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TIN AND LEAD DERIVATIVES OF TETRAKIS(DIMETHOXYBORYL)METHANE*

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SUMMARY

Treatment of tetrakis(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, with lithium methoxide or butyllithium followed by triphenyltin chloride yields (triphenylstannyl)tris(dimethoxyboryl)methane, $Ph_3SnC[B(OMe)_2]_3$, which on further treatment with butyllithium disproportionates to form bis(triphenylstannyl)bis(dimethoxyboryl)methane, $(Ph_3Sn)_2C[B(OMe)_2]_2$. The analogous monolead compound proved too base-sensitive to isolate, and only bis(triphenylplumbyl)bis(dimethoxyboryl)methane, $(Ph_3Pb)_2C[B(OMe)_2]_2$, was obtained from $C[B(OMe)_2]_4$, BuLi, and Ph_3PbCl. A brief study of protodeboronation and other reactions of these compounds has been carried out.

INTRODUCTION

Tetrametallomethanes might be expected to show unusual properties resulting from the proximity of the four metal atoms. The silicon[2], lead[3], and mercury[4] tetrametallomethanes so far reported have been characterized mainly in inertness resulting from steric shielding of the central carbon atom, though complete demercuration of $C(HgBr)_4$ by bromine has been observed[4]. In contrast, boron provides a reactive leaving group in tetrakis(dimethoxyboryl)methane (I)[5], which reacts with bases such as butyllithium or lithium methoxide to form either the tris(dimethoxyboryl)methide anion (II) or perhaps some more complex species from which (II) is readily transferred to electrophiles. Reactions of anion (II) with protons[5], aldehydes and ketones[6], and alkyl halides[7] have been reported.

RESULTS AND DISCUSSION

At the time this work was begun, we had recently found that mercuric acetate would react directly with $C[B(OMe)_2]_4$ (I)[4] and we explored the possibility that

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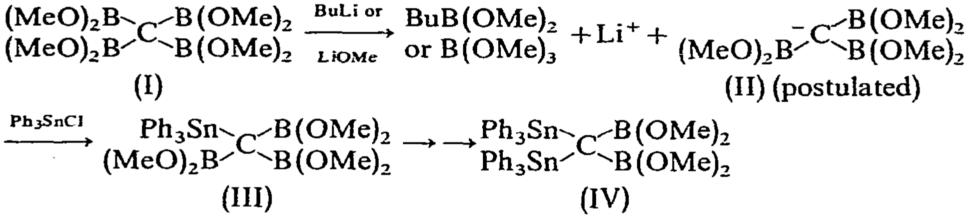
triphenyltin acetate might also react. These attempts failed, and we therefore turned to the anionic route, which easily yielded (triphenylstannyl)tris(dimethoxyboryl)methane (III) and bis(triphenylstannyl)bis(dimethoxyboryl)methane (IV).



Our first attempt to prepare the monotin compound (III) yielded the ditin compound (IV) instead. The reaction conditions involved treatment of $C[B(OMe)_2]_4$ (I) in tetrahydrofuran with one equivalent of butyllithium followed by one equivalent of triphenyltin chloride and refluxing. Evidently the triborylmethide anion (II) is able to act as the base in the abstraction of a $(MeO)_2B^+$ group from the monotin compound (III) to form the anion $Ph_3SnC^-[B(OMe)_2]_2$, which reacts with triphenyltin chloride to form the ditin compound (IV).

Isolation of the monotin compound (III) was first accomplished by using a deficiency of triphenyltin chloride and converting the excess anion, $[(MeO)_2B]_3C^-$ or $Ph_3SnC^-[B(OMe)_2]_2$ or both, back to the dimethoxyboryl compounds $C[B(OMe)_2]_4$ (I) and $Ph_3SnC[B(OMe)_2]_3$ (III) by treatment with dimethoxyboron chloride, $(MeO)_2BCl$. We also routinely added 2,2-dimethoxypropane, which is known to convert boronic acids to their methyl esters[8], at the end of each reaction to reverse any accidental hydrolysis.

The approach just described is wasteful of expensive $C[B(OMe)_2]_4$ (I) and we therefore looked for alternatives. The best synthesis of the monotin compound (III) was accomplished by adding a solution of the triborylmethide anion (II) to excess triphenyltin chloride or bromide. Under these conditions, exposure of the monotin compound (III) to base is minimized, and yields as high as 60% were obtained.

In the earlier experiments we used butyllithium as the base, but we then began to suspect that ligand exchange on boron might occur to yield $B(OMe)_3$ and $[(MeO)_2B]_2^-CB(Bu)OMe$ in addition to the desired cleavage to $BuB(OMe)_2$ and $[(MeO_2B]_3C^-$ (II). The *B*-butylated side product would decrease yields and interfere with crystallization. We therefore decided to try lithium methoxide as the base to preclude this possibility, and although we never proved the suspected side reaction, lithium methoxide provided our highest yields. The solubility of lithium methoxide in tetrahydrofuran is slight, but it readily yielded clear solutions on reaction with $C[B(OMe)_2]_4$ (I).

Several reaction conditions tested and the resulting yields are summarized in Table 1.

The most surprising reaction of the monotin compound (III) was its facile disproportionation on treatment with butyllithium to form the ditin compound (IV) and presumably $[(MeO)_2B]_3C^-$ (II), though we did not succeed in isolating the expected derivative $C[B(OMe)_2]_4$ (I) from treatment of (II) with dimethoxyboron chloride. In order to form $(Ph_3Sn)_2C[B(OMe)_2]_2$ (IV) the triphenyltin cation must be released in some manner from $Ph_3SnC[B(OMe)_2]_3$ (III). Direct displacement on tin of one bulky

TABLE 1

CONDITIONS AND YIELDS FOR PREPARATION OF $Ph_3SnC[B(OMe)_2]_3$ (III)

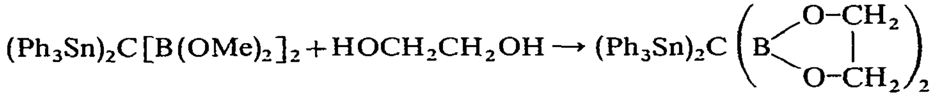
X in Ph_3SnX	*Base*	*Ratio (II)/Ph_3SnX*	*Solvent*	*Mode of addition*[a]	*% Yield based on (I)*
Cl	BuLi	1	THF[b]	regular	0[c]
Cl	BuLi	2	THF	regular	32
Cl	BuLi	2	DME[d]	regular	32
Cl	LiOMe	1	THF	inverse	22
Cl	LiOMe	0.67	THF	inverse	58
Br	LiOMe	1	THF	inverse	62
Cl	LiOMe	1	DME	regular	0

[a] Regular addition is addition of Ph_3SnX to anion (II), inverse is addition of (II) to Ph_3SnX. [b] THF = tetrahydrofuran. [c] A 24% yield of $(Ph_3Sn)_2C[B(OMe)_2]_2$ (IV) was obtained instead. [d] DME = 1,2-dimethoxyethane.

boron-substituted carbanion by another does not seem a likely mechanism for tin transfer, but perhaps methoxide ion (generated by displacement from boron by butyllithium) can remove the tin as triphenyltin methoxide, which could react with $Ph_3Sn\text{-}C^-[B(OMe)_2]_2$ to form $(Ph_3Sn)_2C[B(OMe)_2]_2$ (IV) and MeO^-.

When we attempted to extend this chemistry to the analogous lead compounds, we were unable to obtain any of the monolead compound, $Ph_3PbC[B(OMe)_2]_3$. Even the addition of the solution of anion (II) to excess triphenyllead chloride yielded only the dilead compound, $(Ph_3Pb)_2C[B(OMe)_2]_2$ (V). Addition of triphenyllead chloride to excess anion (II) likewise gave only (V).

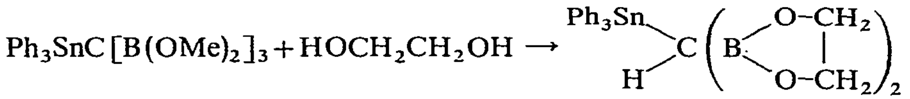
The tin compounds (III) and (IV) are sensitive to atmospheric moisture because of the ease of hydrolysis of the boronic methyl ester groups. In the hope of obtaining a more stable derivative, we reacted the ditin compound (IV) with ethylene glycol and obtained the expected cyclic boronic ester (VI).



$$(Ph_3Sn)_2C[B(OMe)_2]_2 + HOCH_2CH_2OH \longrightarrow (Ph_3Sn)_2C\left(B\begin{matrix}O\text{-}CH_2\\ |\\ O\text{-}CH_2\end{matrix}\right)_2$$

(IV) (VI)

However, reaction of the monotin compound (III) with ethylene glycol resulted in the loss of one of the three boron atoms to form (triphenylstannyl)bis(ethylenedioxyboryl)methane (VII).

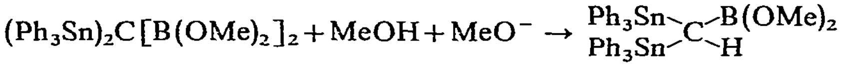


$$Ph_3SnC[B(OMe)_2]_3 + HOCH_2CH_2OH \longrightarrow \begin{matrix}Ph_3Sn\\ H\end{matrix}\!\!>C\left(B\begin{matrix}O\text{-}CH_2\\ |\\ O\text{-}CH_2\end{matrix}\right)_2$$

(III) (VII)

This reaction is particularly surprising in view of the stability of the triboryl compound (III) toward methanol, which is used as a cosolvent in the recrystallization of (III). Evidently the ethylene glycol boronic ester is much more susceptible to protodeboronation.

We then investigated the susceptibility of the ditin compound (IV) to deboronation and found that it could be converted to the monoboronic ester (VIII) by treatment with sodium methoxide in methanol.



$$(Ph_3Sn)_2C[B(OMe)_2]_2 + MeOH + MeO^- \rightarrow \begin{matrix} Ph_3Sn \\ Ph_3Sn \end{matrix} C \begin{matrix} B(OMe)_2 \\ H \end{matrix}$$

(IV) (VIII)

One of our objectives in synthesizing the monotin compound (III) was to see whether it might react with bromine to form $BrC[B(OMe)_2]_3$, which had eluded synthesis directly from the anion (II) and bromine. Not too surprisingly, the only product that could be isolated from the bromination of (III) was bromobenzene. There was also a tarry residue which probably contained $[(MeO)_2B]_3CSnBr_2Ph$ and related compounds. Preferential phenyl cleavage also evidently occurs in the reaction of $Ph_3SnCH(BO_2C_2H_4)_2$ (VIII) with mercuric acetate, which yielded diphenylmercury as the only isolable product.

We undertook the synthesis of the trimethyltin compound $Me_3SnC[B(OMe)_2]_3$ in the hope that the tin-methyl groups might be more resistant to cleavage by bromine, but the compound proved to be a liquid (b.p. 80–105°/0.2 mmHg) and we were unable to obtain a pure sample. The structure was supported by the NMR spectrum (CCl_4): δ 0.01 (singlet, $SnCH_3$, ^{119}Sn and ^{117}Sn satellites, J 52 and 50 Hz) and δ 3.40 (singlet, $BOCH_3$).

At this point it was concluded that many of the troublesome properties of compounds (III), (IV) and (V) might be avoided by the use of more stable cyclic boronic esters, which might be less susceptible to disproportionations such as that of monotin compound (III) to ditin compound (IV), and which should certainly be easier to crystallize. The successful synthesis of the cyclic boronic esters will be described in the next paper in this series[9].

EXPERIMENTAL

All reactions and filtrations were carried out under an atmosphere of nitrogen or argon. Tetrahydrofuran was distilled from lithium aluminum hydride and stored under argon. NMR chemical shifts are relative to internal tetramethylsilane. Melting points were taken in capillaries and are uncorrected.

(Triphenylstannyl) tris(dimethoxyboryl) methane (III)

Method A. With butyllithium. Forty-two ml (0.067 mole) of 1.6 M butyllithium in hexane was added to a stirred solution of 18.2 g (0.060 mole) of tetrakis(dimethoxyboryl)methane (I) in 60 ml of tetrahydrofuran. The yellow solution was stirred 15 min and 11.6 g (0.030 mole) of triphenyltin chloride was added in one portion. The resulting solution was refluxed 2 h and stirred 20 h at 25°, then treated with 10 ml of dimethoxyboron chloride, filtered through a fritted funnel to remove lithium chloride, and concentrated under vacuum. The gummy solid residue was triturated with 75 ml of methanol and yielded 11.0 g [65% based on Ph_3SnCl, 32% based on (I)] of crude (triphenylstannyl)tris(dimethoxyboryl)methane (III), m.p. 145–147°. The analytical sample was recrystallized from methanol/acetone, m.p. 155–156°; IR (CCl_4): 3100 (C_6H_5), 2900–3000 (CH), and 1300 cm^{-1} (BO); NMR (CCl_4): δ 7.17 (m, 15, C_6H_5)

and 3.34 (s, 18, OCH_3). (Found: C, 51.53; H, 5.67; B, 5.37; Sn, 20.69. $C_{25}H_{33}B_3O_6Sn$ calcd.: C, 51.71; H, 5.73; B, 5.59; Sn, 20.44%.)

Method B. With lithium methoxide. Lithium methoxide powder was prepared by dissolving lithium metal in methanol and evaporating the solution under vacuum. A 0.42 g (0.11 mole) portion of lithium methoxide was added to a solution of 3.0 g (0.010 mole) of tetrakis(dimethoxyboryl)methane (I) in 15 ml of tetrahydrofuran at 25°. The mixture was refluxed 10 min and the resulting orange solution was transferred by means of a syringe and added dropwise over a period of 10 min to a stirred, refluxing solution of 5.8 g (0.015 mole) of triphenyltin chloride in 20 ml of tetrahydrofuran. After 15 min additional refluxing 0.2 ml of dimethoxyboron chloride and 3 ml of 2,2-dimethoxypropane were added and the solution was decanted from the lithium chloride precipitate and concentrated under vacuum. The semisolid residue was recrystallized from a mixture of 30 ml of methanol and 5 ml of acetone and yielded 3.0 g (52%) of (triphenylstannyl)tris(dimethoxyboryl)methane (III), m.p. 155–156°.

Bis(triphenylstannyl)bis(dimethoxyboryl)methane(IV)

A solution of 1 g (1.7 mmoles) of triphenylstannyltris(dimethoxyboryl)methane (III) in 10 ml of tetrahydrofuran was chilled with a Dry Ice/acetone bath and 1.2 ml (1.9 mmoles) of 1.6 *M* butyllithium in hexane was added. The mixture was allowed to warm to 25°, then treated with 0.2 ml of dimethoxyboron chloride and 1 ml of 2,2-dimethoxypropane. The solution was concentrated under vacuum and the residue was recrystallized from 40 ml of methanol to yield 0.69 g (93%) of bis(triphenylstannyl)bis(dimethoxyboryl)methane (IV), m.p. 159–160°; IR (CCl_4): 3100 (C_6H_5), 3000 (CH), 1450 (C_6H_5), 1320 (BO), and 730 and 690 cm^{-1} (C_6H_5); NMR (CCl_4): δ 7.13 (m, 30, C_6H_5) and 3.34 (s, 12, OCH_3). (Found: C, 57.35; H, 4.93; B, 2.74; Sn, 27.46. $C_{41}H_{42}B_2O_4Sn_2$ calcd.: C, 57.40; H, 4.94; B, 2.52; Sn, 27.68%.)

Bis(triphenylstannyl)bis(dimethoxyboryl)methane (IV) was also obtained in 21% yield from the treatment of 6.1 g (0.020 mole) of tetrakis(dimethoxyboryl)methane (I) in 30 ml of tetrahydrofuran with 14 ml (0.022 mole) of 1.6 *M* butyllithium in hexane at 25° followed by the addition of 7.2 g (0.020 mole) of triphenyltin chloride in one portion, refluxing 1 h, filtering, concentrating under vacuum, and recrystallizing the residue from carbon tetrachloride/methanol.

Bis(triphenylplumbyl)bis(dimethoxyboryl)methane (V)

Method *A* (with butyllithium) for the preparation of (triphenylstannyl)tris(dimethoxyboryl)methane (III) was followed, substituting triphenyllead chloride for triphenyltin chloride. The product was bis(triphenylplumbyl)bis(dimethoxyboryl)methane (V), which was recrystallized from carbon tetrachloride/methanol, yield 30%, m.p. 174–175°; NMR (CCl_4): δ 7.15 (m, 30, C_6H_5) and 3.34 (s, 12, OCH_3). (Found: C, 47.02; H, 4.07; B, 2.34; Pb, 40.35. $C_{41}H_{42}B_2O_4Pb_2$ calcd.: C, 46.97; H, 4.14; B, 2.16; Pb, 40.52%.)

Bis(triphenylstannyl)bis(ethylenedioxyboryl)methane (VI)

A mixture of 1.0 g (1.2 mmoles) of bis(triphenylstannyl)bis(dimethoxyboryl)methane (IV), 5 ml of acetone, and 1.4 g (2.3 mmoles) of ethylene glycol rapidly yielded crystalline bis(triphenylstannyl)bis(ethylenedioxyboryl)methane (VI), which was recrystallized from acetone/chloroform, yield 0.6 g (59%), m.p. 165–167°; NMR

($CDCl_3$): δ 7.32 (m, 30, C_6H_5) and 3.70 (s, 8, OCH_2CH_2O). (Found: C, 57.29; H, 4.65; B, 2.80; Sn, 27.42. $C_{41}H_{38}B_2O_4Sn_2$ calcd.: C, 57.68; H, 4.49; B, 2.53; Sn, 27.81%.)

(Triphenylstannyl)bis(ethylenedioxyboryl)methane (VII)

Treatment of 1.0 g (1.7 mmoles) of (triphenylstannyl)tris(dimethoxyboryl)-methane (III) with 0.40 g (6.5 mmoles) of ethylene glycol and 5 ml of acetone yielded a solution after about 2 min and a solid precipitate after 30 min. After stirring 2½ h at 25° the mixture was filtered, yielding 0.80 g (90%) of the monodeboronated product, (triphenylstannyl)bis(ethylenedioxyboryl)methane (VII), m.p. 142–143°; NMR ($CDCl_3$): δ 7.50 (m, 15, C_6H_5), 3.83 (s, 8, OCH_2CH_2O), and 1.20 (s, 1, B_2SnCH, with ^{119}Sn and ^{117}Sn satellites, J 80 and 78 Hz, respectively). (Found: C, 54.53; H, 4.86; B, 4.05; Sn, 23.34. $C_{24}H_{24}B_2O_4Sn$ calcd.: C, 54.73; H, 4.79; B, 4.29; Sn, 23.52%.)

Bis(triphenylstannyl)dimethoxyborylmethane (VIII)

A solution of 0.78 g (0.9 mmole) of bis(triphenylstannyl)bis(dimethoxyboryl)-methane (IV) and 0.05 g (0.9 mmole) of sodium methoxide in 10 ml of methanol was refluxed 2 h and the crystals of bis(triphenylstannyl)dimethoxyborylmethane (VIII) were filtered, 0.40 g (57%), m.p. 104–105°; NMR (CCl_4): δ 7.19 (m, 30, C_6H_5), 3.34 (s, 6, OCH_3), and 0.03 (s, 1, BSn_2CH). (Found: C, 59.44; H, 4.84; B, 1.34; Sn, 30.32. $C_{39}H_{37}BO_2Sn_2$ calcd.: C, 59.60; H, 4.75; B, 1.38; Sn, 30.21%.)

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