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ORGANIC DERIVATIVES OF TIN

V SYNTHESIS AND REACTIONS OF ALKYLTIN TRIALKOXIDES

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SUMMARY

Alkyltin trialkoxides, $RSn(OR')_3$ (R = Et, n-Bu and R′ = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9 and t-C_4H_9) have been synthesised from alkyltin trichlorides and the corresponding sodium alkoxide. Mixed derivatives of the type $BuSnX_n(OPr\text{-}i)_{3-n}$ (X = Cl, CH_3CO_2 and $C_2H_5CO_2$) were obtained by exchange reactions. Reactions of butyltin triisopropoxide with protic reagents (*e.g.*, H_2O, $(CH_3)_2C{=}NOH$, *o*-HOC_6H_4OH, $C_6H_5CH_2NH_2$, $NH_2CH_2CH_2NH_2$, i-$PrNHCOCH_3$, n-$BuNHCOCH_3$, $HCONH_2$ and CH_3CONH_2) have been studied. Dialkyltin acetamido derivatives have also been synthesised. IR and NMR spectra and molecular weights of the new products are reported and discussed.

INTRODUCTION

Tin(IV), dialkyltin(IV) and trialkyltin(IV) alkoxides have been studied extensively[1]. However, no systematic study of alkyltin(IV) trialkoxides appears to have been undertaken to date, excepting a brief report by Lorberth and Kula[2] describing a few examples of this series obtained by alcoholysis of alkyltin tris-(diethylamide):

$$RSn(NEt_2)_3 + 3R'OH \rightarrow RSn(OR')_3 + 3Et_2NH$$

(R = Me, Et, Bu and Ph; R′ = Me and Et).

In this paper, we describe the direct preparation of alkyltin trialkoxides from alkyltin trichlorides. Reactions with protic reagents as well as exchange reactions of butyltin triisopropoxide are also discussed.

RESULTS AND DISCUSSION

In contrast to total halide–alkoxide interchange between organotin halides and sodium alkoxides in trialkyltin and dialkyltin derivatives, Davies *et al*[3] have recently reported that alkyltin trihalides undergo only partial replacement even under forcing conditions:

$$BuSnCl_3 + NaOMe \rightarrow BuSnCl_2(OMe)$$

On the contrary, our results indicate that all the chlorines of alkyltin trichlorides are replaced smoothly by alkoxy groups and the method has been utilised to synthesise a number of new alkyltin trialkoxides (Table 1):

$$\mathrm{RSnCl_3 + 3NaOR'} \xrightarrow[\text{reflux}]{C_6H_6} \underset{\text{(I)}}{\mathrm{RSn(OR')_3}}$$

$(\mathrm{R = Et, n\text{-}Bu};\ \mathrm{R' = CH_3, C_2H_5, i\text{-}C_3H_7, n\text{-}C_4H_9}$ and $\mathrm{t\text{-}C_4H_9})$

The appropriate alkyltin trichloride was added to a freshly prepared hot solution of sodium alkoxide in the corresponding alcohol and benzene and the mixture was refluxed for 3–4 h. It was found difficult to remove the finely precipitated sodium chloride by filtration and, in absence of a centrifuging device, either the supernatant liquid was decanted off or in some cases the tin product was distilled without prior removal of sodium chloride. These operations resulted in reduced yields of products.

An attempt was made to prepare butyltin trialkoxides by alcoholysis of butyltin oxide with simultaneous azeotropic removal of water. When the reaction was carried out with ethanol or isopropanol in benzene a clear solution was obtained after refluxing, but no ethanol–water–benzene azeotrope formed; the product, after removal of solvents analysed for the original $\mathrm{BuSnO_{3/2}}$. However, with n-butanol some water was liberated, the amount of which as well as the analysis of the colourless viscous liquid product corresponded to attachment of only one n-butoxy group to tin *i.e.*, the formation of $\mathrm{BuSnO(OC_4H_9\text{-}n)}$.

The alkyltin trialkoxides prepared in this work are colourless or yellow volatile liquids (methoxides are white solids which decomposed during attempted distillation) The products are associated as shown by their molecular weights determined ebullioscopically in benzene The degree of association decreases with increasing ramification of alkoxy group. The degrees of molecular complexity are: methoxides, polymeric; ethoxides, 3; isopropoxides, 1.5; butoxides, 1. It is noteworthy that trialkyltin alkoxides are monomeric, whereas dialkyltin dialkoxides are slightly associated in refluxing benzene

In the NMR spectrum of $\mathrm{EtSn(OEt)_3}$, the methyl and methylene protons of ethoxy groups appear as a triplet and a quartet at $\tau 8.8$ and 6.08 respectively (J 7 cps) t-Butoxy protons of $\mathrm{EtSn(OBu\text{-}t)_3}$ give a singlet at $\tau 8.83$. The Sn–Et protons in both the compounds appear as a singlet at $\tau 8.63$. In the earlier NMR study of $\mathrm{EtSnX_3}$ derivatives[2], $\mathrm{CH_3}$ and $\mathrm{CH_2}$ protons of Sn–Et groups were separately resolved only when highly electronegative substituents were present on tin

Exchange reactions

Butyltin triisopropoxide reacts exothermically with butyltin trichloride yielding unsymmetrical derivatives by radical interchange:

$$\mathrm{2BuSn(OPr\text{-}i)_3 + BuSnCl_3} \rightarrow \underset{\text{(II)}}{\mathrm{3BuSn(OPr\text{-}i)_2Cl}}$$

$$\mathrm{BuSn(OPr\text{-}i)_3 + 2BuSnCl_3} \rightarrow \underset{\text{(III)}}{\mathrm{3BuSn(OPr\text{-}i)Cl_2}}$$

Butyl(diisopropoxy)tin chloride is a volatile liquid (molecular complexity, ca. 1.8) whereas butyl(isopropoxy)tin dichloride is a white solid (molecular complexity, ca. 1.3) which appears to disproportionate into $BuSnCl_3$ and $BuSn(OPr\text{-}i)_2Cl$ upon attempted vacuum distillation.

Similar codisproportionation of butyltin triisopropoxide have been carried out with butyltin triacetate and tripropionate (obtained readily from the condensation of butyltin oxide with the appropriate acid anhydride).

$$2BuSn(OPr\text{-}i)_3 + BuSn(OCOR)_3 \rightarrow \underset{(IV)}{3BuSn(OPr\text{-}i)_2(OCOR)}$$

$$BuSn(OPr\text{-}i)_3 + 2BuSn(OCOR)_3 \rightarrow \underset{(V)}{3BuSn(OPr\text{-}i)(OCOR)_2}$$

($R = CH_3$ and C_2H_5).

These mixed butyltin isopropoxide carboxylates are yellow viscous liquids, stable in refluxing benzene or cyclohexane, but they decompose upon attempted distillation. The decomposition partially proceeds by intermolecular or intramolecular condensation to give isopropyl carboxylates. These compounds are associated; the molecular complexity of both acetates being ca. 3 and that of both the propionates being ca. 2 in refluxing benzene. It is noteworthy that both butyltin tricarboxylates are monomeric.

In an earlier infrared study of butyltin tricarboxylates[4], the CO stretching bands were observed at ca. ν1570 and 1420 cm^{-1} showing the coordinative nature of the C=O groups. Weak to medium absorption bands were also observed near 1700 cm^{-1} (free C=O region) and this was attributed to the free acid formed by slight hydrolysis. This explanation is supported by our study of mixed isopropoxide carboxylates since these compounds also show peaks in the coordinating CO region at ca. 1570 cm^{-1} together with a weak to medium intensity band at ca. 1700 cm^{-1}. However, when the compounds are dissolved in cyclohexane and the solvent is removed by fractionation and vacuum drying, the peak at 1700 cm^{-1} disappears from the residue. Butyltin triacetate also behaves similarly. It seems that traces of the free acid formed by slight hydrolysis are removed during cyclohexane treatment.

Reactions of butyltin triisopropoxide with protic reagents

Alkyltin trialkoxides are very reactive which may be due to the presence of three negative alkoxy groups making the tin atom highly prone to nucleophilic attack. The compounds are extremely sensitive to hydrolysis and require careful handling. In the presence of water, ethyltin and butyltin triisopropoxides are completely hydrolysed to the corresponding alkyltin oxide:

$$2RSn(OPr\text{-}i)_3 + 3H_2O \xrightarrow[\text{reflux}]{C_6H_6} \underset{(VI)}{2RSnO_{3/2}}$$

(R = Et and Bu)

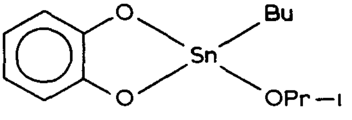
Butyltin triisopropoxide reacts readily and exothermically with hydroxylic reagents giving transalkoxylation products. We have already reported the reactions of butyltin triisopropoxide with glycols[5] and thiols[6]. The isopropoxy groups of

$BuSn(OPr\text{-}i)_3$ are replaced stepwise by acetoxime with the formation of mono-, bis- and tris-acetoximates as distillable liquids:

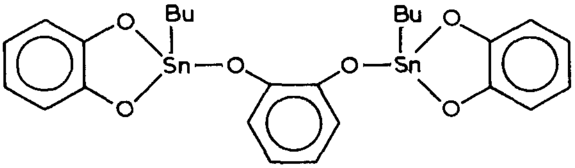
$$BuSn(OPr\text{-}i)_3 + n(CH_3)_2C{=}NOH \xrightarrow[\text{reflux}]{C_6H_6} \underset{\text{(VII)}}{BuSn(OPr\text{-}i)_{3-n}[ON{=}C(CH_3)_2]_n} \quad (7)$$

($n = 1, 2$ and 3).

Reactions of butyltin triisopropoxide with catechol in 1/1 and 2/3 molar ratios yielded monobutyltin catecholate isopropoxide(VIII) and bis(monobutyltin) tris(catecholate) (IX):



(VIII)



(IX)

All mono-, bis- and tris-(acetoximates) are associated (ca. 2) and could be distilled unchanged, the poor yield may be due to partial decomposition of the product at high temperature. Both 1/1 and 2/3 molar catechol derivatives are dark solids, the former being soluble whereas the latter one is insoluble in benzene.

Benzylamine and ethylenediamine react with an equimolar quantity of butyltin triisopropoxide in refluxing benzene and upon azeotropic fractionation thereby removing isopropanol formed, yellow viscous liquid and brown foamy solid were obtained respectively. However, these reactions do not appear to proceed in the cold which may be ascribed to poor reactivity of the amino groups toward alkoxides:

$$BuSn(OPr\text{-}i)_3 + H_2NCH_2C_6H_5 \xrightarrow[\text{reflux}]{C_6H_6} \underset{\text{(X)}}{BuSn(OPr\text{-}i)_2(NHCH_2C_6H_5)}$$

$$BuSn(OPr\text{-}i)_3 + H_2NCH_2CH_2NH_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{\text{(XI)}}{BuSn(OPr\text{-}i)\,(NHCH_2CH_2NH)}$$

Reactions of butyltin triisopropoxide with *N*-alkylacetamides, $RNHCOCH_3$ ($R = i\text{-}C_3H_7$ and $n\text{-}C_4H_9$) in 1/1 and 1/2 molar ratios in refluxing benzene led to the formation of simple mono- and bis-(*N*-alkylacetamido) derivatives:

$$BuSn(OPr\text{-}i)_3 + nRNHCOCH_3 \xrightarrow[\text{reflux}]{C_6H_6} \underset{\text{(XII)}}{BuSn(OPr\text{-}i)_{3-n}(NRCOCH_3)_n}$$

($n = 1$ and 2; $R = i\text{-}C_3H_7$ and $n\text{-}C_4H_9$).

However, the third isopropoxy group in the above derivatives is not replaceable which may be due to steric factors. All mono- and bis-(*N*-alkylacetamido) derivatives of the type (XII) are volatile distillable liquids, highly sensitive to atmospheric moisture. The corresponding reactions of trialkyltin alkoxides with *N*-alkylacetamide, require higher temperature for completion[7].

The reactions of butyltin triisopropoxide with amides, $RCONH_2$($R = H$ and CH_3) in refluxing benzene resulted in the replacement of both the hydrogen atoms of the amino groups yielding BuSn(OPr-i)(NCOR) (XIII), BuSn(NCOR)(HNCOR) (XIV) and $(BuSn)_2(NCOR)_3$ (XV) respectively in 1/1, 1/2 and 2/3 molar ratios. Except for the 1/1 molar yellow product of acetamide, a viscous liquid, all other derivatives are white solids which tend to decompose during vacuum distillation. For the derivatives XIV and XV the possibility of a mixture can be ruled out since as $BuSn(OPr\text{-}i)_3$ and $HCONH_2$ are liquids whereas these derivatives are solids, furthermore, the products XV do not show an NH peak in IR spectra. Molecular weight determinations of the type XIII products in refluxing benzene reveal a highly polymeric structure, although the exact degree of polymerisation needs further investigations

For comparison, the reactions of dialkyltin diethoxides, $R_2Sn(OEt)_2$, with an equimolar ratio of acetamide have been found to lead to similar products as in the case of monoalkyltin(IV) derivatives. Although the reactions are slower, they can nevertheless be pushed to completion by prolonged refluxing:

$$R_2Sn(OEt)_2 + CH_3CONH_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{\text{(XVI)}}{R_2Sn(NCOCH_3)}$$

(R = Et, Pr and Bu).

The products are white insoluble solids which may be polymeric.

Infrared spectra

Infrared spectra of all products were recorded in the region 400–4000 cm^{-1} All derivatives show two bands near 500 and 600 cm^{-1}, which may be assigned to ν_s and ν_{as} (Sn–C)[8,9] respectively. Similar to other organotin alkoxides and chlorides, a band has been observed near 665–670 cm^{-1} which may be assigned to ($Sn{-}CH_2$) rocking vibration arising from *trans* conformations[10]. The band observed at about 500 cm^{-1} may be associated with ν(Sn–O). However, a clear distinction between ν_s(Sn–C) and ν(Sn–O) cannot be made as the bands may overlap. A common feature of all organotin(IV) alkoxides derived from primary alcohols is that they show a strong band in the region 1030–1070 cm^{-1} for ν(C–O)[11] which shifted to a lower region (940–980 cm^{-1}) in branched alkoxides, *i.e.*, in the isopropoxides and tertiary butoxides. All mixed alkoxides derived from carboxylates show a very strong band near 1570 cm^{-1} which may be due to coordinative CO stretching. The acetoximates show a band near 1600 cm^{-1} which may be assigned to the ν(C=N) stretching vibration. Similar bands have been observed in amide derivatives of monobutyltin(IV) and these may be due to either ν(C=N) or coordinating ν(C=O) stretching.

EXPERIMENTAL

All glass apparatus with interchangeable joints were used and the moisture

TABLE 1. SYNTHESIS OF ALKYLTIN TRIALKOXIDES

R in $RSnCl_3$	*R′ in NaOR′*	*Molar ratio*	*Product*	*Yield (%)*	*B p °C/mm (M p °C)*	*Analysis Found(calcd.) (%)*		*Mol.wt Found (calcd)*	*Some characteristic IR bands*[a]
						Sn	*(OR)*		
Et	CH_3	1/3	$EtSn(OCH_3)_3$ white solid	55	Dec (230–235)	49.8 (49.3)		Polymer (241)	
Et	C_2H_5	1/3	$EtSn(OC_2H_5)_3$ colourless liquid	65	125–130/0.2	42.5 (42.0)	46.8 (47.8)	933 (283)	1070–1038 vs(br), 950 vw, 670 s,660 s, 620 (sh), 600 (sh), 590 s(br) 500 s(br)
Et	i-C_3H_7	1/3	$EtSn(OC_3H_7\text{-i})_3$ colourless liquid	56	83–87/0.3	36.6 (36.3)	53.2 (54.5)	496 (325)	1030 (sh), 1020 (sh), 980 vs(br), 958 (sh), 675 m, 610 s, 585 s, 560 s, 505 w(br), 455 m(br)
Et	n-C_4H_9	1/3	$EtSn(OC_4H_9\text{-n})_3$ yellow liquid	54	145–150/0.3	31.7 (32.3)			1075 vs(br), 1055 (sh), 1030 s(br), 960–940 m(br), 675 m, 600 m(br), 525 m, 510 m(br)
Et	t-C_4H_9	1/3	$EtSn(OC_4H_9\text{-t})_3$ colourless liquid	63	75–80/0.9–1.0	31.9 (32.3)		437 (367)	1025–1010 m(br), 960 (sh), 940 s(br), 670 m, 610 (sh), 585 s(br), 500 w(br), 460 m(br)
Bu	CH_3	1/3	$BuSn(OCH_3)_3$ white solid	41	Dec (220–225)	44.9 (44.2)		Polymer (269)	
Bu	C_2H_5	1/3	$BuSn(OC_2H_5)_3$ yellow liquid	57	130–135/0.2	37.6 (38.2)	42.5 (43.4)	1050 (311)	1060 vs, 1020 (sh), 1000 (sh), 960 w, 685 s(br), 665 s(br), 590 s, 560 s(br), 505 s(br)
Bu	i-C_3H_7	1/3	$BuSn(OC_3H_7\text{-i})_3$ colourless liquid changed to yellow on keeping.	55	93–95/0.3	34.1 (33.6)	49.2 (50.2)	527 (353)	988–975 vs(br), 935 vs, 700 (sh), 675 w, 615 s, 590 s(br), 565 s, 460 s(br)
Bu	t-C_4H_9	1/3	$BuSn(OC_4H_9\text{-t})_3$ colourless liquid	58	93–94/0.4	29.6 (30.0)		388 (395)	950 vs(br), 700 w(br), 665 w, 590 s, 460 m(br)

[a] IR data given above are in cm^{-1} followed by an indication of intensity Following abbreviations are used vs, very strong, s, strong m medium., w, weak, vw, very weak, (sh), shoulder, (br), broad

was strictly excluded throughout these investigations. Benzene (B.D.H.) was dried initially over sodium then finally by azeotropic distillation with ethanol. Methanol and ethanol were dried over calcium oxide, magnesium alkoxide, sodium alkoxide and finally azeotropically distilled with benzene. Isopropanol was dried over NaOPr-i, $Al(OPr\text{-}i)_3$ and then with benzene azeotropically. n- and t-Butanol were dried over the corresponding sodium butoxide.

Molecular weights were determined ebulliometrically in refluxing benzene using a semi-micro ebulliometer (Gallenkamp). Infrared spectra were recorded using Perkin–Elmer 337 grating spectrophotometer. NMR spectra were recorded on an MC 60 instrument in CCl_4 solution.

Tin was estimated as SnO_2. Ethoxy and isopropoxy groups were estimated by dissolving the sample in benzene. Subsequent hydrolysis with water liberated the corresponding alcohol which were fractionated out azeotropically with benzene. The alcohol in the azeotrope was estimated oxidimetrically[12]. Carboxylic groups were estimated by titration with 0.1 *N* NaOH in alcohol solution Nitrogen was estimated by the Kjeldahl method.

(1) *General method for synthesis of alkyltin trialkoxides*

A stoichiometric amount of alkyltin trichloride in benzene solution was added dropwise to a freshly prepared hot solution of sodium alkoxide (3 mole) prepared from sodium and alcohol in the presence of excess of the corresponding alcohol under perfectly anhydrous conditions. Sodium chloride was thus precipitated and the mixture was refluxed for ca. 3–4 h, then set aside to allow the sodium chloride to settle down The supernatant liquid was repeatedly decanted off (filtration of the precipitate was extremely slow, and was avoided due to extremely hydrolysable nature of the products) Excess of solvent was distilled out and the product was finally dried under reduced pressure. Upon vacuum distillation the desired alkyltin trialkoxide was obtained (methoxides decomposed during attempted distillation). The product yield was poor due to loss of the product during repeated decantation, *e.g.*, $BuSn(OPr\text{-}i)_3$ was obtained in 55% yield by the above process, whereas the product was obtained in 90% yield when ca. 40 g of compound was distilled in the presence of sodium chloride without filtration. $BuSn(OPr\text{-}i)_3$ when distilled in the presence of sodium chloride (time required for distillation ca. 3–4 h) it separated together with a white solid insoluble in common organic solvents which may be hydrolysed product.

Similar compounds prepared by above method are summarised in Table 1.

(2) *Reaction of* $BuSnO_{3/2}$ *with* $(CH_3CO)_2O$ *(2/3 molar ratio)*

$BuSnO_{3/2}$ (2.63 g, 13.0 mmole) and $(CH_3CO)_2O$ (2.10 g, 20.6 mmole) on mixing together evolved heat. The mixture was heated at 95–100°C for ca. 2 h and vacuum distillation of the product yielded $BuSn(OCHOCH_3)_3$(ca. 63%) as a yellow liquid b.p. 115–118°C/0 4 mm. (Found: Sn, 33.2; $(OCOCH_3)$, 49.5; mol.wt., 361 $SnC_{10}H_{18}O_6$ calcd.: Sn, 33.6; $(OCOCH_3)$, 50.2%; mol.wt , 353).

(3) *Reaction of* $BuSnO_{3/2}$ *with* $(C_2H_5CO)_2O$ *(2/3 molar ratio)*

Using the above procedure, a mixture of $BuSnO_{3/2}$ (3.83 g, 19.2 mmole) and $(C_2H_5CO)_2O$ (3.74 g, 28.8 mmole) yielded $BuSn(OCOC_2H_5)_3$ as a pale yellow liquid b.p. 142–148°C/0 3 mm (ca. 61%). (Found: Sn, 29.6; $(OCOC_2H_5)$, 55.0; mol.wt, 383. $SnC_{13}H_{24}O_6$ calcd.: Sn, 30.0; $(OCOC_2H_5)$, 55.7%; mol. wt., 395).

TABLE 2

REACTIONS OF BUTYLTIN TRIISOPROPOXIDES WITH BUTYLTIN TRICHLORIDE AND TRICARBOXYLATES

X in $BuSnX_3$	*Molar ratio of the reactants*	*Product*	*Yield (%)*	*Analysis Found (calcd) (%)*		*Mol wt Found (calcd)*	*Some characteristic IR bands*[d]
				Sn	*OCOR*		
$OCOCH_3$	2/1	$BuSn(OC_3H_7\text{-i})_2(OCOCH_3)$[a] yellow viscous liquid	100	33 0 (33 6)	16 5 (16 7)	1033 (353)	1575 (sh), 1565 vs, 1460 (sh), 1075 w, 1020 m(br), 975 s(br), 960 s(br), 665 m(br), 612 s, 580 s(br), 535 m(br), 455 w(br)
$OCOCH_3$	1/2	$BuSn(OC_3H_7\text{-i})(OCOCH_3)_2$[a] yellow viscous liquid	100	32 8 (33 6)	32 6 (33 5)	980 (353)	1595 vs(br), 1560 vs, 1450 vs, 1080 w, 1020 s, 955 s, 660 vs, 615 vs(br), 585–570 s(br), 550 s, 505 w, 430 vw
$OCOC_2H_5$	2/1	$BuSn(OC_3H_7\text{-i})_2(OCOC_2H_5)$[a] yellow viscous liquid	100	31 8 (32 3)	19 7 (19 9)	920 (367)	1560 vs, 1545 vs, 1460 vs, 1075 s, 1010 m, 980–960 s(br), 670 s(br), 605 vs(br), 570 vs(br), 525 vs
$OCOC_2H_5$	1/2	$BuSn(OC_3H_7\text{-i})(OCOC_2H_5)_2$[a] yellow viscous liquid	100	30 8 (31 2)	37 3 (38 4)	801 (381)	1590 vs, 1560 vs, 1465 vs, 1080 vs, 1010 w, 950 w, 675 s(br), 610 vs, 575 vs(br), 510 (sh), 455 vw
Cl	2/1	$BuSn(OC_3H_7\text{-i})_2Cl$[b] colourless liquid	73	35 3 (36 1)		588 (329)	1080 m, 1025 m(br), 975 vs, 950 vs, 700 (sh), 675 m(br), 615 vs(br), 560 s, 460 m(br)
Cl	1/2	$BuSn(OC_3H_7\text{-i})Cl_2$[c] white solid	100	38 3 (38 8)		400 (306)	1080 (sh), 1020 w, 915 vs, 688 w, 665 (sh), 610 s, 595 s, 558 vs, 460 s

[a] Product decomposed on attempted vacuum distillation

[b] b p , 110–112°C/0 2 mm, Found Cl, 10.6, calcd; Cl, 10 8 %

[c] Disproportionated on distillation Found Cl, 22.9, calcd. Cl, 23 2%

[d] Abbreviations see Table 1

(4) *Reaction of $BuSn(OPr\text{-}i)_3$ with $BuSnCl_3$ (2/1 molar ratio)*

To $BuSn(OPr\text{-}i)_3$(2.60 g, 7.37 mmole) was added $BuSnCl_3$ (1.06 g, 3.68 mmole); an exothermic reaction occurred after shaking the mixture The product on distillation under reduced pressure gave a colourless liquid which changed to yellow on keeping (2.64 g, ca 73%) b.p. 110–112°C/0.2 mm. (Found: Sn, 35 3; Cl, 10 6; mol.wt., 588 $SnC_{10}H_{23}O_2Cl$ calcd.: Sn, 36.1; Cl, 10.8%; mol. wt., 329).

Similarly the products obtained by the reactions of $BuSn(OPr\text{-}i)_3$ and $BuSnCl_3$ in 1/2 molar ratio and that of $BuSn(OPr\text{-}i)_3$ with $BuSn(OCOCH_3)_3$ and $BuSn(OCOC_2H_5)_3$ in 2/1 and 1/2 molar ratios are summarised in Table 2

(5) *Reaction of $BuSn(OPr\text{-}i)_3$ with $HCONH_2$ (1/1 molar ratio)*

A mixture of $BuSn(OPr\text{-}i)_3$ (3 67 g, 10.4 mmole) and $HCONH_2$ (0.47 g, 10.4 mmole) in benzene (ca. 80 ml) was refluxed at 120–125°C bath temperature for about 3 h and the binary azeotrope (isopropanol–benzene) was slowly fractionated out. On removal of the excess of solvent by distillation and finally drying under reduced pressure a white solid was obtained (2.83 g, ca. 98%) which decomposed on attempted vacuum distillation. (Weight of isopropanol in azeotrope, found: 1.20 g; calcd. (for 2 mole): 1.25 g) (Found: N, 4.99; Sn, 43.5: $C_8H_{17}NO_2Sn$ calcd.: N, 5.04; Sn, 42.7%).

Using the above procedure, the products obtained by the reactions of $BuSn(OPr\text{-}i)_3$ with $HCONH_2$, CH_3CONH_2, $i\text{-}C_3H_7NHCOCH_3$, $n\text{-}C_4H_9NHCOCH_3$, $(CH_3)_2C{=}NOH$, $C_6H_5CH_2NH_2$, $H_2NCH_2CH_2NH_2$ and $o\text{-}OHC_6H_4OH$ in different molar ratios are summarised in Table 3.

(6) *Reaction of $Et_2Sn(OEt)_2$ with CH_3CONH_2 (1/1 molar ratio)*

To $Et_2Sn(OEt)_2$ (3.31 g, 12.4 mmole) was added CH_3CONH_2 (0.73 g, 12 4 mmole) in benzene (ca. 70 ml). The mixture was refluxed for about 4 h and the binary azeotrope (ethanol–benzene) was very slowly fractionated whereby an insoluble solid was separated. The alcohol estimation showed that the reaction was not complete, hence, about 70 ml more benzene was added to the reaction mixture. The mixture was again refluxed for about 4 h and azeotrope was collected. On drying the product under reduced pressure a white solid was obtained (2.88 g, ca. 99%) as $Et_2Sn(NCOCH_3)$. (Weight of ethanol in azeotrope, found: 1.08 g; calcd. (for 2 mole): 1.14 g.) (Found: N, 5.95; Sn, 51.6. $SnC_6H_{13}NO$ calcd.: N, 5.99; Sn, 50.7%).

(7) *Reaction of $Pr_2Sn(OEt)_2$ with CH_3CONH_2 (1/1 molar ratio)*

Using the above procedure, a mixture of $Pr_2Sn(OEt)_2$ (3 71 g, 12.6 mmole) and CH_3CONH_2 (0 74 g, 12.6 mmole) in benzene gave a white insoluble product on drying under reduced pressure (3.25 g, ca. 99%).(Weight of ethanol in azeotrope, found: 1.12 g; calcd. (for 2 mole): 1.16 g) (Found: N, 5.31; Sn, 45.8. $SnC_8H_{17}NO$ calcd.: N, 5 35; Sn, 45.3%).

(8) *Reaction of $Bu_2Sn(OEt)_2$ with CH_3CONH_2 (1/1 molar ratio)*

Similarly, a mixture of $Bu_2Sn(OEt)_2$ (3 36 g, 10 4 mmole) and CH_3CONH_2 (0.62 g, 10.5 mmole) in benzene gave a white insoluble product, drying under reduced pressure (2.92 g, ca. 97%). (Weight of ethanol in azeotrope, found: 0.93 g; calcd. (for 2 mole): 0.96 g.) (Found: N, 4.79; Sn, 39.8. $SnC_{10}H_{21}NO$ calcd.: N, 4.83; Sn, 40.9%).

TABLE 3. REACTIONS OF $BuSn(OPr\text{-}i)_3$ WITH PROTIC REAGENTS

Protic reagent	Molar ratio of reactants	Product	Yield (%)	B p °C/mm (M p.°C)	Analysis Found (calcd)(%)		Mol wt Found (calcd)
					Sn	N	
$(CH_3)_2C{=}NOH$	1/1	$BuSn[ON{=}C(CH_3)_2](OPr\text{-}i)_2$ yellow liquid	48	110–115/0.3	31.7 (32.4)	3.79 (3.83)	725 (366)
$(CH_3)_2C{=}NOH$	1/2	$BuSn[ON{=}C(CH_3)_2]_2(OPr\text{-}i)$ yellow liquid	42	122–127/0.2	30.8 (31.4)	7.33 (7.39)	950 (379)
$(CH_3)_2C{=}NOH$	1/3	$BuSn[ON{=}C(CH_3)_2]_3$ yellow liquid	38	135–140/0.2	29.9 (30.3)	10.6 (10.7)	923 (392)
o-HOC_6H_4OH	1/1	$BuSn(o\text{-}OC_6H_4O)(OPr\text{-}i)$ dark solid	98	Dec (178–180)	35.4 (34.6)		
o-HOC_6H_4OH	2/3	$[BuSn(o\text{-}OC_6H_4O)]_2(o\text{-}OC_6H_4O)$ dark insoluble solid	97	Dec (218–222)	34.8 (35.1)		
$C_6H_5CH_2NH_2$	1/1	$BuSn(NHCH_2C_6H_5)(OPr\text{-}i)_2$ brown viscous liquid	98		29.4 (29.7)	3.45 (3.50)	
$H_2NCH_2CH_2NH_2$	1/1	$BuSn(NHCH_2CH_2NH)(OPr\text{-}i)$ brown foamy solid	97	Dec (118–222)	42.5 (40.5)	9.50 (9.56)	
$HCONH_2$	1/1	$BuSn(NCOH)(OPr\text{-}i)$ white solid	98	Dec (166–170)	43.5 (42.7)	4.99 (5.04)	Polymer (278)
$HCONH_2$	1/2	$BuSn(NCOH)(NHCOH)$ pale yellow solid	(98)	Dec (158–162)	46.3 (45.1)	10.6 (10.7)	
$HCONH_2$	2/3	$(BuSn)_2(NCOH)_3$ white solid	97	Dec (152–156)	50.3 (49.4)	8.69 (8.74)	
CH_3CONH_2	1/1	$BuSn(NCOCH_3)(OPr\text{-}i)$ yellow viscous liquid	(98)	Dec	42.0 (41.7)	4.71 (4.80)	Polymer (292)
CH_3CONH_2	1/2	$BuSn(NCOCH_3)(NHCOCH_3)$ white solid	97	Dec (120–125)	42.5 (40.8)	9.53 (9.63)	
CH_3CONH_2	2/3	$(BuSn)_2(NCOCH_3)_3$ white solid	96	Dec (Does not melt upto 300)	46.5 (45.4)	7.95 (8.04)	
$CH_3CONHC_3H_7$-i	1/1	$BuSn(i\text{-}C_3H_7NCOCH_3)(OPr\text{-}i)_2$ yellow liquid	70	105–110/0.2	29.7 (30.1)	3.50 (3.56)	378 (394)
$CH_3CONHC_3H_7$-i	1/2	$BuSn(i\text{-}C_3H_7NCOCH_3)_2(OPr\text{-}i)$ yellow liquid	68	125–130/0.2	27.7 (27.3)	6.40 (6.44)	421 (435)
$CH_3CONHC_4H_9$-n	1/1	$BuSn(n\text{-}C_4H_9NCOCH_3)(OPr\text{-}i)_2$ colourless liquid	60	108–112/0.2	29.7 (29.1)	3.40 (3.43)	398 (408)
$CH_3CONHC_4H_9$-n	1/2	$BuSn(n\text{-}C_4H_9NCOCH_3)_2(OPr\text{-}i)$ yellow liquid	55	140–145/0.2	25.2 (25.6)	5.98 (6.05)	450 (463)

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