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STANNOBOROXANES

I. SYNTHESIS OF 2-(TRIBUTYLSTANNOXY)-1,3,2-DIOXABOROLANES AND RELATED COMPOUNDS

S. K. MEHROTRA, G. SRIVASTAVA and R. C. MEHROTRA
The Chemical Laboratories, University of Rajasthan, Jaipur 4 (India)

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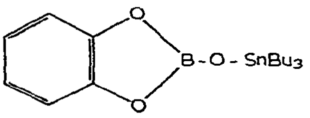
SUMMARY

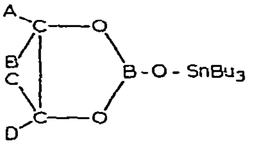
Various methods for establishing B–O–Sn bonds have been explored. Tris(tributylstannyl) borate and a number of 2-(tributylstannoxy)-1,3,2-dioxaborole, -borolanes and -borinanes have been prepared.

Wide industrial applications of siloxane polymers have led to a great deal of work in the field of heterometalloxanes containing M–O–M′ bonds[1]. Metalloboroxanes containing M–O–B bonds have also received considerable attention, but stannoboroxanes (compounds with Sn–O–B bonds) have been little studied[2]. Three uncharacterised stannyl borates, $(R_3SnO)_3B$, (R = Pr, Bu and Ph) have been described in patents[3–6], and the preparation of a few orthoborates, having insecticidal and fungicidal activity, and containing one or two stannyl groups, as well as dibutyltin borate[7], have also been claimed.

In this paper, we describe the synthesis of some simple 2-(tributylstannoxy)-1,3,2-dioxaborole (I), -borolanes (II) and -borinanes (III) and tris(tributylstannyl) borate by several routes:

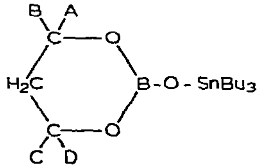


(I)



(II)

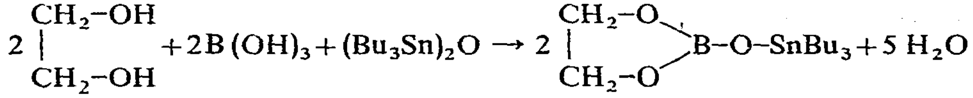
(a) A,B,C,D = H
(b) A,B,C=H; D=Me
(c) A,B,C,D = Me



(III)

(a) A,B,C,D = H
(b) A,B,C = Me; D = H

These compounds were obtained by azeotropic removal of water with benzene from a mixture of bis(tri-n-butyltin) oxide, boric acid and appropriate glycol, *e.g.*,



$$2\begin{array}{l}CH_2\text{-}OH\\ |\\ CH_2\text{-}OH\end{array} + 2B(OH)_3 + (Bu_3Sn)_2O \rightarrow 2\begin{array}{l}CH_2\text{-}O\\ |\\ CH_2\text{-}O\end{array}\!\!\!>B\text{-}O\text{-}SnBu_3 + 5\,H_2O$$

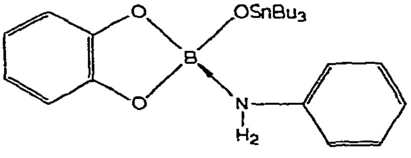
Tris(tributylstannyl) borate was prepared similarly.

$$2\,B(OH)_3 + 3\,(Bu_3Sn)_2O \rightarrow 2\,(Bu_3SnO)_3B + 3\,H_2O$$

The completion of the above reaction is indicated by the complete disappearance of the broad Sn–O–Sn peak at 763–787 cm^{-1} in the reaction mixture. The yields were quantitative in every case.

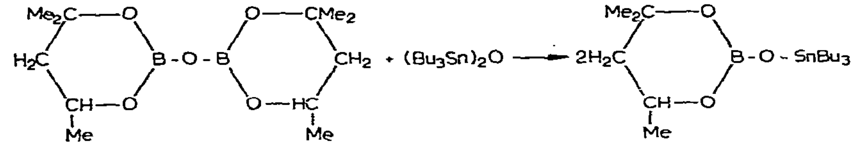
Attempts to prepare mixed products of the type $(Bu_3SnO)_nB(OH)_{3-n}$ ($n=1$ or 2), as described in the patent literature, were not successful, even when the reactions were carried out with various stoichiometric ratios of reactants.

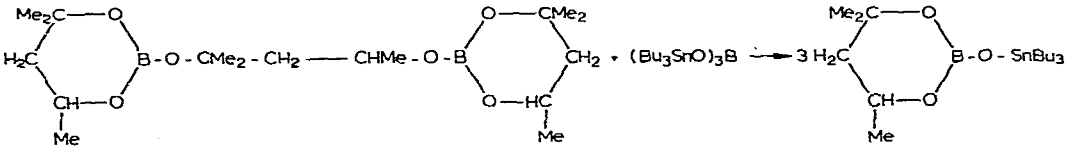
Tris(tributylstannyl) borate and compounds (I)–(III) are all colourless volatile liquids, monomeric in boiling benzene. They show high thermal stability except for (I), which is slightly yellowish when freshly distilled, but changes into a dark brown semi-solid within a couple of days. Like simple 2-alkoxy-1,3,2-benzodioxaboroles[8], compound (I) shows a tendency to form complexes (IV) with amines such as aniline.



(IV)

The ready interchangeability of boroxy and stannoxy groups has been demonstrated by the following reactions:





However, in the second case, the reaction can be taken to completion only by using a slight excess of 2,2′-(1,1,3-trimethyltrimethylenedioxy)bis(4,4,6-trimethyl-1,3,2-dioxaborinane).

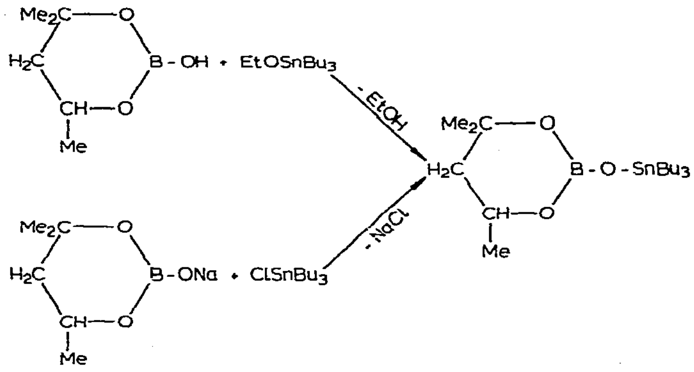
Stannoxy and isopropoxy groups attached to boron interchange readily in the following exothermic reactions:

$$2\,(Bu_3SnO)_3B + (i\text{-}PrO)_3B \rightarrow 3\,(Bu_3SnO)_2BO\text{-}i\text{-}Pr$$

$$(Bu_3SnO)_3B + 2\,(i\text{-}PrO)_3B \rightarrow 3\,Bu_3SnOB(O\text{-}i\text{-}Pr)_2$$

However, on distillation tris(tributylstannyl) borate was obtained as the major fraction in both cases.

The following two different routes were also employed for the synthesis of (IIIb):



Preparation of stannyl borates was also attempted by the reaction of tributyltin acetate with alkyl borates. The reaction with 2-isopropoxy-1,3,2-benzodioxaborole in cyclohexane was extremely slow, and the distillation of the product always resulted in a mixture of (I) and unchanged reactants. Similar results were obtained with triisopropyl borate. used in various molar ratios, even when toluene was used as solvent.

INFRA-RED SPECTRA

The spectrum of tris(tributylstannyl) borate is similar to that of bis(tributyltin) oxide, but there are two significant differences. The strong, broad peak at 784 cm^{-1} due to Sn–O–Sn asymmetric stretch observed in bis(tributyltin) oxide[9] completely disappears, and a strong, broad peak appears at 1290–1275 cm^{-1}; this may be assigned to the B–O–Sn asymmetric stretch. The ν_{as}(B–O) vibration in trialkyl borates[10] has been observed as a very strong peak at 1350–1310 cm^{-1}. In tris(trialkylsilyl) borates[11] also it appears in the same range (1333 ± 8 cm^{-1}). On replacing silicon by a heavier atom such as tin, a shift is expected towards lower frequencies, as observed for tris(tributylstannyl) borate.

2-(Tributylstannoxy)-1,3,2-dioxaborolane and borinanes show two types of ν_{as}(B–O) peaks in the regions 1430–1330 cm^{-1} and 1280–1270 cm^{-1}; the former may be due to B–O–C and the latter to B–O–Sn [(IIa): 1365–1345 vs(br), 1280–1270 vs(br); (IIc): 1430 vs, 1365 s, 1270 vs; (IIIa): 1400 vs, 1350 vs, 1280 vs, 1260 vs; (IIIb): 1375–1330 vs(br), and 1282 s cm^{-1}.]

In compound (I), ν_{as}(B–O–C)(aromatic) appears as a strong band at 1450 cm^{-1}, and is in the same range as observed for other 2-substituted-1,3,2-benzodioxaborole derivatives[10]. In the lower frequency region there is a very strong, broad peak at 1240 cm^{-1}, which may be due to both ν_{as}(B–O–Sn) and C–O. The lowering of ν_{as}(B–O–Sn) by 30 wave numbers is probably due to the strong $-I$ effect of the catecholate group.

EXPERIMENTAL

All glass apparatus was used, and special precautions were taken to exclude moisture.

Benzene (BDH, LR) was kept overnight over sodium wire then distilled, and finally dried azeotropically with ethanol. All the glycols were distilled before use. Bis(tri-n-butyltin) oxide (Nitto Kasei & Co. Japan) was used after distillation at 150–157°/0.05 mmHg.

Analytical methods

Boron was determined by hydrolysing the compound with 80% ethanol and titrating the boric acid produced against standard sodium hydroxide solution in the presence of mannitol, using phenolphthalein as indicator.

Tin was estimated as tin oxide by decomposing the compound with fuming nitric and sulphuric acids, and precipitating tin hydroxide by addition of ammonium hydroxide, ammonium nitrate ($\approx$30 g) being added to avoid coagulation.

Molecular weights were determined ebullioscopically in boiling benzene with a semi-micro ebulliometer employing thermistor sensing.

(1). *Reaction between bis(tri-n-butyltin) oxide and boric acid in* (3/2) *molar ratio in presence of benzene*

Azeotropic removal of water from a mixture of bis(tri-n-butyltin) oxide (7.76 g) and boric acid (0.54 g) in benzene (60 ml) gave tris(tributylstannyl) borate (7.64 g, 95% yield), b.p. 200–205°/0.2 mmHg, as a colourless liquid. (Found: B, 1.19; Sn, 38.01. $C_{36}H_{81}BO_3Sn_3$ calcd.: B, 1.18; Sn, 38.1%.)

(2). *Reaction between bis(tri-n-butyltin) oxide, boric acid and 2-methyl-2,4-pentanediol in* (1/2/2) *molar ratio*

Azeotropic removal of water with benzene (60 ml) from a mixture of bis(tri-n-butyltin) oxide (4.89 g), diol (1.93 g) and boric acid (1.016 g) gave a colourless liquid (6.66 g, 94% yield), b.p. 155°/0.5 mmHg. (Found: B, 2.5; Sn, 27.87. $C_{18}H_{39}BO_3Sn$ calcd.: B, 2.50; Sn, 27.41%.)

Compounds similarly prepared from other glycols are listed in Table 1.

TABLE 1

PREPARATIONS AND ANALYSES OF SOME NEW STANNOBOROXANES

Bis(tri-n-butyltin)-oxide (g)	*Glycol (g)*	*Boric acid (g)*	*Yield (%)*	*B.p. (°C/mmHg)*	(n_D^{30})	*Analysis found (calcd.) (%)*	
						B	*Sn*
4.89	2-Methyl-2,4-pentanediol (1.93)	1.016	94	155/0.5	1.4612	2.50 (2.50)	27.87 (27.41)
5.87	2,3-Dimethyl-2,3-butanediol (2.48)	1.29	89	161/0.8	1.4619	2.53 (2.50)	27.35 (27.41)
8.81	1,2-Ethanediol (1.92)	1.84	85	125–135/0.2	1.4798	3.12 (2.87)	30.63 (31.50)
3.06	1,2-Propanediol (0.79)	0.64	91	120–121/0.2	1.4678	2.84 (2.77)	30.90 (30.35)
2.56	1,3-Propanediol (0.71)	0.56	87	132/0.1	1.4738	3.14 (2.77)	30.24 (30.35)
4.82	1,2-Benzenediol (1.77)	1.02	82	143–148/0.1		2.58 (2.54)	27.80 (27.93)

(3). *Reaction between 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and bis(tri-n-butyltin) oxide in 1/1 molar ratio*

Heating a mixture of bis(tri-n-butyltin) oxide (3.95 g) and pyroborate (1.87 g) and distilling under reduced pressure, gave a colourless compound (5.7 g, 98 % yield) b.p. 158°/0.6 mmHg. (Found: B, 2.56; Sn, 26.98. $C_{18}H_{39}BO_3Sn$ calcd.: B, 2.50; Sn, 27.41 %.)

(4). *Reaction between tributyltin ethoxide and 2-hydroxy-4,4·6-trimethyl-1,3,2-dioxaborinane in 1/1 molar ratio*

A mixture of tributyltin ethoxide (2.44 g) and 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane (1.054 g) was heated for about 6 h. After drying *in vacuo* at 27°/0.4 mmHg, distillation gave a colourless liquid, b.p. 127–129°/0.2 mmHg, (2.85 g, 91 % yield). (Found: B, 2.61; Sn, 27.82. $C_{18}H_{39}BO_3Sn$ calcd.: B, 2.50; Sn, 27.41 %.)

(5). *Reaction between 2,2'-(1,1,3-trimethyltrimethylenedioxy)bis(4,4,6-trimethyl-1,3,2-dioxaborinane) and tris(tributylstannyl) borate*

A mixture of tris(tributylstannyl) borate (3.02 g) and excess 2,2'-(1,1,3-trimethyltrimethylenedioxy)bis(4,4,6-trimethyl-1,3,2-dioxaborinane) (2.92 g) was heated for about 5 h. Distillation gave (IIIb) at 152–155°/1 mmHg (2.03 g, 66 % yield) (identified by authentic spectrum as 2-(tributylstannoxy)-4,4,6-trimethyl-1,3,2-dioxaborinane).

(6). *Reaction between sodium salt of 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane and tributyltin chloride in 1/1 molar ratio*

A mixture of sodium salt of 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane (2.55 g) and tri-n-butyltin chloride (5.1 g) was refluxed in benzene (30 ml) for about 8 h. Sodium chloride was filtered off, and the solvent removed, and the residue was distilled at 118–133°/0.2 mmHg (5.9 g, 89 % yield). (Found: B, 2.47; Sn, 27.6. $C_{18}H_{39}BO_3Sn$ calcd.: B, 2.50; Sn, 27.41 %.)

(7). *Reaction between tributyltin acetate and triisopropylborate in 1/1 molar ratio*

A mixture of tributyltin acetate (5.17 g) and triisopropyl borate (3.07 g) was refluxed in toluene for about 10 h with slow fractionation. It was then dried and distilled to give a white solid, b.p. 96°/0.05 mmHg (2.57 g). (Found: B, 0.6; Sn, 35.07; OAc, 16.8. $C_{18}H_{41}BO_3Sn$ calcd.: B, 2.5; Sn, 27.16 %.)

(8). *Reaction between 2-(tributylstannoxy)-1,3,2-dioxaborole and aniline in 1/1 molar ratio*

A brown complex (2.50 g), m.p. 160°, was precipitated immediately on adding aniline (0.57 g) to the borole (2.04 g) in benzene (10 ml). It was filtered and dried *in vacuo*. (Found: B, 2.24; N, 2.75; Sn, 20.4. $C_{24}H_{38}BNO_3Sn$ calcd.: B, 2.1; N, 2.71; Sn, 22.94 %.)

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