Journal of Organometallic Chemistry, 65 (1974) 195—204

ORGANIC DERIVATIVES OF TIN

VI. REACTIONS OF BUTYLTIN TRIISOPROPOXIDE WITH ALKANOLAMINES

D.P. GAUR, G. SRIVASTAVA and R.C. MEHROTRA
The Chemical Laboratories, University of Rajasthan, Jaipur 302004 (India)

(Received June 5th, 1973)

Summary

Butyltin triisopropoxide, $BuSn(OPr\text{-}i)_3$, reacts with various alkanolamines, viz. $HOCH_2CH_2NH_2$, $HOCH_2CH_2CH_2NH_2$, $HOCH_2CH_2NHMe$, $(HOCH_2CH_2)_2NH$ and $(HOCH_2CH_2)_3N$ in different molar ratios to yield cyclic derivatives. Identical products are obtained by the reactions of $BuSnO_{3/2}$ with $HOCH_2CH_2NHMe$ and $(HOCH_2CH_2)_3N$. Alcoholysis reactions of $BuSn(OPr\text{-}i)_3$ with $HOXNMe_2$ ($X = CH_2CH_2$ and $CHMeCH_2$) yield distillable $BuSn(OPr\text{-}i)_{3-n}(OXNMe_2)_n$ ($n = 1$, 2 and 3) according to molar ratios of the reactants. Molecular weights and IR spectra are reported.

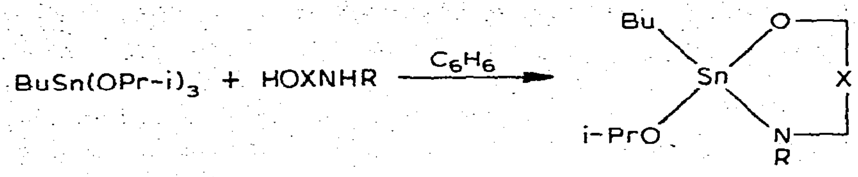
Introduction

In view of an interesting trend observed in the reactions of alkanolamines with tin(IV) [1], dibutyltin(IV) [1,2] and tributyltin(IV) [3] moieties it was considered worthwhile to complete the series by a study of the reactivity of monobutyltin(IV) moiety towards alkanolamines. A survey of literature reveals that no work has been carried out on monoalkyltin(IV) derivatives of alkanolamines except for the synthesis of a few derivatives of triethanolamine by Davies et al. [4]. The high reactivity of butyltin triisopropoxide towards glycols [5], thiols [6], β-diketones [7], unsaturated substrates [7] and various protic reagents [8] has already been investigated. We describe below studies of the reactions of butyltin triisopropoxide and sesquioxide with various alkanolamines in different molar ratios under various experimental conditions.

Results and discussion

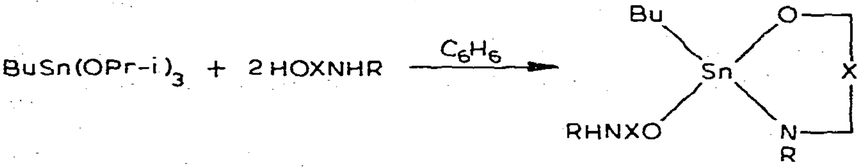
Butyltin triisopropoxide reacts exothermally with a variety of alkanol amines, HOXNHR, in different molar ratios to give cyclic products arising from the replacement of isopropoxy groups by both hydroxyl and amino groups

The reactions are quite facile, and proceed to completion at ambient temperature as represented in eqns. (1)-(4):



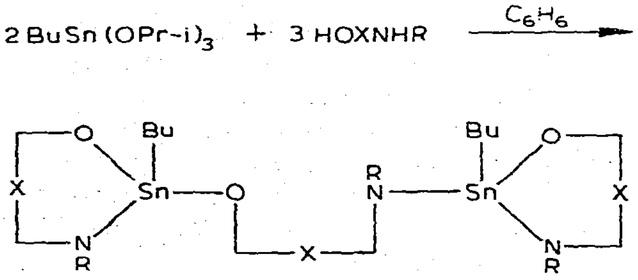
(1)

(I)



(2)

(II)



(3)

(III)

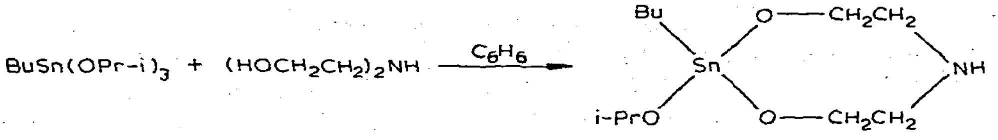
$$BuSn(OPr\text{-}i)_3 + 3\ HOXNHR \xrightarrow{C_6H_6} \underset{(IV)}{BuSn(OXNHR)_3} \qquad (4)$$

($X = CH_2CH_2$, $CH_2CH_2CH_2$ and $R = H$; $X = CH_2CH_2$ and $R = Me$.)

However, when the alcoholysis reactions of $BuSn(OPr\text{-}i)_3$ with $HOXNH_2$ ($X = CH_2CH_2$ and $CH_2CH_2CH_2$) were carried out in 1/1 and 2/3 molar ratios in refluxing benzene, the reactions appear to proceed further, slowly yielding products with higher tin contents. In order to force this second stage of the reactions, an equimolar mixture of $BuSn(OPr\text{-}i)_3$ and $HOCH_2CH_2NH_2$ was refluxed in a high boiling solvent such as *m*-xylene (b.p. 139°) and the progress of the reaction was followed by estimating the isopropanol fractionated out along with the solvent. All the three isopropoxy groups appear to be replaced under these conditions, yielding the product (V).

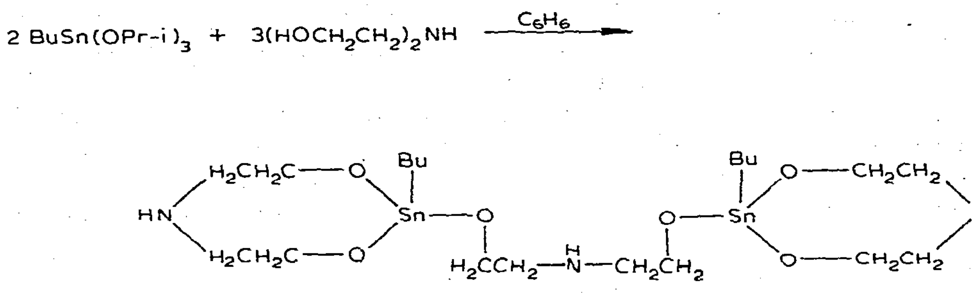
$$BuSn(OPr\text{-}i)_3 + HOCH_2CH_2NH_2 \xrightarrow[\text{reflux}]{m\text{-xylene}} \underset{(V)}{BuSn(OCH_2CH_2N)} \qquad (5)$$

The reactions of $BuSn(OPr\text{-}i)_3$ with $(HOCH_2CH_2)_2NH$ carried out at ambient temperature yield products (VI) and (VII).



(VI)

(6)

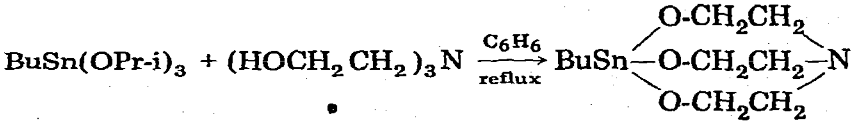


(VII)

(7)

However, as for ethanolamine and propanolamine, the reactions of diethanolamine also seem to proceed further to give products with high tin contents when carried out in refluxing benzene.

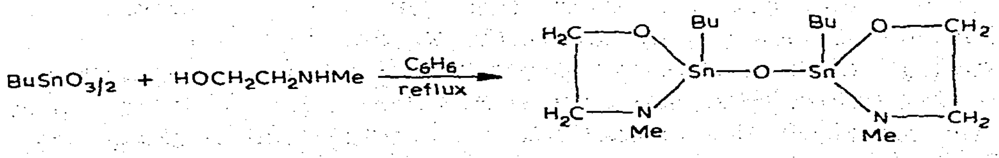
The reaction of $BuSn(OPr\text{-}i)_3$ with $(HOCH_2CH_2)_3N$ in equimolar ratio in refluxing benzene yielded butylstannatrane (eqn. 8):



$$BuSn(OPr\text{-}i)_3 + (HOCH_2CH_2)_3N \xrightarrow[\text{reflux}]{C_6H_6} BuSn\begin{cases} O\text{-}CH_2CH_2 \\ O\text{-}CH_2CH_2 \\ O\text{-}CH_2CH_2 \end{cases} N \qquad (8)$$

(VIII)

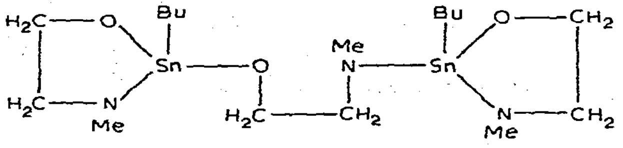
With *N*-methylethanolamine and triethanolamine, further reactions are not of course, possible and pure products, [(III), (VIII) and (IX)] are thus obtained from the reactions between these alkanolamines and $BuSnO_{3/2}$ in refluxing benzene followed by azeotropic removal of water. On the other hand, $BuSnO_{3/2}$ reacts with ethanolamine and propanolamine in refluxing benzene to liberate water and a mixture of products similar to those obtained from $BuSn(OPr\text{-}i)_3$ under similar conditions.



(IX)

(9)

$$2\,BuSnO_{3/2} + 3\,HOCH_2CH_2NHMe \xrightarrow[\text{reflux}]{C_6H_6}$$



(III)

(10)

$$BuSnO_{3/2} + (HOCH_2CH_2)_3N \xrightarrow[\text{reflux}]{C_6H_6} (VIII) \tag{11}$$

The ethanolamine, diethanolamine, and triethanolamine derivatives are white solids readily or moderately soluble in benzene, whereas those of *N*-methylethanolamine and propanolamine are either viscous liquids or low melting solids. Product (V) is a brown solid insoluble in benzene. All these derivatives decomposed on attempted vacuum distillation. Pyrolysis of the ethanolamine derivatives of type (I) and (II) at 190-205°/0.2-0.4 mm yielded SnO_2 as the final product. Molecular weight determinations on the ethanolamine derivatives of type (I) and the low solubility of other derivatives indicate their associated nature.

The butylstannatrane (VIII) synthesised by either methods (eqns. 8 and 11) is identical to that reported by Davies et al. [4], and may be compared with germatranes [9], silatranes [10] and stannatranes [1,11] described earlier by Voronkov et al. and other workers. Molecular weight determination ebulliometrically in benzene shows butylstannatrane to be associated in the solid state, but it undergoes a slow dissociation in refluxing benzene and finally the degree of association of ca. 1.6 is obtained.

The formation of mixtures in derivatives of type (II), (III) and (VII) may be excluded, as the IR spectra of *N*-methylethanolamine derivatives do not show any OH absorption due to unreacted alkanolamine, and furthermore in most of the cases crystalline solids or low melting solid products are obtained, whereas both $BuSn(OPr\text{-}i)_3$ and alkanolamines are liquids.

Butyltin triisopropoxide reacts exothermally with $HOXNMe_2$ in 1/1, 1/2 and 1/3 molar ratios in refluxing benzene yielding mono-, bis- and tris-aminoalkoxides respectively. The progress of the reactions can be followed by determination of the alcohol in the azeotrope:

$$BuSn(OPr\text{-}i)_3 + n\,HOXNMe_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{(X)}{BuSn(OPr\text{-}i)_{3-n}(OXNMe_2)_n} \tag{12}$$

$(X = CH_2CH_2 \text{ and } CHMeCH_2)$

All the products obtained by the reaction shown in eqn. (12) are colourless or yellow liquids, and distilled pure in 50-86% yields. Molecular weight determinations in refluxing benzene reveal them to be monomeric. They all are very sensitive towards atmospheric moisture, and their identity is confirmed by elemental analysis, molecular weight measurements, and IR spectra.

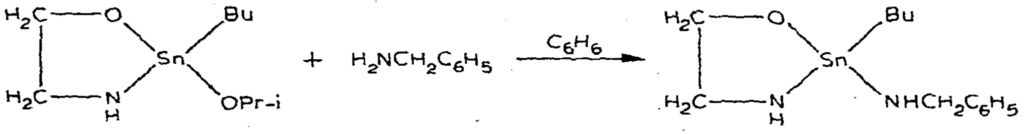
In the light of the above observations, it is interesting to compare the reactivities of various alkyltin derivatives with alkanolamines. In the reactions of tributyltin ethoxide with alkanolamines [3], only the hydroxyl group reacts in refluxing benzene, yielding $Bu_3SnOXNH_2$. However, the amino group enters into reaction at higher temperatures, yielding *O,N*-stannyl derivatives, e.g., $Bu_3SnOXNH(SnBu_3)$ and $Bu_3SnOXN(SnBu_3)_2$. Dibutyltin diethoxide appears to be more reactive towards ethanolamine, and a cyclic derivative, $Bu_2Sn(OCH_2CH_2NH)$, is obtained in refluxing benzene [1]. However, with substituted ethanolamines, only the hydroxyl group appears to be reactive, yielding distillable derivatives [2] of the type $Bu_2Sn(OEt)(OXNH_2)$ and $Bu_2Sn(OXNH_2)_2$. In contrast, butyltin triisopropoxide reacts exothermally at ambient temperatures even with substituted ethanolamines to give cyclic products or the type (I)-(III). Tin tetraisopropoxide also gives cyclic products with ethanolamine [1].

These observations indicate that the reactivity of alkyltin alkoxides towards amino groups of alkanolamines increases with increase in the number of alkoxy groups on tin:

$$R_3SnOR < R_2Sn(OR)_2 < RSn(OR)_3 \approx Sn(OR)_4$$

It is reasonable to assume that with increasing number of electronegative alkoxy groups, the induced positive charge on the central tin atoms tends to make them more electrophilic, and also causes contraction of their diffused *d* orbitals, bringing about a greater overlap with the orbitals of donor nitrogen atoms of amino group, and thus assisting the attack by the latter.

The same order of reactivity has been found in the reactions of amines with alkyltin(IV) alkoxides. Trialkyltin and dialkyltin alkoxides do not appear to undergo replacement reactions on treatment with amines in refluxing benzene [7], whereas butyltin triisopropoxide [8], and tin tetraisopropoxide [1] react with primary amines under these conditions. The replaceability of the isopropoxy group of ethanolamine derivative of type (I) by benzylamine has also been demonstrated:



(13)

(I) (XI)

The greater strength of Sn—O and Sn—N bonds in the chelate derivative appears to make the tin atoms even more electrophilic, and increases the reactivity towards benzylamine.

IR spectra

The IR spectra of these derivatives have been recorded in the region 400-4000 cm^{-1}. They show two bands, one near 1070 cm^{-1} of strong intensity, and one at about 1020 cm^{-1}, of rather low intensity, which may be assigned to the ν_{as}(C—O) and ν_s(C—O) stretching frequencies, respectively, of the alkanolamine system [2,3,12]. On the other hand, mixed derivatives containing both isoproxy as well aminoalkoxy groups, show, in addition to above bands, a strong band near 980 cm^{-1}, which may also be assigned to the ν(C—O) stretching frequency of the isopropoxy group. A similar band has been

(continued on p. 202)

TABLE 1

REACTIONS OF BUTYLTIN TRIISOPROPOXIDE WITH ALKANOLAMINES

Alkanolamine	Molar ratio of reactants	Product[a]	Yield (%) [M.p.(°C)]	Analysis, found (calcd.) (%) Sn	N	Characteristic[b] IR bands (cm^{-1})
$HOCH_2CH_2NH_2$	1/1	$BuSn(OCH_2CH_2NH)(OPr\text{-}i)^{c,d}$ (White solid)	99 (92-96)	40.9 (40.4)	4.69 (4.77)	1072vs, 965-55w(b), 655vw, 600m(b), 555m, 515m, 480m
$HOCH_2CH_2NH_2$	1/2	$BuSn(OCH_2CH_2NH)(OCH_2CH_2NH_2)^{e}$ (Pink solid changes to white on keeping)	98 (88-90)	39.7 (40.2)	9.40 (9.50)	1070vs, 1020sh, 655vw, 595-565w(b), 520w, 490-75w(b)
$HOCH_2CH_2NH_2$	2/3	$[BuSn(OCH_2CH_2NH)]_2(OCH_2CH_2NH)^{c}$ (White solid)	98 (98-100)	44.0 (44.9)	7.90 (7.94)	1080-1055vs(b), 1015sh, 660m, 595s(b), 520s(b), 465s(b)
$HOCH_2CH_2NHMe$	1/1	$BuSn(OCH_2CH_2NMe)(OPr\text{-}i)$ (Yellow viscous liquid)	99	38.9 (38.5)	4.52 (4.55)	1065vs(b), 1010w, 980s(b), 670m, 590vs(b), 520s, 480s
$HOCH_2CH_2NHMe$	1/2	$BuSn(OCH_2CH_2NMe)(OCH_2CH_2NHMe)$ (Yellow viscous liquid)	100	36.2 (36.8)	8.60 (8.68)	1075-1065vs(b), 1010m, 670m, 655w, 585s(b), 515m, 490s
$HOCH_2CH_2NHMe$	1/3	$BuSn(OCH_2CH_2NHMe)_3$ (Yellow viscous liquid)	97	29.6 (29.8)	10.5 (10.6)	1070vs(b), 1010m, 670w, 600sh, 570m, 520w, 485m
$HOCH_2CH_2NHMe$	2/3	$[BuSn(OCH_2CH_2NMe)]_2(OCH_2CH_2NMe)$ (Yellow viscous liquid)	99	40.8 (41.6)	7.30 (7.36)	1065vs(b), 1015m, 665m, 595m, 505w, 485m
$(HOCH_2CH_2)_2NH$	1/1	$BuSn[(OCH_2CH_2)_2NH](OPr\text{-}i)^{c,e}$ (White solid)	98 (265-270)	34.5 (35.1)	4.10 (4.15)	1070vs, 1020s, 670sh, 660s, 600s, 565s, 520s, 460s
$(HOCH_2CH_2)_2NH$	2/3	$\{BuSn[(OCH_2CH_2)_2NH]\}_2[(OCH_2CH_2)_2NH]^{c,e}$ (White solid)	97 (178-182)	35.3 (35.9)	6.30 (6.36)	1068vs, 1045vs, 1015s, 665w, 590w, 562w, 545w, 518w
$(HOCH_2CH_2)_3N$	1/1	$BuSn[(OCH_2CH_2)_3N]^{c,f}$ (White solid)	99 (142-146)	36.6 (36.9)	4.33 (4.35)	
$HOCH_2CH_2CH_2NH_2$	1/1	$BuSn(OCH_2CH_2CH_2NH)(OPr\text{-}i)^{c}$ (White foamy solid)	98	39.1 (38.5)	4.49 (4.55)	1060vs(b), 1025sh, 978m, 660w, 600s, 565m, 525m, 475m(b)
$HOCH_2CH_2CH_2NH_2$	1/2	$BuSn(OCH_2CH_2CH_2NH)(OCH_2CH_2CH_2NH_2)$ (Low-melting solid)	97	36.3 (36.8)	8.58 (8.68)	1070-1055vs(b), 1020sh, 675m, 660m, 605s, 570s, 528s, 475s(b)
$HOCH_2CH_2CH_2NH_2$	2/3	$BuSn[(OCH_2CH_2CH_2NH)]_2(OCH_2CH_2CH_2NH)^{c}$ (White foamy low melting solid)	98	41.0 (41.6)	7.30 (7.36)	1075-1060vs(b), 1020sh, 660vw, 595w, 560w, 500sh

[a] All these products decomposed on attempted vacuum distillation. [b] Refer Table 2. [c] Reaction was carried out at ambient temperature. [d] Mol.wt in refluxing benzene, found: polymer, calcd: 294. [e] Compound is moderately soluble in benzene. [f] Mol.wt. in refluxing benzene, found: 508, calcd: 322.

TABLE 2

REACTIONS OF BUTYLTIN TRIISOPROPOXIDE WITH *N*, *N*-DIALKYLALKANOLAMINES ($HOXNMe_2$)

X in $HOXNMe_2$	Molar ratio of reactants	Product	B.p. (°C/mm) [yield (%)]	Analysis found (calcd.) (%)		M.wt. found (calcd.)	Characteristic IR bands (cm^{-1})[a]
				Sn	N		
CH_2CH_2	1/1	$BuSn(OCH_2CH_2NMe_2)(OPr\text{-}i)_2$ (Colourless liquid)	105-108/0.1 (63)	31.9 (31.1)	3.65 (3.67)	369 (382)	1075m, 1035m, 980vs, 660w, 590s, 495w
CH_2CH_2	1/2	$BuSn(OCH_2CH_2NMe_2)_2(OPr\text{-}i)$ (Colourless liquid)	125-30/0.3 (51)	29.3 (28.9)	6.70 (6.82)	402 (411)	1075sh, 1040vs, 1020sh, 975s, 665w, 595s, 495w
CH_2CH_2	1/3	$BuSn(OCH_2CH_2NMe_2)_3$ (Yellow liquid)	158-65/0.5 (68)	27.5 (27.0)	9.50 (9.55)	425 (420)	1098-1065vs(b), 1025sh, 665w(b), 600s(b), 500m(b)
$CHMeCH_2$	1/1	$BuSn(OCHMeCH_2NMe_2)(OPr\text{-}i)_2$ (Colourless liquid)	98-100/0.1 (79)	29.5 (30.0)	3.50 (3.54)	389 (396)	1095s, 1020s, 980vs, 665w, 605-595s(b), 522w
$CHMeCH_2$	1/2	$BuSn(OCHMeCH_2NMe_2)_2(OPr\text{-}i)$ (Colourless liquid)	118-20/0.1 (86)	27.3 (27.0)	6.30 (6.38)	445 (439)	1095vs, 1030s, 1020s, 980s, 665w, 595s, 520m, 490vw
$CHMeCH_2$	1/3	$BuSn(OCHMeCH_2NMe_2)_3$ (Colourless liquid)	130-35/0.3 (63)	25.0 (24.6)	8.58 (8.72)	465 (482)	1095vs, 1080sh, 1032s, 665w, 595s, 520w

[a] For the intensity of IR bands following abbreviations are used: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, (b) = broad. IR spectra of solid products were run in Nujol mull.

observed in $RSn(OPr\text{-}i)_3$ and $RSn(OBu\text{-}t)_3$ [8].

These derivatives also show 3 characteristic bands in the range 670-500 cm^{-1}, which are considered to arise from various $\nu(Sn-C)$ and $\nu(Sn-O)$ stretchings. The band at 665 ± 5 cm^{-1} may be assigned to $(Sn-CH_2)$ rocking vibration arising from the *trans* conformation [13]. The bands at 595 ± 5 and 510 ± 15 cm^{-1} may be ascribed to $\nu_{as}(Sn-C)$ and $\nu_s(Sn-C)$ stretching modes, respectively [14-16]. The band at 510 ± 15 cm^{-1} could also be associated with $\nu(Sn-O)$, and a clear differentiation cannot be made due to overlapping.

Table 1 gives reactions of butyltin triisopropoxide with alkanolamines, and Table 2 those reactions with *N,N*-dialkylalkanolamines.

Experimental

Rigorous precautions were taken to exclude moisture. Alkanolamines were distilled before use. $BuSn(OPr\text{-}i)_3$ was synthesised by the sodium method [8]. The $BuSnO_{3/2}$ was used as supplied as a gift from Nitto Kasei Co. Ltd., Japan. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp). IR spectra were recorded on a Perkin - Elmer 337 grating spectrophotometer.

Tin was estimated as SnO_2. Nitrogen was estimated by the Kjeldahl method. Isopropanol in the azeotrope was estimated by an oxidimetric method [8].

(1). Reaction of $BuSn(OPr\text{-}i)_3$ with $HOCH_2CH_2NH_2$ at ambient temperature (1/1 molar ratio)

A mixture of $BuSn(OPr\text{-}i)_3$ (2.13 g, 6.03 mmole) and $HOCH_2CH_2NH_2$ (0.37 g, 6.06 mmole) in ca. 10 ml benzene reacted exothermically. The mixture was set aside at room temperature for ca. 5-6 h, and the excess of the solvent was then removed in vacuum. The product was obtained after drying as white solid (2.11 g, 99%), which decomposed on vacuum distillation (m.p. 92-96°). (Found: N, 4.69; Sn, 40.9; mol. wt., polymer. $C_9H_{21}NO_2Sn$ calcd.: N, 4.77: Sn, 40.4%; mol. wt., 294.)

The products obtained from the analogous reactions of $BuSn(OPr\text{-}i)_3$ with $HOCH_2CH_2NH_2$, $HOCH_2CH_2CH_2NH_2$, $HOCH_2CH_2NHMe$, $(HOCH_2CH_2)_2NH$ and $(HOCH_2CH_2)_3N$ in different molar ratios are summarised in Table 1.

(2). Reaction of $BuSn(OPr\text{-}i)_3$ with $HOCH_2CH_2NH_2$ in refluxing m-xylene (1/1 molar ratio)

To $BuSn(OPr\text{-}i)_3$ (2.27 g, 6.43 mmole) was added $HOCH_2CH_2NH_2$ (0.39 g, 6.40 mmole) in *m*-xylene (ca. 80 ml). The mixture was refluxed (bath temperature 180-90°) for ca. 6 h and the isopropanol liberated was fractionated very slowly with solvent. About 50 ml more *m*-xylene was added and the mixture was again refluxed for ca. 2 h (any isopropanol left was fractionated out) to ensure the completion of the reaction. During the fractionation a brown solid separated. The excess of solvent was distilled off, and the residue was dried under reduced pressure at 70-75°/0.2 mm bath temperature to give a brown insoluble solid (1.50 g, 100%) (Wt. of isopropanol in distillate; found: 1.08 g, calcd. (for 3 mole): 1.16 g). (Found: N, 5.95; Sn, 49.7; $C_6H_{13}NOSn$ calcd.: N, 5.99; Sn, 50.7%.)

(3). Reaction of $BuSn(OPr\text{-}i)_3$ with $HOCH_2CH_2NMe_2$ (1/1 molar ratio)

A mixture of $BuSn(OPr\text{-}i)_3$ (2.51 g, 7.11 mmole) and $HOCH_2CH_2NMe_2$ (0.63 g, 7.08 mmole) in benzene (ca. 80 ml) was refluxed (bath temperature 120-25°) for ca. 2 h, and the binary azeotrope (isopropanol/benzene) was very slowly fractionated out. The excess of solvent was distilled out, and the product was dried in vacuum. Distillation under reduced pressure gave a colourless liquid (1.71 g, 63%) b.p. 105-108°/0.1 mm (Wt. of isopropanol in azeotrope; found: 0.43 g, calcd.: 0.43 g). (Found: N, 3.65; Sn, 31.9; mol, wt., 369. $C_{14}H_{33}NO_3Sn$ calcd.: N, 3.67; Sn, 31.1%; mol. wt., 382.)

(4). Reaction of $BuSnO_{3/2}$ with $HOCH_2CH_2NHMe$(1/1 molar ratio)

To a suspension of $BuSnO_{3/2}$ (2.42 g, 12.1 mmole) in benzene (ca. 60 ml) was added $HOCH_2CH_2NHMe$ (0.91 g, 12.1 mmole). The reaction mixture was refluxed (bath temperature 115-120°) for ca. 3 h, and the binary azeotrope (water/benzene) was continuously fractionated out. Distillation of the remaining solvent and drying of the residue under reduced pressure gave a white foamy low melting solid (3.05 g, 98%) (Found: N, 5.40; Sn, 46.9; $C_{14}H_{32}N_2O_3Sn_2$ calcd.: N, 5.45; Sn, 46.2%). It underwent decomposition on attempted vacuum distillation.

(5). Reaction of $BuSnO_{3/2}$ with $HOCH_2CH_2NHMe$ (2/3 molar ratio)

Similarly, from a suspension of $BuSnO_{3/2}$ (2.15 g, 10.8 mmole) in benzene (ca. 70 ml) and $HOCH_2CH_2NHMe$ (1.21 g, 16.1 mmole), with azeotropic removal of water and final drying in vacuum, a yellow viscous liquid (2.99 g, 97%) was obtained. (Found: N, 7.31; Sn, 42.2; $C_{17}H_{39}N_3O_3Sn$ calcd.: N, 7.36; Sn, 41.6%.)

(6). Reaction of $BuSnO_{3/2}$ with $(HOCH_2CH_2)_3N$ (1/1 molar ratio)

Similarly, a suspension of $BuSnO_{3/2}$ (2.08 g, 10.4 mmole) in benzene (ca. 60 ml) and $(HOCH_2CH_2)_3N$ (1.55 g, 10.4 mmole) gave a white solid (3.12 g, 93%). Found: N, 4.29; Sn, 36.5; $C_{10}H_{21}NO_3Sn$ calcd.: N, 4.35; Sn, 36.9%.)

Acknowledgements

One of the authors (D.P.G.) thanks the U.G.C., New Delhi for the award of a Junior Research Fellowship.

References

1 R.C. Mehrotra and V.D. Gupta, Indian J. Chem., 5 (1967) 643.
2 D.P. Gaur, G. Srivastava and R.C. Mehrotra, J. Organometal Chem., 63(1973) 213.
3 D.P. Gaur, G. Srivastava and R.C. Mehrotra, Z. Anorg. Allgem. Chem., 398 (1973) 72.
4 A.G. Davies, L. Smith and P.J. Smith, J. Organometal. Chem., 39 (1972) 279.
5 D.P. Gaur, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., 47 (1973) 95.
6 D.P. Gaur, G. Srivastava and R.C. Mehrotra, Indian J. Chem., 11 (1973) 691.
7 D.P. Gaur, G. Srivastava and R.C. Mehrotra, unpublished work.
8 D.P. Gaur, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., 63 (1973) 221.
9 M.G. Voronkov, G. Zelcans, V.F. Mironov, J. Bleidelis and A. Kemme, Khim. Geterotsikl. Soedin, (1968) 227; Chem. Abstr. 69 (1968) 87129.
10 M.G. Voronkov and G. Zelcans, Khim. Geterotsikl Soedin, (1966) 511; Chem. Abstr., 66 (1967) 85780.

11 R.G. Kostyanovskii, A.K. Prokof'ev, V.I. Gol'danskii, V.V. Khrapov and V.Y. Rochev, Izv. Akad. Nauk SSSR, Ser. Khim. 2 (1968) 270.
12 J. Mendelsohn, A. Marchand and J. Valade, J. Organometal. Chem., 6 (1966) 25.
13 R.A. Cummins and J.V. Evans, Spectrochim. Acta 21 (1965) 1016.
14 R.A. Cummins, Aust. J. Chem., 18 (1965) 985.
15 T. Tanaka, Organometal. Chem., Rev. Sect. A, 5 (1970) 1.
16 R.C. Poller, The Chemistry of Organotin Compounds, Logos Press, London, 1970, p. 221.