II) in tetrahydrofuran at −75°. The change in appearance to a fine precipitate suggested immediate reaction. The suspension was allowed to warm slowly to 0°, with apparent change to a much coarser crystalline solid, and the triphenyltin chloride was then added. The precipitate dissolved rapidly, and the product (V) was isolated by concentrating, dissolving the (V) in chloroform, and precipitating with ether, which gave 70% of (V).

When the initial addition of the butyllithium to the $C(BO_2C_3H_6)_4$ (II) was carried out at 0°, the yield of (V) was only 50%. These experiments were repeated several times. An explanation for the lower yield might be that liberation of the by-product boronic ester, $BuBO_2C_3H_6$, at 0° leads to consumption of butyllithium to form $Li^+Bu_2BO_2C_3H_6^-$. At −75°, persistence of the undissociated anion (III) without liberation of $BuBO_2C_3H_6$ would lead to more efficient utilization of butyllithium. However, the use of two equivalents of butyllithium under warmer conditions led to crude (V) which was difficult to purify.

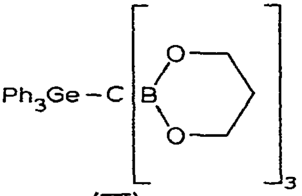
The major constituent of the precipitate from $C(BO_2C_3H_6)_4$ (II) and butyllithium is the triborylmethide salt (IV). The best samples obtained in this study were prepared from a half-equivalent of butyllithium added slowly to a tetrahydrofuran solution of (II) at 0°. These were pyrophoric in air but could be collected by filtration under argon and then reacted with triphenyltin chloride in tetrahydrofuran to yield 50% of $Ph_3SnC(BO_2C_3H_6)_3$ (IV). No nondestructive solvent for the precipitate could be found, but in perdeuterodimethyl sulfoxide the NMR spectra indicated that n-butyl groups were absent in some samples and present in others up to a value that could represent as much as about 50% (III) if that were the source, though $Bu_2BO_2C_3H_6$ seems more likely. There were some other complexities in the NMR spectra. In more recent work, we have obtained better samples and cleaner NMR spectra indicating that the precipitate is the triborylmethide (IV)[6].

Several other schemes were tried for producing the triborylmethide salt (IV), but none worked as well as the procedures already described. The lithium salt of *N,N*-dimethylethanolamine, $LiOCH_2CH_2N(CH_3)_2$, was tried in the hope of chelating the boron removed from the tetraborylmethane (II), but it failed to react with (II). Methylmagnesium bromide, which had been successfully used with $C[B(OMe)_2]_4$ in an alkylation[7], failed in an attempted conversion of $C(BO_2C_3H_6)_4$ (II) to the triphenyltin derivative (V).

Having found good conditions for preparing the triphenyltin compound (V), we turned to the lead and germanium analogs (VI) and (VII), which had not been obtained in the dimethoxyboryl series[1]. In the present series, (VI) and (VII) were obtained easily.



(VI)



(VII)

The lead compound (VI) decomposes to a tar in a sealed tube at 150° and turns black in refluxing toluene, but no identifiable products were isolated from these reactions. The tin and germanium compounds (V) and (VII) show no signs of thermal instability up to 200°, and (V) sublimes unchanged at 200° (0.1 mmHg).

In contrast to the other Group IV compounds, triphenylchlorosilane failed to yield any $Ph_3SiC(BO_2C_3H_6)_3$ on reaction with the triborylmethide (IV). Instead, an air-sensitive white paste which was insoluble in tetrahydrofuran was obtained.

Benzyl bromide likewise failed to react with the triborylmethide (IV) in the manner expected on the basis of previous[7,8] alkylations of $[(MeO)_2B]_3C^-$. Again, an intractable white paste was obtained, but this time its nature was revealed by carbonation with solid carbon dioxide, which converted the benzyllithium to phenylacetic acid in 58% yield.

$$\underset{\text{(IV)}}{Li^+\,{}^-C(BO_2C_3H_6)_3} + PhCH_2Br \rightarrow$$

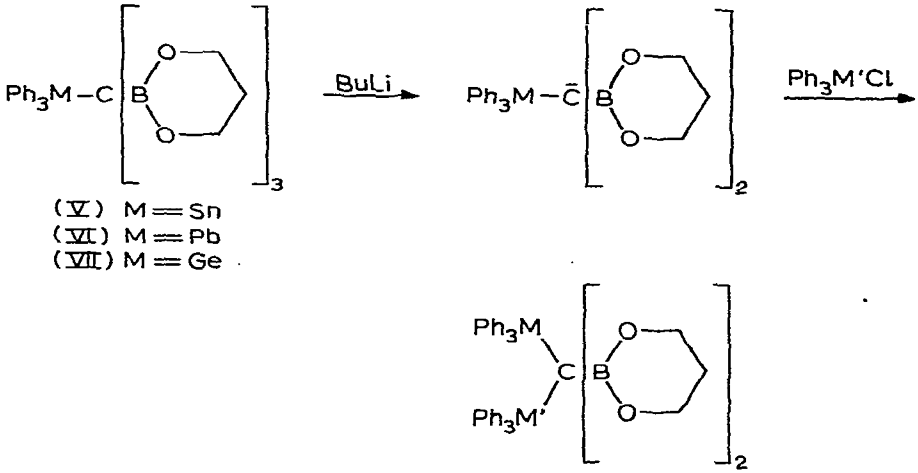
$$\rightarrow \underset{\text{(not isolated)}}{BrC(BO_2C_3H_6)_3} + PhCH_2Li \xrightarrow[\text{(2) }H_3O^+]{\text{(1) }CO_2} PhCH_2CO_2H$$

Perhaps triphenylchlorosilane undergoes a similar metal–halogen interchange to form $Ph_3SiLi$ and $ClC(BO_2C_3H_6)_3$, but this was not proved.

The halogen compounds such as $BrC(BO_2C_3H_6)_3$ are unstable under the conditions of their preparation and were not isolated in this work. Attempts were made to react the triborylmethide (IV) with bromine, and an impure crystalline solid which appeared to be $BrC(BO_2C_3H_6)_3$ was obtained several times, but it always decomposed to tar on attempted recrystallization. The problem of synthesizing $BrC[B(OR)_2]_3$ has been solved by the use of the pinacol boronic ester[9].

## DISUBSTITUTION PRODUCTS

In view of the previous results in the dimethoxyboryl series[1], we anticipated that compounds of the general formula $(Ph_3M)_2C(BO_2C_3H_6)_2$ could be made, though there might be some difficulty in preparing compounds having two different metal atoms M and M′ if base-catalyzed disproportionation of $Ph_3MC[B(OR)_2]_3$ occurred. No such difficulty developed. The ditin (VIII), dilead (IX), tin-lead (X), tin-germanium (XI), and lead-germanium (XII) compounds were obtained in good yields.



(V) M = Sn
(VI) M = Pb
(VII) M = Ge

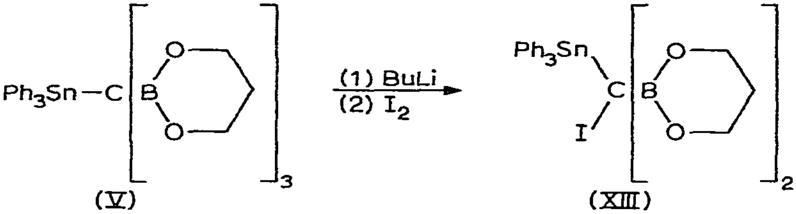
(VIII) M = M′ = Sn; (IX) M = M′ = Pb; (X) M = Sn, M′ = Pb
(XI) M = Sn, M′ = Ge or M = Ge, M′ = Sn
(XII) M = Pb, M′ = Ge or M = Ge, M′ = Pb

The best procedure for preparing the lithium derivatives of the $Ph_3MC(BO_2C_3H_6)_3$ series (V), (VI), and (VII) was the same as that which had been successful with $C(BO_2C_3H_6)_4$ (II), treatment with butyllithium at −75° followed by slow warming to 0°. However, the lithium salts $Li^+Ph_3MC^-(BO_2C_3H_6)_2$ remained in solution in tetrahydrofuran.

As might be expected, the ditin compound (VIII) and tin-lead compound (XI) have very similar physical properties. The melting points, infrared spectra, and NMR spectra of these two compounds are so similar that they cannot be used to prove the two are different compounds, though of course the elemental analyses did so. We also checked the possibility that the monotin compound (V) might disproportionate on treatment with butyllithium in tetrahydrofuran followed by dimethoxyboron chloride, but obtained only a 20% recovery of unchanged (V) and no ditin compound (VIII).

The tin–germanium and lead–germanium compounds (XI) and (XII) were first made from the monotin and monolead compounds (V) and (VI), but it proved difficult to separate (XI) and (XII) from triphenylgermanium chloride by crystallization from methanol. Reversing the order of substitution, starting from the monogermanium compound (VII) with triphenyltin or triphenyllead chloride, resulted in samples of (XI) and (XII) which were easily purified.

The substitution of $Ph_3M$ groups for boron increases the stability of the compounds toward atmospheric moisture and makes them generally easier to crystallize and purify. We were therefore encouraged to try to make a halogen derivative from $Ph_3SnC(BO_2C_3H_6)_3$ (V). We first tried bromination of $Li^+ Ph_3Sn\bar{C}(BO_2C_3H_6)_2$ but obtained only an intractable mixture. It appeared that the bromine might be cleaving phenyl groups from the tin. In contrast, iodine reacted readily to produce iodo(triphenylstannyl)bis(trimethylenedioxyboryl)methane (XIII), a stable crystalline solid.



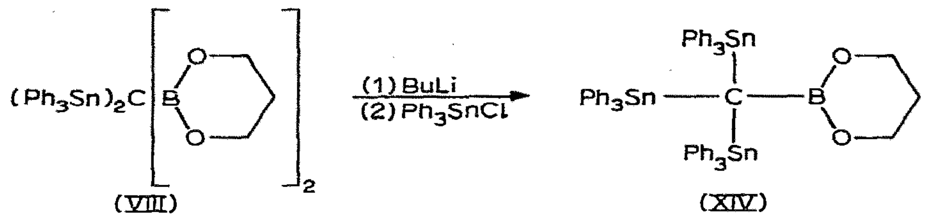
(V) (XIII)

Heating the tin–iodo compound (XIII) at 200° in cyclohexene in a bomb for 24 h led to a quantitative recovery of unchanged (XIII). The lead analog of (XIII) ought to decompose under such conditions, perhaps to form a diborylcyclopropane derivative of the alkene, but attempts to iodinate $Li^+ Ph_3Pb\bar{C}(BO_2C_3H_6)_2$ derived from (VI) did not yield the desired lead–iodo analog of (XIII), and it appeared that the iodine might be cleaving phenyl groups from the lead.

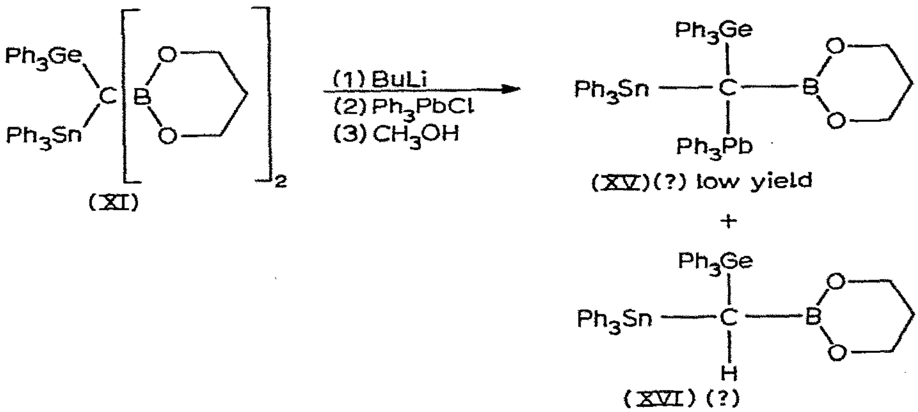
## TRISUBSTITUTION PRODUCTS

In previous work, we had found a definite tendency for replacement of boronic ester groups to stop at the stage where two remained[1,7,8]. For example, reaction of $C[B(OMe)_2]_4$ with lithium ethoxide followed by methyl iodide yields $CH_3C[B(OMe)_2]_3$ and $(CH_3)_2C[B(OMe)_2]_2$ but no evidence for $(CH_3)_3CB(OMe)_2$[8]. There was therefore no assurance that a boron atom could be removed from $(Ph_3M)_2C(BO_2C_3H_6)_2$ and replaced by a Group IV metal to form $(Ph_3M)_3CBO_2C_3H_6$. On the other hand, $Ph_3Sn\bar{C}R_2$ is isoelectronic with the antimony ylide $Ph_3SbCR_2$, and it is therefore conceivable that the tin atoms could assist the stability of the required carbanion intermediate.

The conversion of the ditin compound (VIII) to the tritin compound (IX) actually proceeded smoothly and routinely. Evidently the boron atom in the tritin compound (XIV) is extremely sterically hindered, and this boronic ester is so stable toward hydrolysis that the analytical sample was allowed to stand in air for a week without loss of purity.



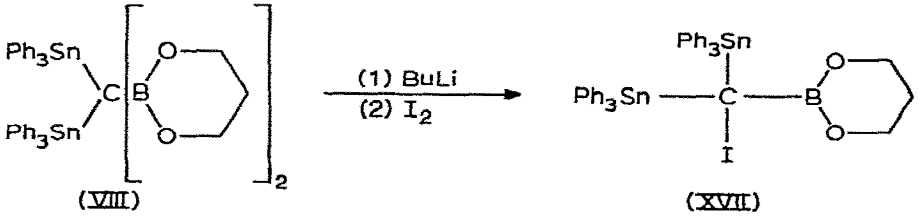
In contrast to the easy synthesis of the tritin compound (XIV), the germanium–tin–lead compound (XV) was obtained in very small yield at best and was not fully characterized.



The major product from the germanium–tin compound (XI) appeared from its NMR spectrum to be the simple protodeboronation product (XVI), though this was never purified and characterized. Thin layer chromatography yielded a small amount of material which showed the right NMR spectrum for the germanium–tin–lead compound (XV), but not enough was obtained for characterization. Attempts were also made to synthesize (XV) from the germanium–lead (XII) and tin–lead (X) compounds, but these also yielded mixtures which seemed to contain a large amount of simple protodeboronation product.

It is not immediately apparent why the tritin compound (XIV) should be so easy to make and the germanium–tin–lead compound (XV) so difficult. Steric hindrance might be greater in (XV) than in (XIV), or the carbon–lead bond of (XIV) might be vulnerable to some sort of cleavage.

Iodination of the carbanion from the ditin compound (VIII) proceeded readily to form the ditin–iodo compound (XVII).



Refluxing the ditin–iodo compound (XVII) with lithium methoxide in dimethoxyethane followed by treatment with methanol resulted in protodeboronation to $(Ph_3Sn)_2CHI$ (XVIII). Cyclohexene was included in the reaction mixture in the hope that the lithium compound $(Ph_3Sn)_2CILi$ might transfer the $(Ph_3Sn)_2C$ group to the double bond to form a cyclopropane, but no evidence for such a reaction was found. Since it appeared that the lithium methoxide was removing the boron atom from (XVII) to form the anion $(Ph_3Sn)CI^-$, an attempt was made to trap this anion by the addition of triphenyltin chloride, but this time the deiodination product, $(Ph_3Sn)_2CHBO_2C_3H_6$ (XIX), was obtained. A small amount of tris(triphenylstannyl)methane, $(Ph_3Sn)_3CH$, was also isolated from this reaction. There was not enough to purify for analysis, but the $Sn_3CH$ absorption in the NMR at $\delta$ 1.95 with satellite peaks having the right strength for three neighboring tin atoms is strong evidence for the structure. This work leaves many unresolved questions about what governs loss of iodine *versus* loss of boron from (XVII).

An attempt was made to react the lithium derivative of (VIII), $Li^+(Ph_3Sn)_2C^-BO_2C_3H_6$, with acetone or cyclopentanone, but the only compound isolated was the protodeboronation product, $(Ph_3Sn)_2CHBO_2C_3H_6$. It was not determined whether the proton source was the ketone or accidental moisture introduced during work-up.

We of course attempted to replace the last boronic ester group of the tritin compound (XIV), $(Ph_3Sn)_3CBO_2C_3H_6$, but this compound proved extremely resistant to base attack. Refluxing with lithium methoxide in methanol left (XIV) unchanged. Butyllithium appeared to react, and triphenyltin chloride was added, but the product was a mixture which still contained boron and was definitely not the desired $(Ph_3Sn)_4C$. Evidently the butyllithium attacks the protons of the phenyl groups in preference to the sterically hindered boron atom of (XIV).

## EXPERIMENTAL

All reactions were carried out under nitrogen. Tetrahydrofuran and 1,2-dimethoxyethane were distilled from lithium aluminum hydride. NMR spectra were taken on a Varian A-60 spectrometer and an external tetramethylsilane reference was used to avoid obscuring any peaks near $\delta$ 0[8]. NMR and IR spectra of selected compounds are reproduced in R. J. Wilcsek's Ph.D. thesis, 1973 (available from University Microfilms, Ann Arbor, Michigan). Microanalyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., or Galbraith Laboratories, Knoxville, Tenn.

### *Tetrakis(ethylenedioxyboryl)methane (I)*

A solution of 8.2 g of ethylene glycol in 10 ml of tetrahydrofuran was added to a solution of 10.0 g of tetrakis(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, in 100 ml of tetrahydrofuran. The product precipitated almost immediately, but the mixture was stirred overnight before filtration. The yield of (I) was 8.0 g (83%); m.p. 180–182°; NMR ($CDCl_3$) $\delta$ 4.23 (s, $-OCH_2-$). (Found: C, 36.75; H, 5.69; B, 14.60. $C_9H_{16}B_4O_8$ calcd.: C, 36.63; H, 5.45; B, 14.60%.)

### *Tetrakis(trimethylenedioxyboryl)methane (II)*

One hundred ml (1.3 moles) of 1,3-propanediol was added to a solution of

89.6 g (0.295 mole) of tetrakis(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, in 500 ml of tetrahydrofuran. Subsequent work has shown that about 1–3 ml of boron trifluoride etherate should be added to catalyze the reaction, which sometimes fails in the absence of a catalyst. The product began to crystallize after about 1 h. After stirring 48 h, the product was filtered and the mother liquor was concentrated and recrystallized from 100 ml of tetrahydrofuran, yielding a second crop as large as the first. The total yield of (II) was 76 g (73 %); m.p. 217–218° ; NMR ($CDCl_3$) $\delta$ 3.90 (t, 16, $-OC\underline{H}_2-$) and 2.10 (quintet, 8, $-CH_2C\underline{H}_2CH_2-$). (Found: C, 44.18; H, 6.92; B, 12.10. $C_{13}H_{24}B_4O_8$ calcd.: C, 44.42; H, 6.83; B, 12.30 %.)

*(Triphenylstannyl)tris(trimethylenedioxyboryl)methane (V)*

A suspension of 17.55 g (0.05 mole) of tetrakis(trimethylenedioxyboryl)-methane (II) in 500 ml of tetrahydrofuran was stirred at −75° and 31.3 ml of 1.6 *M* butyllithium in hexane (Foote Mineral Co.) was added dropwise. The mixture was stirred 15 min. in the Dry Ice/acetone bath. The bath was then removed and stirring was continued until the frost which condensed on the outside of the flask just finished melting. At this point a white precipitate remained in the flask, and this coagulated to a gum if the mixture warmed to room temperature but the yield of (V) was not affected. A 19.3-g portion of triphenyltin chloride was added and the mixture was stirred, producing a turbid solution. Stirring was continued overnight at 25°. If any precipitate remained at this point, the mixture was filtered. The solution was concentrated under vacuum and 200 ml of ether was added to the white powdery residue. The mixture was stirred 10 min and filtered under nitrogen. The solid was dissolved in 100 ml of chloroform, the solution was filtered, and the filtrate was concentrated to about 25 ml. Addition of 200 ml of anhydrous ether, cooling in an ice bath and stirring, and filtration under nitrogen yielded 21.5 g (70 %) of (triphenylstannyl)tris(trimethylenedioxyboryl)methane (V); m.p. 182–183° ; NMR ($CDCl_3$) $\delta$ 7.50 (m, 15, $C_6\underline{H}_5$), 3.75 (t, 12, $-OC\underline{H}_2-$), and 1.75 (quintet, 6, $-CH_2C\underline{H}_2CH_2-$). (Found: C, 54.53; H, 5.38; B, 5.18; Sn, 19.03. $C_{28}H_{33}B_3SnO_6$ calcd.: C, 54.54; H, 5.36; B, 5.26; Sn, 19.27 %.)

*(Triphenylplumbyl)tris(trimethylenedioxyboryl)methane (VI)*

Triphenyllead chloride was substituted for triphenyltin chloride in the procedure described for the preparation of (V) and the reaction was carried out on a 0.009 mole scale. The yield of (VI) was 3.0 g (48 %); m.p. 181–183° (dec.); NMR ($CDCl_3$) $\delta$ 7.50 (m, 15, $C_6\underline{H}_5$), 3.80 (t, 12, $-OC\underline{H}_2-$), and 1.55 (m, 6, $-CH_2C\underline{H}_2CH_2-$). (Found: C, 47.81; H, 4.83; B, 4.92; Pb, 29.08. $C_{28}H_{33}B_3PbO_6$ calcd.: C, 47.69; H, 4.68; B, 4.60; Pb, 29.44 %.)

*(Triphenylgermyl)tris(trimethylenedioxyboryl)methane (VII)*

Triphenylgermanium chloride was substituted for triphenyltin chloride in the procedure described for the preparation of (V) and the reaction was carried out on a 0.025 mole scale. The yield of (VII) was 10.6 g (74 %); m.p. 174–176° ; NMR ($CDCl_3$) $\delta$ 7.50 (m, 15, $C_6\underline{H}_5$), 3.75 (t, 12, $-OC\underline{H}_2-$), and 1.55 (quintet, 6, $-CH_2C\underline{H}_2CH_2-$). (Found: C, 58.81; H, 6.20; B, 5.26; Ge, 12.47. $C_{28}H_{33}B_3GeO_6$ calcd.: C, 58.95; H, 5.79; B, 5.68; Ge, 12.74 %.)

*Bis(triphenylstannyl)bis(trimethylenedioxyboryl)methane (VIII) and other $Ph_3MC(M'Ph_3)(BO_2C_3H_6)_2$ (IX)–(XII)*

The scale of these reactions ranged from 1.4–6.0 mmoles. For example, a 6.0

mmole sample of $Ph_3MC(BO_2C_3H_6)_3$ (V), (VI), or (VII) was stirred with 75 ml of tetrahydrofuran and cooled with a Dry Ice/acetone bath, and 3.75 ml of 1.6 *M* butyllithium was added dropwise from a syringe to the vigorously stirred mixture. The mixture was stirred 1 h at −75°, then allowed to warm slowly to 20–25°. There was no precipitate at this point and the solution was colorless in each case. A 6.1 mmole portion of $Ph_3M'Cl$, where M′ = Sn or Pb, was added and the solution was stirred 1 h at 25°. If the solution was not clear, it was filtered under nitrogen. The solution was concentrated under vacuum to 5–10 ml, 50 ml of methanol was added, and the mixture was stirred 15 min. in an ice bath to complete crystallization of the product, which was recrystallized from chloroform/methanol. The properties of these products are summarized in Table 1.

TABLE 1

PROPERTIES OF $(Ph_3M)_2C(BO_2C_3H_6)_2$ AND $Ph_3MC(M'Ph_3)(BO_2C_3H_6)_2$ (VIII)–(XII), $C_{43}H_{42}B_2MM'O_4$

| *No.* | *M* | *M′* | *M.p.* (°*C*) | *Yield* (%) | *NMR* ($CDCl_3$), δ | | | *Analyses, found (calcd.)* (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $C_6\underline{H}_5$ *m* | $OC\underline{H}_2$ *t* | $CC\underline{H}_2C$ *m* | *C* | *H* | *B* | *M* | *M′* |
| (VIII) | Sn | | 196–198 | 84 | 7.26 | 3.56 | 1.32 | 58.34<br>58.55 | 5.16<br>4.77 | 2.19<br>2.45 | 27.14<br>26.94 | |
| (IX) | Pb | | 180–181 | 39 | 7.33 | 3.68 | 1.42 | 48.70<br>48.77 | 4.28<br>3.97 | 2.21<br>2.04 | 39.40<br>39.17 | |
| (X) | Sn | Pb | 194–195 | 79 | 7.30 | 3.62 | 1.23 | 53.30<br>53.21 | 4.54<br>4.33 | 2.02<br>2.23 | 12.64<br>12.24 | 20.92<br>21.37 |
| (XI) | Ge | Sn | 202–203 | 67 | 7.32 | 3.57 | 1.38 | 61.54<br>61.80 | 5.07<br>5.03 | 2.80<br>2.59 | 8.90<br>8.70 | 14.15<br>14.22 |
| (XII) | Ge | Pb | 204–206 | 69 | 7.30 | 3.60 | 1.38 | 55.91<br>55.88 | 4.59<br>4.55 | 2.36<br>2.34 | 7.47<br>7.86 | 22.21<br>22.44 |

### *Tris(triphenylstannyl)(trimethylenedioxyboryl)methane (XIV)*

The starting material was 1.75 g (1.98 mmoles) of bis(triphenylstannyl)bis(trimethylenedioxyboryl)methane (VIII) and the procedure was the same as that described for the preparation of (VIII) itself. The yield of (XIV) was 2.23 g (98 %); after recrystallization from chloroform/methanol, m.p. 276–280°; NMR ($CDCl_3$) δ 7.14 (apparent singlet, 45, $C_6\underline{H}_5$), 3.71 (t, 4, $-OCH_2-$), and 1.52 (quintet, 2, $-CH_2C\underline{H}_2-CH_2-$). (Found: C, 60.35; H, 4.60; B, 1.10; Sn, 30.88. $C_{58}H_{51}BSn_3O_2$ calcd.: C, 60.60; H, 4.45; B, 0.94; Sn, 31.05%.)

### *Iodo(triphenylstannyl)bis(trimethylenedioxyboryl)methane (XIII)*

In the usual manner, 10.0 g (16.2 mmoles) of $Ph_3SnC(BO_2C_3H_6)_3$ (V) in 200 ml of tetrahydrofuran was treated with 10.5 ml of 1.6 *M* butyllithium in hexane at −75° and allowed to warm to 25°. Iodine was added in small portions until the color was no longer discharged. The consumption was 3.09 g (12.2 mmoles). The solution was concentrated under vacuum to about 10 ml, then treated with 25 ml of ethanol followed by 250 ml of hexane. After stirring $\frac{1}{2}$ h the solid iodo compound (XIII) was filtered, yield 5.6 g (50%); after recrystallization from chloroform/methanol, m.p. 147–148°; NMR ($CDCl_3$) $\delta$ 7.50 (m, 15, $C_6\underline{H}_5$), 3.90 (t, 8, $-OC\underline{H}_2-$), and 1.60 (quintet, 4, $-CH_2C\underline{H}_2CH_2-$). (Found: C, 45.71; H, 4.12; B, 3.45; I, 19.11; Sn, 18.05. $C_{25}H_{25}B_2IO_4Sn$ calcd.: C, 45.58; H, 4.10; B, 3.28; I, 19.28; Sn, 18.03%.)

*Iodobis(triphenylstannyl)(trimethylenedioxyboryl)methane (XVII)*

In the usual manner, 6.37 g (7.24 mmoles) of $(Ph_3Sn)_2C(BO_2C_3H_6)_2$ (VIII) in 75 ml of tetrahydrofuran was treated with 4.52 ml of 1.6 *M* butyllithium in hexane at −75° and allowed to warm to 0°, and 1.84 g (7.24 mmoles) of iodine was added. After stirring overnight, the solution was concentrated and the residue was treated with anhydrous ether. The yield of crystalline (XVII) was 4.0 g (60%); after recrystallization from chloroform/hexane, m.p. 178–180°; NMR ($CDCl_3$) $\delta$ 7.40 (m, 30, $C_6\underline{H}_5$), 3.70 (t, 4, $-OC\underline{H}_2-$), and 1.42 (quintet, 2, $-CH_2C\underline{H}_2CH_2-$). (Found: C, 51.91; H, 4.14; B, 1.23; I, 13.58; Sn, 25.67. $C_{40}H_{36}BIO_2Sn_2$ calcd.: C, 52.00; H, 3.90; B, 1.17; I, 13.75; Sn, 25.72%.)

*Iodobis(triphenylstannyl)methane (XVIII)*

One g (1.09 mmoles) of $(Ph_3Sn)_2CIBO_2C_3H_6$ (XVIII) and 0.04 g (1.0 mmole) of lithium methoxide in 25 ml of 1,2-dimethoxyethane and 5 ml of cyclohexene were refluxed overnight, yielding a colorless solution. Concentration to 5 ml and addition of 30 ml of methanol yielded 0.63 g of solid, which was recrystallized 3 times from chloroform/methanol to yield 0.12 g of $(Ph_3Sn)_2CHI$ (XVIII); m.p. 154–155°; NMR ($CDCl_3$) $\delta$ 7.30 (m, 30, $C_6\underline{H}_5$) and 2.89 (s, 1, $Sn_2CHI$, $^{117}Sn$ and $^{119}Sn$ satellites *J* 42 and 43 Hz). (Found: C, 53.16; H, 3.80; I, 14.86; Sn, 28.60. $C_{37}H_{31}ISn_2$ calcd.: C, 52.90; H, 3.69; I, 15.12; Sn, 28.29%.)

*Bis(triphenylstannyl)(trimethylenedioxyboryl)methane (XIX) and tris(triphenylstannyl)methane*

One g of $(Ph_3Sn)_2CIBO_2C_3H_6$ (XVII) and 0.04 g of lithium methoxide in 25 ml of tetrahydrofuran were refluxed overnight, treated with 0.43 g of triphenyltin chloride, and concentrated under vacuum to 5 ml. Addition of 25 ml of pentane precipitated 0.42 g of crude product, which was recrystallized from hexane to yield 0.27 g of $(Ph_3Sn)_2CHBO_2C_3H_6$ (XIX); m.p. 138–140°; NMR ($CDCl_3$) $\delta$ 7.18 (m, 30, $C_6\underline{H}_5$), 3.48 (t, 4, $-OC\underline{H}_2-$), 1.20 (quintet, 2, $-CH_2C\underline{H}_2CH_2-$), and 0.98 (s, 1, $Sn_2CHB$, $^{117}Sn$ and $^{119}Sn$ satellites *J* 66 and 67 Hz). (Found: C, 59.97; H, 4.68; B, 1.60; Sn, 29.48. $C_{40}H_{37}BO_2Sn$ calcd.: C, 60.21; H, 4.64; B, 1.35; Sn, 29.78%.) The mother liquor from the first precipitation with pentane was concentrated to half its original volume and cooled to −15°, yielding 0.57 g of solid. Recrystallization from 10 ml of hexane yielded 0.07 g of $(Ph_3Sn)_3CH$, NMR ($CDCl_3$) $\delta$ 7.3 (m, 45, $C_6\underline{H}_5$) and 1.95 (s, 1, $Sn_3CH$, $^{117}Sn$ and $^{119}Sn$ satellites, *J* 90 and 91 Hz).

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