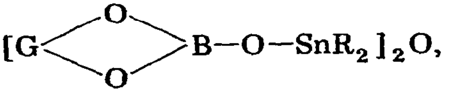
Journal of Organometallic Chemistry, 65 (1974) 367—376

STANNOBOROXANES

III*. SYNTHESIS AND REACTIONS OF 1,3-BIS(BORYLOXY)TETRAALKYLDISTANNOXANES AND RELATED COMPOUNDS

S K MEHROTRA, G. SRIVASTAVA and R C MEHROTRA
The Chemical Laboratories, Rajasthan University, Jaipur 302004 (India)
(Received June 15th, 1973)

Summary

1,3-Bis(boryloxy)tetraalkyldistannoxanes,  $[G\langle^{O}_{O}\rangle B{-}O{-}SnR_2]_2O$, R = Me, Bu; G = CMe_2CH_2CHMe—, —CMe_2—CMe_2— and —$CHMe$—CH_2— have been prepared from dialkyltin oxide and pyroborate, or directly from dialkyltin oxide, boric acid and glycol A dimeric structure for these compounds is proposed on the basis of molecular weight, IR and PMR studies. The reactivity of the Sn—O—B bond towards PhNCO and Me_3SiCl has been demonstrated.

Introduction

Tributyltin(IV) boroxanes have been synthesized recently by a number of routes [1]. In continuation of this work, we now report the synthesis and a few reactions of some novel dialkyltin(IV) boroxanes

Results and discussion

Azeotropic dehydration of a mixture of alkyltin oxide and boric acid constitutes one of the most convenient methods of forming B—O—Sn bonds, and the method has been utilized to synthesize tris(tributyltin) borate [1] and other tris(trialkyltin) borates [2].

$$3\,(Bu_3Sn)_2O + 2\,H_3BO_3 \xrightarrow{C_6H_6} 2\,(Bu_3SnO)_3B + 3\,H_2O\uparrow \qquad (1)$$

The method is not successful, however, in case of dibutyltin oxide and contrary

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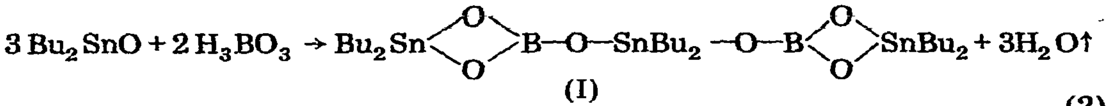
* For part II see ref 2

to Ramsen's claim [3] to have isolated cyclic stannoboroxane (I) by the following method (2),



$$3\,Bu_2SnO + 2\,H_3BO_3 \rightarrow \underset{(I)}{Bu_2Sn{<}(O)_2{>}B{-}O{-}SnBu_2{-}O{-}B{<}(O)_2{>}SnBu_2} + 3H_2O\uparrow \qquad (2)$$

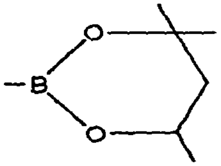
We obtained a mixture of unreacted dibutyltin oxide and boric anhydride (irrespective of molar ratio of reactants) after azeotropic removal of water with toluene. It seems that dibutyltin oxide and boric acid (or its anhydride), being isoluble in the reaction medium (benzene or toluene) are unable to enter into reaction.

Dibutyltin oxide also fails to dissolve in an excess of isopropylborate even on refluxing for 10-12 h, showing that there is no transfer of isopropoxy groups from boron to tin.

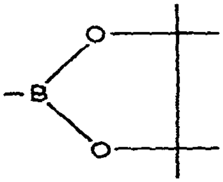
On the other hand, cyclic pyroborates, e g , 2,2′-oxybis(4,4,6-trimethyl-1,3,2-dioxaborinane), dissolve dibutyltin oxide at 120-130° (2 h) to give a clear liquid, which solidifies at room temperature This solid gives a clear solution in benzene showing that no Bu_2SnO is present. The reactions were run at different molar ratios (eqns. 3 and 4)·

$$2\,Bu_2SnO + QOQ \xrightarrow{\Delta} \underset{(II)}{QOSnBu_2OSnBu_2OQ} \qquad (3)$$

(IIa) Q =



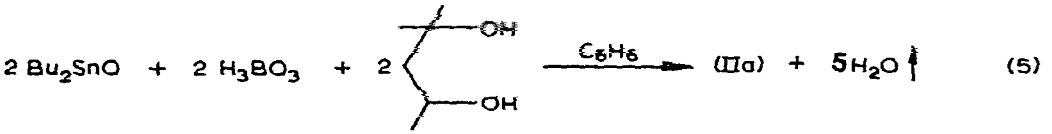
(IIb) Q =



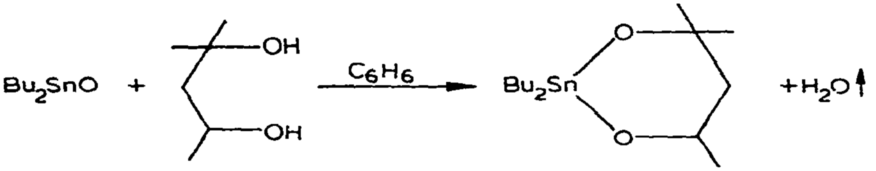
$$2\,Bu_2SnO + 2\,QOQ \begin{cases} \xrightarrow{X}\!\!\!\!\!\!/\;\; \underset{(III)}{2\,Bu_2Sn(OQ)_2} \\ \xrightarrow{Y} (II) + QOQ \end{cases} \qquad (4)$$

The stannoboxanes (II) are obtained in quantitative yields, and can be recrystallized from acetonitrile. Reaction (4) appears to follow course (Y) rather than (X). The infrared spectrum of the product showed it to be a mixture of (II) and unchanged pyroborate. The latter could be easily removed by washing the product with acetonitrile, so that pure (II) was left.

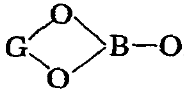
Derivatives (II) could also be prepared directly from a mixture of dibutyltin oxide, boric acid and the glycol (hexylene glycol or pinacol) by removing water azeotropically with benzene, e g.,



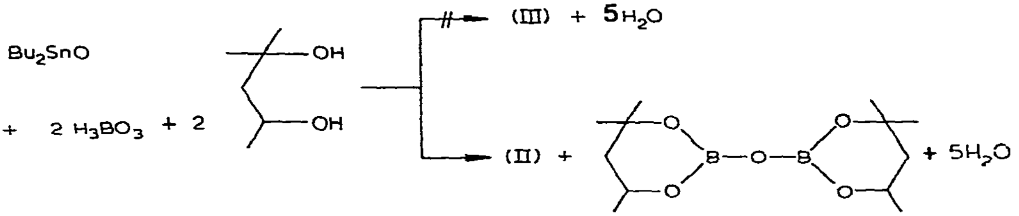
It should be mentioned that dibutyltin glycolates [4] are also obtained by azeotropic dehydration of a mixture of dibutyltin oxide and the glycol, e g.,



(6)

Thus, the absence of any dibutyltin glycolate in the reaction (5) indicates that the glycol reacts preferentially with boric acid with the formation of alkylene hydrogen borate,  which, unlike boric acid, is soluble in benzene and is capable of reacting with Bu_2SnO. It is also possible that the hydrogen borate is first dehydrated to pyroborate, which reacts with Bu_2SnO as in eqn (3).

Attempts to prepare derivatives (III) by reaction (7) also failed, and instead a mixture of (II) and pyroborate was obtained



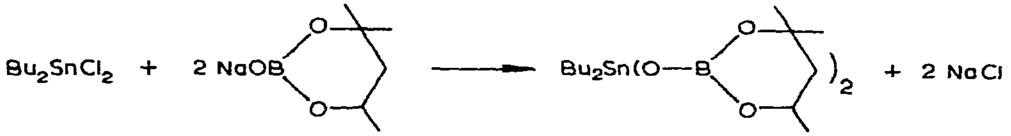
(7)

It is noteworthy that earlier attempts to prepare the silicon analogues [5] of (III), i.e. $R_2Sn(OSiMe_3)_2$, by cohydrolysis of a mixture of R_2SnCl_2 and Me_3SiCl were unsuccessful, for example, with R = Me the product was invariably 1,3-bis(trimethylsiloxy)tetraalkyldistannoxane, $(Me_3SiOSnR_2)_2O$. Schmidbauer [6] prepared $Me_2Sn(OSiMe_3)_2$ by another route (8)

$$Me_2SnCl_2 + 2LiOSiMe_3 \rightarrow Me_2Sn(OSiMe_3)_2 + 2LiCl \qquad (8)$$

and reported that whereas $Me_3SnOSiMe_3$ is stable up to 200°, the former decomposes above 150° and intermediates of the type $Me_3SiO(SnMe_2O)_nSiMe_3$ may be detected in the decomposition products by IR and NMR spectroscopy.

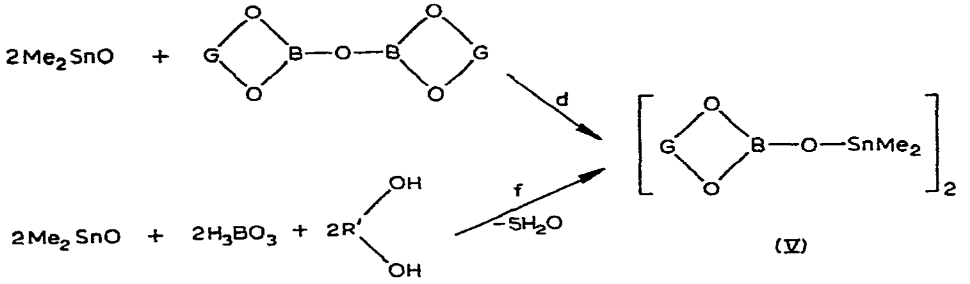
Attempted synthesis of (III) by route (9) was not successful, mainly because of the very low solubility of (IV) in the reaction medium Even with large excess of (IV), the product contained some chlorine. On the other hand, this route was satisfactory for the preparation of the corresponding tributyltin derivative [1] ·



(9)

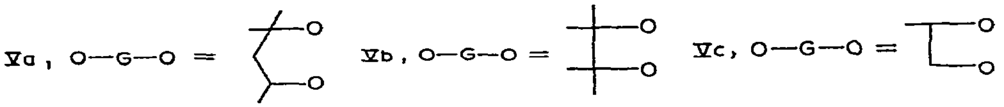
(IV)

Reactions of type (3) and (5) with Me_2SnO are comparatively slower and require longer reaction times and a higher boiling solvent (e.g. toluene):

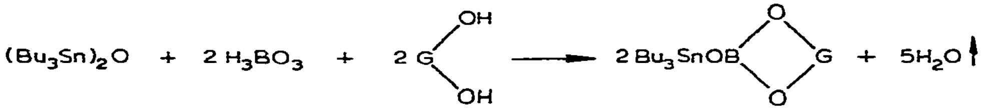


(V)

(10)



The lower reactivity of $(Me_2SnO)_n$ may be related to its higher degree of polymerization. It should be mentioned that reaction (10f) failed with ethylene and trimethylene glycols; $(Me_2SnO)_n$ remained insoluble even after refluxing for about 12 hours. In case of ethylene glycol, the non-reactivity may be due to the insolubility of the pyroborate itself. However, the pyroborate of trimethylene glycol is a miscible liquid [7], and its non-reactivity with $(Me_2SnO)_n$ is somewhat surprising. Perhaps it indicates a relationship between the nucleophilicity of boryloxy oxygen of the pyroborate and its capacity to attach and react with dialkyltin oxides. However, it should be remembered that reactions of type (11) were quite facile even with ethylene and trimethylene glycol [1]:

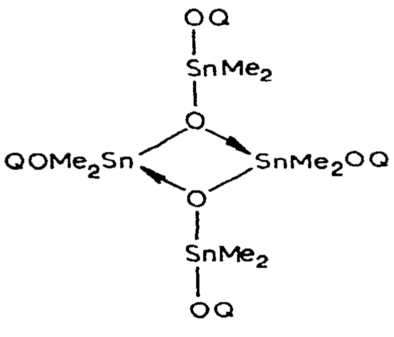


(11)

Distannoxanes of the type $XR_2SnOSnR_2X$, where X is an electronegative substituent (e.g.. Cl, Br, I, OAc, OPh, $OSiMe_3NCS$, etc) have been prepared in recent years and there has been some interest in their structure [8]. Molecular weight, infrared, PMR and X-ray data as well as a recent ^{119}Sn NMR and Mossbauer study show dimeric nature and ladder like structure for these compounds. The data available to us for derivatives (II) and (V) indicate that these fit into the general pattern.

Compounds (II) and (V) are dimeric in benzene at room temperature (osmometry) but in refluxing benzene the association tends to break down to some extent The dimeric nature is further confirmed by the PMR spectra of (V) In all three derivatives, the methyls on tin appear as two singlets, which is consistent with structure (VI).

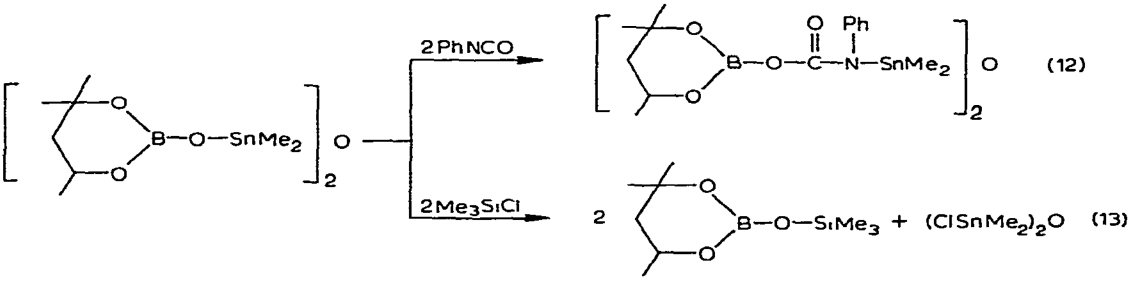
IR spectra of (II) and (V) also show two peaks for the B—O—Sn stretch at 1280 ± 10 and 1260 ± 10 cm^{-1}. These and the Sn—O—Sn peaks of (II) and (V) are shown in Table 1. In view of the reduced donor character of the oxygen, it



(VI)

will be interesting to confirm these ladder-like structures by other techniques.

In an initial study of the reactions of the Sn—O—B bond in the distannoxanes (II) and (V) the compounds were treated with phenyl isocyanate and trimethylchlorosilane. An insertion reaction (12) occurs with the former whereas with the latter, cleavage of Sn—O bond takes place (13).



The completeness of reaction (12), which was exothermic in benzene, was indicated by the complete disappearance of ν(—N=C=O) at 2270 ± 10 cm^{-1} [9] and the appearance of ν(C = O) at 1625 cm^{-1} In view of the greater ionic character of the Sn—O bond than of the B—O bond, insertion of PhNCO should presumably occur with the former. Insertion into B—O bond is very rare, and has been demonstrated only in the case of $Ph_2B(OMe)$ [10] Reaction (13) is also exothermic and the borosiloxane obtained has recently been pre-

(Continued p 374)

TABLE 1

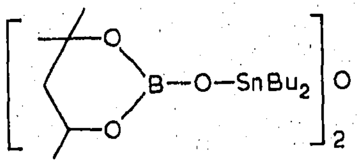
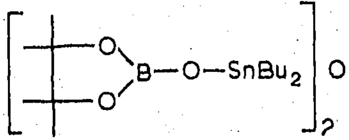
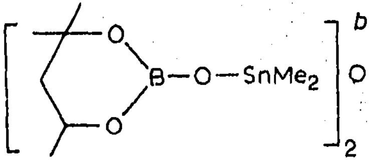
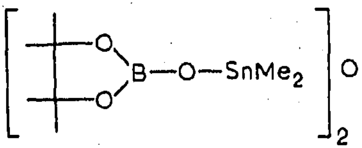
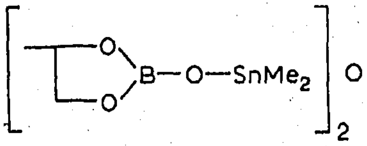
IR SPECTRA

Compound	ν_{as}(B—O—Sn) (cm^{-1})	ν_{as}(Sn—O—Sn) (cm^{-1})	Me_2Sn peaks (τ)
(IIa)	1285 1267	595, 577	
(IIb)	1272 1255	595 575	
(Va)	1290 1270	615 590	9 40 9 5[b]
(Vb)	1285 1255	605, 580	9 36 9 43[c]
(Vc)	[a]	610, 585	9 30, 9 38[d]

[a] Assignment with any amount of certainty is difficult as strong peaks are absent in 1250—1300 cm^{-1} region. [b] At τ 8.83 ppm doublet J 6 Hz (6 protons), τ 8 80 singlet (12 protons), τ 8 13—8 53 multiplet (4 protons) τ 5 4—6 25 complex multiplet (2 protons) [c] At τ 8 90 singlet (24 protons) [d] At τ 8 75 doublet J 6 Hz (6 protons) τ 6 17—6 63 multiplet (4 protons)· τ 5 28—6 08 complex multiplet (2 protons)

TABLE 2

SOME REACTIONS OF DIALKYLTIN OXIDE

Dialkyltin oxide (g) (mmoles)	Boric acid (g) (mmoles)	Glycol (g) (mmoles)	Product	M.p. (°C)	Yield (%)	Analysis, found (calcd.) (%)		
						B	C	H
5.28 (21.21)	1.53 (24.19)	2.51 (21.27)		56–57	98	2.8 (2.8)	43.8 (43.8)	7.9 (7.9)
[a]3.45 (13.87)	1.70 (26.79)	3.28 (27.54)		57	53	2.7 (2.8)		
3.75 (15.08)	0.94 (15.16)	1.78 (15.09)		84–86	99	2.7 (2.8)	43.5 (43.8)	7.9 (7.9)
[a]3.21 (12.90)	1.64 (26.44)	3.05 (25.84)		86	46	2.6 (2.8)		
2.07 (12.57)	0.79 (12.60)	1.49 (12.63)	 [b]	166–168	72	3.4 (3.6)	32.6 (32.1)	6.2 (6.1)
[a]1.31 (7.95)	1.00 (16.13)	1.88 (15.93)		167	42	3.8 (3.6)		
2.71 (16.45)	1.03 (16.62)	1.94 (16.44)		287–288	94	3.5 (3.6)	31.8 (32.1)	5.9 (6.1)
[a]1.42 (8.62)	1.07 (17.26)	2.03 (17.20)		288	40	3.3 (3.6)		
1.53 (9.29)	0.58 (9.33)	0.70 (9.21)		188–190	54	4.1 (4.2)	23.3 (23.3)	4.6 (4.2)

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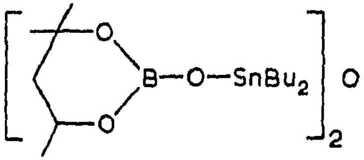
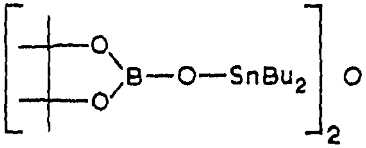
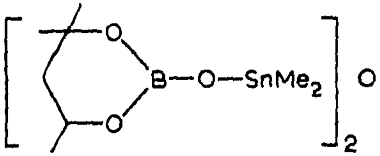
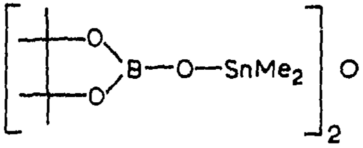
[a] In all these cases the final products were obtained after washing with acetonitril the washings gave the corresponding pyroborates, the infrared spectra of the washed products were similar to those of samples prepared by processes (10f) or (5). [b] Mol. wt. found osmometrically 895, ebullioscopically 664; calcd. 599.

TABLE 3

SOME REACTIONS OF DIALKYLTIN OXIDE WITH PYROBORATE

Dialkyltin-oxide (g) (mmoles)	Pyroborate (g) (mmoles)	Product[a]	M p. (°C)	Yield (%)	Analysis, found (cald) (%) B	C	H
2 70 (10 83)	1 49 (5 52)		57	98	2 7 (2 8)		
[b] 4 70 (18 91)	5 10 (18 91)		56	44	2 6 (2 8)		
3 30 (13 26)	1 77 (6,57)		87	97	2 8 (2 8)		
[b] 1 77 (7 12)	1 90 (7 05)		86	52	3 0 (2 8)		
1 35 (8 19)	1 12 (4 15)		162	90	3 4 (3 6)	32 6 (32 1)	6 2 (6 1)
[b] 1.36 (8 26)	2 22 (8 16)		164–5	41	3 3 (3 6)		
1 41 (8 56)	1 16 (4 30)		288	96	3 5 (3 6)	32 2 (32 1)	6 1 (6 1)
[b] 1 45 (8 80)	2 39 (8 86)		286	42	3 8 (3 6)		

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[a] In all cases, the IR spectra were similar to those of samples prepared by process (5) or (10f) [b] The spectra of the solids (after washing with acetonitrile) were, similar to those of samples prepared by process (5) or (10f) Evaporation of the washings gave products showing the IR spectra of the corresponding pyroborates

pared by a similar reaction of 2-(tributylstannoxy)-4,4,6-trimethyl-1,3,2-dioxaborinane.

The reactions of dialkyltin oxide with boric acid and glycol are summarised in Table 2, and with pyroborate in Table 3.

Experimental

All the glycols were distilled before use Dibutyltin oxide (Nitto Kasei and Co, Japan), dimethyltin oxide (Ventron, Alpha, Alpha corpn. USA), and boric acid (E. Merk, India) were used as supplied. The pyroborates of hexylene glycol and pinacol* were prepared by removing water azeotropically from a mixture of boric acid and the glycol in benzene

Boron was estimated by Thomas' [11] method, Carbon and hydrogen analyses were carried out by the Australian microanalytical service CSIRO, Melbourne, Australia. Infrared spectra were recorded with Nujol mulls on Perkin - Elmer model 337-grating spectrophotometer using KBr optics. PMR spectra were recorded on a Varian A60 spectrophotometer. Molecular weights were determined both ebullioscopically and osmometrically in benzene.

(1). Reaction between dibutyltin oxide, boric acid and hexylene glycol

(a) Removal of water azeotropically with benzene from a mixture of dibutyltin oxide (5 28 g, 21.21 mmoles), boric acid (1.53 g, 24.19 mmoles) and hexylene glycol (2 51 g, 21 27 mmoles) followed by drying of the product in vacuo yielded (IIa) (m.p. 57°) (8 g, 98% yield) as a white solid, recrystallized from acetonitrile (Found: C, 43.8, H, 7 9, B, 2.8. $C_{28}H_{60}B_2O_7Sn_2$ calcd: C, 43.8; H, 7.9, B, 2 8%.)

(*b*). Removal of water azeotropically with benzene from a mixture of dibutyltin oxide (3 45 g, 13.87 mmoles), boric acid (1.70 g, 26 79 mmoles), and hexylene glycol (3.28 g, 27 54 mmoles) yielded a viscous liquid, which was then treated with acetonitrile to give (IIa) as insoluble white solid yield (2 8 g, 53%) (m.p 57%). Evaporation of the washings left pyroborate (authentic IR spectrum). Similar reactions are summarized in Table 2.

(2). Reaction between dibutyltin oxide and 2,2'-oxybis(4,4,6-trimethyl-1,3,2-dioxaborinane)

(*a*) A mixture of dibutyltin oxide (2.7 g, 10 83 mmoles) and pyroborate (1 49 g, 5 52 mmoles) was heated for about 4 h at a bath temperature of 120-40°. On cooling a white solid (which was completely miscible with benzene) was obtained, and gave (IIa) after recrystallizing from acetonitrile (m p. 57°) (4 18 g, 98% yield). (Found B, 2 7. $C_{28}H_{60}B_2O_7Sn_2$ calcd.: B, 2.8%.)

(*b*). A mixture of dibutyltin oxide (4.7 g, 18.91 mmoles) and pyroborate (5.1 g, 18.91 mmoles) was heated for about 4 h at a bath temperature of 120-40° to yield a mixture of white solid and viscous liquid This was then treated with acetonitrile to give (IIa) as an insoluble product (m.p. 56°) (3 2 g, 44%). Evaporation of the washings gave pyroborate (authentic IR spectrum).

Similar reactions are summarized in Table 3.

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* Hexylene glycol = 2-methyl-2,4-pentanediol pinacol = 2,3-dimethyl-2 3-butanediol.

(3). Reaction between dimethyltin oxide, boric acid and ethylene glycol

Removal of water azeotropically with benzene from a mixture of dimethyltin oxide (1.29 g, 7.83 mmoles), boric acid (0.48 g, 7 74 mmoles), ethylene glycol (0.48 g, 7.74 mmoles) and benzene (≈ 60 ml) gave soluble (0.38 g) and insoluble (1.64 g) portions on decantation. The analysis of the insoluble product (Found: B, 3.2, 5.9, 4.7. $C_8H_{20}B_2O_7Sn_2$ calcd.: B, 4.4%.) and its infrared spectrum showed that the reaction does not proceed in the forward direction.

(4) Reaction between dimethyltin oxide, boric acid and trimethylene glycol

Azeotropic removal of water from a mixture of dimethyltin oxide (1 40 g, 8.5 mmoles), boric acid (0.53 g, 8 55 mmoles), trimethylene glycol (0.68 g, 8.94 mmoles) and benzene (≈ 60 ml) yielded soluble (0.66 g) and insoluble (1 57 g) portions. (Found: B, 2 86, 2 63 $C_{10}H_{24}B_2O_7Sn_2$ calcd.: B, 4 2%) The infrared spectrum revealed that the reaction had not proceeded in the forward direction.

(5) Reaction between (Va) and phenyl isocyanate

Phenyl isocyanate (0.29 g, 2.44 mmoles) was added dropwise to a solution of (Va) (0.74 g, 1 24 mmoles) in benzene (≈ 5 ml). The reaction proceeded exothermally with the separation after 20 min of a light brown solid, which showed no free isocyanate peak. (Found B, 2 4. $C_{30}H_{46}B_2N_2O_9Sn_2$ calcd : B, 2.6%.)

(6) Reaction between (Va) and trimethylchlorosilane

Trimethylchlorosilane (0.42 g, 3.87 mmoles) was added dropwise to a solution of (Va) (0 96 g, 1.60 mmoles) in benzene (≈ 5 ml). The reaction was exothermic, with separation of white solid. Distillation gave 2-(trimethylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane, as a colourless liquid at 76-77°/8 mm (0 16 g) and left 1,3-dichlorotetramethylstannoxane as white solid (0.6 g) in the distillation flask (Found: C, 13.1; H, 2.8. $C_4H_{12}Cl_2OSn_2$ calcd.: C, 12.5; H, 3.1%.)

(7) Reaction between dibutyltin oxide and boric acid

Azeotropic dehydration with toluene (≈ 60 ml) from a mixture of dibutyltin oxide (4.71 g, 18.93 mmoles) and boric acid (0 78 g, 12 58 mmoles) yielded a white solid (yield calcd. 5.15 g, found 5.26 g), with an IR spectrum identical with that of authentic Bu_2SnO

Acknowledgements

One of the authors (S.K.M.) is grateful to CSIR for a Junior Research fellowship. Thanks are also due to Prof. G.B. Singh for his generous help in recording the PMR spectra of the compounds.

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