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STANNOBOROXANES

II*. SYNTHESIS AND REACTIONS OF TRIS(TRIALKYLTIN) BORATES

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Summary

Tris(trialkyltin) borates $B(OSnR_3)_3$ (R = Me, Et, Pr, Bu, i-Bu and Ph) have been prepared by esterification of boric acid with trialkyltin hydroxide or bis(trialkyltin) oxide. These reacted with boric anhydride to give the corresponding trialkyltin metaborates $(R_3SnOBO)_3$ Reactions of tris(tributyltin) borate with hydrogen chloride, acetyl chloride, acetic acid, acetic anhydride, phenol, butanethiol, thiophenol and isopropyl acetate have been studied. The infrared spectra of these compounds are discussed

Introduction

In the first part of this series [1], we described the synthesis of 2-(tributylstannoxy)-1,3,2-dioxaborolanes, boroles and borinanes by various routes. The present paper deals with some new tris(trialkyltin) borates

Results and discussion

The new compounds were prepared in quantitative yields by the following general route·

$$2\ B(OH)_3 + 3\ (R_3Sn)_2O\ (\text{or } 6\ R_3SnOH) \xrightarrow{C_6H_6} 2\ (R_3SnO)_3B + 3\ H_2O\ (\text{or } 6\ H_2O)$$

Water formed during the reactions was fractionated out azeotropically with benzene. The completion of the reactions was confirmed by the complete disappearance of Sn—O—Sn or OH peak and also by the formation of a new broad band due to B—O—Sn in the range 1270-1300 cm^{-1} range [1]. The

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* For part I see ref 1

TABLE 1
PREPARATION OF TRIS (TRIALKYLTIN) BORATES

Organotin hydroxide or oxide (g)(mmoles)	Boric acid (g) (mmoles)	Product	Yield (%)	B p [°C(mm)]	ν_{as}(BOSn)	Analysis (%) Found				Calcd			
						B	C	H	Sn	B	C	H	Sn
4.1[a] (22.69)	0.47 (7.58)	$B(OSnMe_3)_3$	89	130 132(14)	1300-1285	2 1	20 8	5.2		1.96	19.6	5.0	
3.4[a] (15.26)	0 34 (5.48)	$B(OSnEt_3)_3$	70	140 145(0.5)	1300-1286	1.4				1.6			
3 2 (9 01)	0 25 (4.03)	$B(OSnPr_3)_3$	98	152-153(0.1)	1290-75	1 4	40 5	7 9		1 4	40 4	7.9	
17 2 (28.89)	1 22 (19.68)	$B(OSnBu_3)_3$	91	195-200(0 1)	1290-75	1 2			38.0	1.2			38 1
3 3 (5 54)	0.22 (3.55)	$B(OSnBu\text{-}i_3)_3$	99	180-185(0 05)	1290-70	1 1	47 4	8.7		1.2	46 6	8 8	
2 8[a] (7.64)	0.16 (2.58)	$B(OSnPh_3)_3$	98	128-130[b]	1270	0 98	57 8	4 0		0 98	58 5	4.1	

[a] In all these cases respective hydroxides are taken [b] The compound does not distil, so m p is reported

TABLE 2
PREPARATION OF TRIALKYLTIN METABORATES

$B(OSnR_3)$ (g) (mmoles)	B_2O_3 (g) (mmoles)	Temp (°C) (h)	Product	$\nu_{as}(BOSn)$ (cm^{-1})	Metaborate peak (cm^{-1})	Boron found (calcd.) (%)
0.84 (1.26)	0.09 (1.29)	100 (1)	$(OBOSnEt_3)_3$	1295	732m 742m	4.2 (4.4)
0.92 (1.15)	0.09 (1.29)	140 (3)	$(OBOSnPr_3)_3$	1295	732m 742m	3.7 (3.8)
2.68 (2.88)	0.20 (2.87)	240 (3)	$(OBOSnBu_3)_3$	1296	730m 742m	3.3 (3.3)
0.67 (0.72)	0.05 (0.72)	180 (4)	$(OBOSnBu\text{-}i_3)_3$	1290	732vs, 744s	3.1 (3.3)

reactions are complete within 4-5 hours. On distillation under reduced pressure, these compounds undergo slight disproportionation into bis(trialkyltin) oxide and boric anhydride, as is demonstrated by the appearance of a weak Sn—O—Sn peak in the range 740-84 cm^{-1}.

Data for the tris(trialkyltin) borates are presented in Table 1.

On heating tris(trialkyltin) borates with boric anhydride, the latter slowly dissolves with the formation of trialkyltin metaborate (Table 2), and the temperature of dissolution increases from 120-240° from ethyl to butyl derivatives. The ease of such group exchange, leading to metaborates, appears to increase in the following order.

C[3] < Si[2] < Ge[4] < Sn

Like tris(trialkyltin) borates, trialkyltin metaborates may also be prepared directly from bis(trialkyltin) oxide and boric anhydride. These are colourless, viscous liquids, miscible with common organic solvents Like other metaborate esters they have high thermal stability, but disproportionate into orthoborates on attempted distillation under reduced pressure:

$$(R_3Sn)_2O + B_2O_3 \xrightarrow{\Delta} (R_3SnOBO)_3 \xrightleftharpoons[+B_2O_3,\,120\text{-}240^\circ]{\text{in vacuo},\,-B_2O_3} (R_3SnO)_3B$$

Reactions of tris(tributyltin) borate with hydrogen chloride and acetyl chloride are exothermic, and give tributyltin chloride.

$$B(OSnBu_3)_3 + 3\,HCl \longrightarrow 3\,Bu_3SnCl + H_3BO_3$$

$$B(OSnBu_3)_3 + AcCl \longrightarrow 3\,Bu_3SnCl + B(OAc)_3$$

Reactions of tris(tributyltin) borate with acetic acid, phenol, butanethiol and thiophenol also proceed with the cleavage of tin—oxygen bond and the negative group attaches to the organotin moiety.

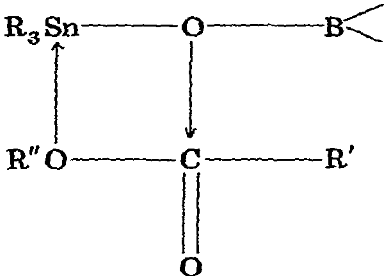
$$B(OSnBu_3)_3 + 3\,AH \longrightarrow 3\,Bu_3SnA + H_3BO_3$$

$A = CH_3COO$, SBu, SPh, OPh

It is advantageous to carry out these reactions in benzene medium, as one of the products, boric acid, is precipitated out, and can be easily separated by filtration. All these reactions are quite fast, as shown by their exothermic nature, but to ensure completion, the reaction mixtures were kept overnight at room temperature.

Tris(tributyltin) borate also reacts exothermically with acetic anhydride with the formation of tributyltin acetate and boron triacetate (or diboron tetraacetate oxide), but it is rather difficult to separate the products, fractrional crystallization from benzene gave tributyltin acetate in 50% yield.

Analogous reactions of trialkyltin alkoxides, R_3SnOR with AcCl [5], RSH [6], acetic acid [7], have been previously reported. Qualitatively, there does not appear any appreciable difference in the reactivities of Sn—O—C and Sn—O—B bonds towards these reagents. However, there is a notable difference towards alkyl acetates. In the case of former, transesterification is facile, but there appears to be no reaction with the latter. Because of $(p \rightarrow p)\pi$ bonding between boron and oxygen, the nucleophilicity of boroxy-oxygen may be somewhat reduced, and the following intermediate necessary for transesterification is less likely to be formed:



It should be mentioned that trialkyl borates likewise fail to react with esters under normal conditions [8].

IR and NMR spectra

Like tris(tributyltin) borate [1], other tris(trialkyltin) borates and trialkyltin metaborates show the strongest peak in their infrared spectra in the range 1270-1300 cm^{-1}. This may be assigned to ν_{as}(B—O—Sn). The exact positions are given in Tables 1 and 2. The assignment is supported by the fact that on cleavage of the B—O—Sn bond, this peak disappears completely.

In metaborates, a strong absorption appears near 1360-1365 cm^{-1}, which may be due to ν(B—O) in the ring Exact positions are as follows. $(OBOSnEt_3)_3$ 1360 cm^{-1}, $(OBOSnPr_3)_3$ 1365 cm^{-1}, $(OBOSnBu_3)_3$ 1365 cm^{-1}, $(OBOSnBu\text{-}i_3)_3$ 1365 cm^{-1}.

Strong absorptions near 720 and 735 cm^{-1} are characteristic of metaborates, and probably arise from out-of-plane vibrations of the B_3O_6 skeleton. These peaks appear at 732 and 742 cm^{-1} in trialkyltin metaborates, and are absent in $(R_3SnO)_3B$.

The purity of $(Me_3SnO)_3B$ [singlet at τ 9.80 ppm; $J(^{119}Sn—C—H)$ 59 Hz; $J(^{117}Sn—C—H)$ 57 Hz] and $(Ph_3SnO)_3B$ (complex multiplet at τ 2.52 ppm) was also checked by PMR spectra.

Experimental

All the trialkyltin hydroxides or bis(trialkyltin) oxides were used as supplied. Benzene (B.D.H , L R.) was kept overnight on sodium wire and distilled, and was finally dried azeotropically with ethanol.

Methods of analysing boron and tin have been described earlier [1]. Carbon and hydrogen analyses were carried out by M/s Australian Microanalytical Service CSIRO, Melbourne, Australia.

Infrared spectra were recorded on Perkin - Elmer 337 grating spectrophotometer. PMR spectra were recorded on an Mz 60 D machine.

(1) Preparation of tris(trimethyltin) borate

Azeotropic removal of water from a mixture of trimethyltin hydroxide (4 1 g, 22.69 mmoles) and boric acid (0.47 g, 7.58 mmoles) gave a colourless liquid (4.0 g, 89% yield), b.p. 130-132° /14 mm (Found B, 2 1, C, 20 8, H, 5.2 $C_9H_{27}O_3BSn_3$ calcd.. B, 2.0; C, 19.6, H, 5 0%)

Tris(trialkyltin) borates prepared by this method are listed in Table 1.

(2) Preparation of tributyltin metaborate

(a) On heating a mixture of tris(tributyltin) borate (2.68 g, 2 89 mmoles) and boric anhydride (0 202 g, 2 902 mmoles) at 240° ca 3 h, the latter dissolved to give clear colourless liquid, miscible with benzene

(b). Heating a mixture of bis(tributyltin) oxide (4 16 g, 6 99 mmoles) and boric anhydride (0 49 g, 7.04 mmoles) for ca 2 h at 200° yielded tributyltin metaborate (characterized by IR spectrum)

(3) Reaction between tris(tributyltin) borate and hydrogen chloride

On passing dry HCl gas through a solution of tris(tributyltin) borate (2 56 g) in benzene ($\approx$ 70 ml) for ca 3 h, an exothermic reaction took place with precipitation of boric acid (0.16 g, 95% yield) (Found: B, 17 0. H_3BO_3 calcd.· B, 17.4%.) Drying and distillation of the filtrate gave tributyltin chloride (2 3 g, 85% yield) (authentic IR spectrum).

(4) Reaction between tris(tributyltin) borate and acetyl chloride

Acetyl chloride (0.54 g, 6 88 mmoles) and tris(tributyltin) borate (1.68 g, 1.81 mmoles) reacted exothermically in benzene ($\approx$ 10 ml) A white gelatineous solid separated and was removed by decantation The liquid on distillation gave tributyltin chloride, b.p 89°/0 1 mm (1.4 g, 79% yield) (authentic IR spectrum)

(5) Reaction between tris(tributyltin) borate and acetic acid

On adding acetic acid (0.35 g, 5.84 mmoles) dropwise to a solution of tris(tributyltin) borate (1.80 g, 1.94 mmoles) in benzene ($\approx$ 10 ml), an exothermic reaction occurred with immediate separation of boric acid (0.106 g, 91% yield) (Found: B, 16.7. H_3BO_3 calcd.: B, 17.4%.). The filtrate after removal of solvent gave tributyltin acetate, m.p. 84° ; 2 0 g, 98% yield (Found: OAc, 17.0 $C_{14}H_{30}O_2Sn$ calcd.: OAc, 17.3%) (authentic IR spectrum).

(6). Reaction between tris(tributyltin) borate and phenol

A solution of phenol (0.41 g, 4.36 mmoles) in benzene (≈ 7 ml) was added to tris(tributyltin) borate (1.41 g, 1.52 mmoles) in benzene (≈ 10 ml); boric acid precipitated out (0.057 g, 77% yield) (Found: B, 17.0. H_3BO_3 calcd.: B, 17.4%). Distillation of the filtrate gave tributyltin phenoxide (1.3 g, 74% yield) at 140°/0.4 mm (lit. b.p. 152°/1 mm.) (Found: Sn, 30.8. $C_{18}H_{32}OSn$ calcd.: Sn, 31%.) (authentic IR spectrum).

(7). Reaction between tris(tributyltin) borate and butanethiol

On adding butanethiol (0.52 g, 5.78 mmoles) dropwise to tris(tributyltin) borate (1.78 g, 1.92 mmoles) in benzene (≈ 10 ml), an exothermic reaction took place with immediate precipitation of boric acid (0.08 g, 67% yield) (Found: B, 17.5. H_3BO_3 calcd.: B, 17.4%.). Tributyltin butanethiolate (2.1 g, 95% yield) (115°/0.1 mm; lit. 122-23°/0.2 mm) was obtained from the filtrate (Found: Sn, 30.1 $C_{16}H_{36}SSn$ calcd.: Sn, 30.6%) (authentic IR spectrum).

(8). Reaction between tris(tributyltin) borate and thiophenol

Similarly, an exothermic reaction between thiophenol (1.4 g, 12.71 mmoles) and tris(tributyltin) borate (3.1 g, 3.34 mmoles) in benzene (≈ 10 ml) gave boric acid (0.098 g, 58% yield) (Found: B, 16.7. H_3BO_3 calcd: B, 17.4%.) and tributyltin benzenethiolate (b.p 148°/0.2 mm lit. 147°/0.2 mm) (3.7 g, 87% yield) (Found: Sn, 29.8. $C_{18}H_{32}SSn$ calcd.: Sn, 29.7%.) (authentic IR spectrum).

(9). Reaction between tris(tributyltin) borate and acetic anhydride

Some heat was evolved on adding acetic anhydride (0.7 g, 6.86 mmoles) dropwise to a solution of tris(tributyltin) borate (1.9 g, 2.05 mmoles) in benzene (≈ 10 ml). On keeping the mixture overnight, white crystals of tributyltin acetate (m.p 83°) (Found: OAc, 17.5. $C_{14}H_{30}O_2Sn$ calcd.: OAc, 17.3%.) were obtained (authentic IR spectrum).

(10). Attempted reaction between tris(tributyltin) borate and isopropyl acetate

A mixture of isopropyl acetate (0.61 g, 5.98 mmoles) and tris(tributyltin) borate (1.65 g, 1.78 mmoles) in benzene was refluxed for ca 5 h. Distillation gave unchanged reactants.

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