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ORGANIC DERIVATIVES OF TIN

IV. REACTIONS OF DIALKYLTIN DIALKOXIDES WITH ALKANOLAMINES

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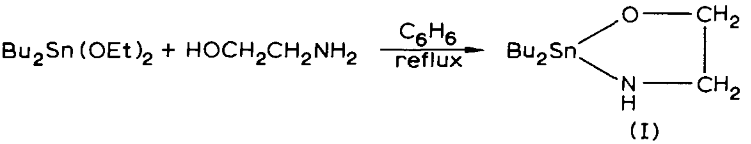
SUMMARY

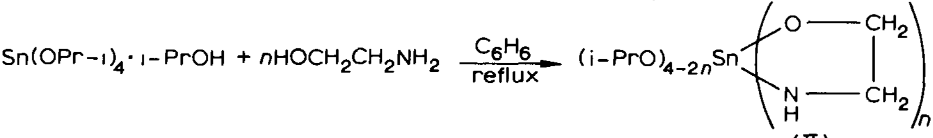
Dibutyltin diethoxide, $Bu_2Sn(OEt)_2$, reacts with various alkanolamines, $HOXNH_2$, ($X=CH_2CH_2CH_2$, $CH(Me)CH_2$), $HOXNR_2$ ($X=CH(Me)CH_2$ and $R=Me$; $X=CH_2CH_2CH_2$ and $R=Et$) in 1/1 and 1/2 molar ratios to yield distillable dibutyl(ethoxy)tin aminoalkoxides, $Bu_2Sn(OEt)(OXNR_2)$ and dibutyltin bis(aminoalkoxides) $Bu_2Sn(OXNR_2)_2$, respectively. For reactions of $R_2Sn(OR')_2$ ($R=Et$, n-Pr and $R'=Et$; $R=Et$ and $R'=t$-Bu) with $HOXNH_2$ ($X=CH_2CH_2$, $CH_2CH_2CH_2$ and $CH(Me)CH_2$), cyclic compounds of the type $R_2Sn(OXNH)$ are obtained. Molecular weights and IR spectra of the new products are reported and discussed.

INTRODUCTION

Dibutyltin diethoxide and tin tetraisopropoxide react with ethanolamine to yield cyclic products[1]:



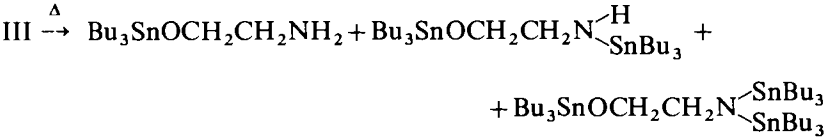
(I) (1)



(II) (2)

By contrast, only hydroxy groups of various alkanolamines react with tributyltin ethoxide in refluxing benzene, although during distillation of the product, thermal decomposition additionally yields *N*-tributylstannyl derivatives[2], *e.g.*:

$$Bu_3SnOEt + HOCH_2CH_2NH_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{(III)}{Bu_3SnOCH_2CH_2NH_2} \rightarrow \quad (3)$$



$$\mathrm{III} \xrightarrow{\Delta} \mathrm{Bu_3SnOCH_2CH_2NH_2 + Bu_3SnOCH_2CH_2N{<}^{H}_{SnBu_3}} + \mathrm{Bu_3SnOCH_2CH_2N{<}^{SnBu_3}_{SnBu_3}} \quad (4)$$

This paper describes the reactions of dialkyltin dialkoxides with a variety of straight- and branched-chain alkanolamines having free as well as substituted amino groups.

RESULTS AND DISCUSSION

Reactions of dibutyltin diethoxide with various alkanolamines have been carried out in refluxing benzene with continuous azeotropic removal of ethanol. The progress of reaction was followed by estimating the quantity of ethanol in the azeotrope. These reactions are represented by equations (5) and (6)

$$\mathrm{Bu_2Sn(OEt)_2 + HOXNR_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{(V)}{Bu_2Sn(OEt)(OXNR_2)}} \quad (5)$$

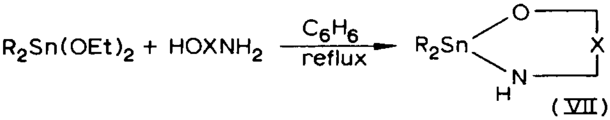
$$\mathrm{Bu_2Sn(OEt)_2 + 2HOXNR_2 \xrightarrow[\text{reflux}]{C_6H_6} \underset{(VI)}{Bu_2Sn(OXNR_2)_2}} \quad (6)$$

($X = CH_2CH_2CH_2$, $CH(Me)CH_2$ and $R = H$; $X = CH_2CH_2$ and $R = H$, Me and H, Et; $X = CH_2CH_2CH_2$, $CH(Me)CH_2$ and $R = Me$ and Et)

Refluxing the reactants for longer periods (10–12 h) or even the use of higher boiling solvents did not cause the amino group to take part in the reactions.

The mixed dibutyltin aminoalkoxides, (V) as well as the dibutyltin bis(aminoalkoxides), (VI) are colourless or yellow hydrolysable liquids, monomeric in refluxing benzene. They are all volatile and can be obtained pure in 40–70% yields upon distillation. A similar dibutyltin derivative $Bu_2Sn(OPr\text{-}i)(OCH_2CH_2NMe_2)$ has been described previously as distillable liquid, whereas the dimethyl- and diethyl-tin derivatives disproportionate during vacuum distillation[3]; the stability of the dibutyltin derivatives (V) is probably steric in origin.

The non-reactivity of the alkanolamine amino groups contrasts with ethanolamine[1] in reaction with dibutyltin diethoxide which may again be due to steric reasons. This fact is supported by the reactions (eqn. 7) of diethyltin diethoxide and dipropyltin diethoxide with alkanolamines in equimolar ratio carried out under similar conditions.



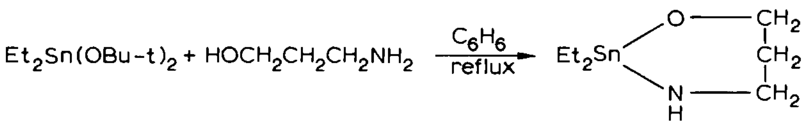
(VII)

($R = Et$ and n-Pr; $X = CH_2CH_2$, $CH_2CH_2CH_2$ and $CHMeCH_2$)

The reaction with diethyltin diethoxide is quite facile and the cyclic product is easily obtained. However, with dipropyltin diethoxide, the reaction slows down after the removal of one mole of ethanol, but may be driven to completion upon prolonged refluxing. It therefore appears that as the length of the alkyl chain attached to the tin atom increases, the reactivity of the amino group of the alkanolamine decreases.

All type VII products are brown or yellow viscous liquids which decompose on attempted vacuum distillation. These are extremely susceptible to hydrolysis by atmospheric moisture.

In order to compare the steric effects of the alkoxy groups also, it was thought worthwhile to study the reaction of diethyltin di-t-butoxide with propanolamine. This alkoxide synthesised by reaction of diethyltin diethoxide with t-butanol, is a volatile liquid (b.p. 57–60/0.2 mm) which is monomeric in benzene. It reacts readily with propanolamine (eqn. 8):



(8)

This ready reaction of the t-butoxide with propanolamine shows that ramification of the alkoxy group does not apparently hinder the ease of reaction with alkanolamines. Similarly, the reaction between equimolar quantities of butyltin triisopropoxide and propanolamine also yields a cyclic product[4].

In both dibutylethoxytin aminoalkoxides and dibutyltin bis(aminoalkoxides) the tin atom may be 5- and 6-coordinate, respectively, as evidenced by IR and Raman spectra[3,5,6]. The dibutyltin bis(aminoalkoxides)may possess distorted octahedral geometry with the alkyl groups attached to tin occupying a *cis*-disposition as shown earlier by Nelson *et al.*[7] for various hexacoordinated dialkyltin derivatives on the basis of their dipole moments and NMR spectra.

IR spectra

IR spectra of some of the products have been recorded in the region 400–4000 cm^{-1}. All those compounds derived from $HOXNH_2$ and HOXNHR show a broad absorption band near 3350 cm^{-1} assigned to the N–H stretching vibration. The bands observed in the region 2960–2850 cm^{-1} are due to ν(C–H) stretching in the various alkyl groups. They also show a very strong band near 1070 cm^{-1} which may be assigned to ν_{as}(C–O) arising from the alkoxy group of the alkanolamines and ethanol. Similar bands have been observed in several dialkyl- and trialkyl-tin compounds[2,8] in the region 960–1100 cm^{-1}. Similar to dialkyltin dialkoxides[9–11] these aminoalkoxy derivatives show four characteristic bands in the region 700–500 cm^{-1}; the bands near 505 ± 5 and 590 cm^{-1} may be assigned to ν(Sn–C) *gauche* and *trans* and those bands near 680 and 660 ± 5 cm^{-1} to (Sn–CH_2) rocking vibrations due to *gauche* and *trans* conformations respectively. The band observed at 505 ± 5 cm^{-1} may also be associated with ν(Sn–O).

EXPERIMENTAL

Moisture was excluded throughout. Benzene, ethanol, t-butanol and alkanol-

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TABLE 1

REACTIONS OF DIBUTYLTIN DIETHOXIDE WITH ALKANOLAMINES

Alkanolamine	*Molar ratio of re-actants*	*Product*	*B p °C/mm*	*Yield (%)*	*Analysis Found (calcd) (%)* Sn	*Analysis Found (calcd) (%)* N	*mol wt. Found (calcd)*	*Some characteristic IR bands*[a]
$HOCH_2CH_2CH_2NH_2$	1/1	$Bu_2Sn(OEt)(OCH_2CH_2CH_2NH_2)$ yellow liquid	140–146/0.1	43	34.1 (33.7)	3.96 (3.98)	370 (352)	1070vs(br), 688m, 665m, 590m, 500w
$HOCH_2CH_2CH_2NH_2$	1/2	$Bu_2Sn(OCH_2CH_2CH_2NH_2)_2$ yellow liquid	155–160/0.1	45	30.6 (31.2)	7.34 (7.36)	369 (381)	1070vs(br), 1020m, 685m, 660m, 590m, 555w, 510w
$HOCHMeCH_2NH_2$	1/1	$Bu_2Sn(OEt)(OCHMeCH_2NH_2)$ yellow liquid	145–150/0.2	37	33.9 (33.7)	3.93 (3.98)	389 (352)	1065vs(br), 1018s, 680m, 655m, 590s, 500w
$HOCHMeCH_2NH_2$	1/2	$Bu_2Sn(OCHMeCH_2NH_2)_2$ colourless liquid	155–165/0.1	36	30.8 (31.2)	7.31 (7.36)	385 (381)	1065vs(br), 1015s(br), 680s(br), 590m, 500w
$HOCH_2CH_2NHMe$	1/1	$Bu_2Sn(OEt)(OCH_2CH_2NHMe)$ colourless liquid	115–120/0.1	54	33.3 (33.7)	3.91 (3.98)	390 (352)	1065vs, 685m, 660m(br), 590m, 505w(br)
$HOCH_2CH_2NHMe$	1/2	$Bu_2Sn(OCH_2CH_2NHMe)_2$ yellow liquid	130–135/0.2	52	30.7 (31.2)	7.30 (7.36)	378 (381)	1060vs, 685m, 650m(br), 590m, 505w(br)
$HOCH_2CH_2NHEt$	1/1	$Bu_2Sn(OEt)(OCH_2CH_2NHEt)$ colourless liquid	120–122/0.2	67	32.0 (32.4)	3.80 (3.83)	372 (366)	1070vs, 1020m, 685m, 660m(br), 590m, 500w(br)
$HOCH_2CH_2NHEt$	1/2	$Bu_2Sn(OCH_2CH_2NHEt)_2$ yellow liquid	135–140/0.2	53	29.3 (29.0)	6.80 (6.85)	390 (409)	1070vs, 1020m, 670–655w (br), 595m(br), 505w
$HOCHMeCH_2NMe_2$	1/1	$Bu_2Sn(OEt)(OCHMeCH_2NMe_2)$ colourless liquid	108–112/0.2	65	30.6 (31.2)	3.68 (3.69)	405 (380)	1090vs, 1055s, 1030s(br), 670–655m(br), 595s(br), 510w(br)
$HOCHMeCH_2NMe_2$	1/2	$Bu_2Sn(OCHMeCH_2NMe_2)_2$ yellow liquid	120–125/0.2	59	26.7 (27.2)	6.40 (6.41)	421 (437)	1075vs, 1038s, 675–660w(br), 590m(br), 510w(br)
$HOCH_2CH_2CH_2NEt_2$	1/1	$Bu_2Sn(OEt)(OCH_2CH_2CH_2NEt_2)$ yellow liquid	150–155/0.8	62	28.5 (29.1)	3.38 (3.43)	415 (408)	1060vs, 1020w, 670w(br), 600vs, 505w
$HOCH_2CH_2CH_2NEt_2$	1/2	$Bu_2Sn(OCH_2CH_2CH_2NEt_2)_2$ yellow liquid	155–160/0.3	64	23.9 (24.1)	5.65 (5.68)	475 (493)	1065vs, 1015m, 670m(br), 600m(br), 500w(br)

[a] For abbreviations see ref 2

TABLE 2

REACTIONS OF $R_2Sn(OR')_2$ WITH ALKANOLAMINES

$R_2Sn(OR')_2$	*Alkanolamine*	*Molar ratio*	*Yield of product Found (calcd.)*	*Product*	*Analysis Found (calcd.) (%)*		*Some characteristic IR bands*[a]
					Sn	*N*	
$Et_2Sn(OEt)_2$	$HOCH_2CH_2NH_2$	1/1	2.01 (2.06)	$Et_2Sn(OCH_2CH_2NH)$ brown viscous liquid	49.6 (50.3)	5.86 (5.94)	
$Et_2Sn(OEt)_2$	$HOCH_2CH_2CH_2NH_2$	1/1	4.70 (4.76)	$Et_2Sn(OCH_2CH_2CH_2NH)$ yellow viscous liquid	47.0 (47.5)	5.55 (5.60)	1060vs(br), 1020vs, 670vs, 610vs(br), 520vs(br), 500w
$Et_2Sn(OEt)_2$	$HOCHMeCH_2NH_2$	1/1	2.01 (2.09)	$Et_2Sn(OCHMeCH_2NH)$ brown viscous liquid	46.8 (47.5)	5.51 (5.60)	
$Et_2Sn(OBu\text{-}t)_2$	$HOCH_2CH_2CH_2NH_2$	1/1	2.40 (2.48)	$Et_2Sn(OCH_2CH_2CH_2NH)$ yellow viscous liquid	46.5 (47.5)	5.53 (5.60)	
$Pr_2Sn(OEt)_2$	$HOCH_2CH_2NH_2$	1/1	3.05 (3.19)	$Pr_2Sn(OCH_2CH_2NH)$ brown viscous liquid	44.1 (45.0)	5.25 (5.31)	
$Pr_2Sn(OEt)_2$	$HOCH_2CH_2CH_2NH_2$	1/1	3.30 (3.37)	$Pr_2Sn(OCH_2CH_2CH_2NH)$ yellow viscous liquid	43.3 (42.7)	4.97 (5.03)	1060vs, 1015m, 665m(br), 600s(br), 510w(br)

[a] IR data are given in cm^{-1} followed by an indication of intensity; vs, very strong, s, strong, m, medium, w, weak; (br), broad

amines were dried as reported earlier[2]. Dibutyltin diethoxide was prepared by the sodium method[12]. Molecular weights were determined ebulliometrically in benzene. IR spectra were recorded on a Perkin–Elmer 337 grating infrared spectrophotometer.

Analyses. Ethanol removed by azeotropic distillation was estimated by an oxidimetric method[13]. Tin was estimated by decomposing the sample with fuming H_2SO_4 and HNO_3 followed by precipitation as the hydroxide and final ignition to SnO_2. Nitrogen was estimated by the Kjeldahl method.

(1) *Reaction of* $Bu_2Sn(OEt)_2$ *with* $HOCH_2CH_2CH_2NH_2$ *(1/1 molar ratio)*

$Bu_2Sn(OEt)_2$ (2.14 g, 6.63 mmole) and $HOCH_2CH_2CH_2NH_2$ (0.50 g, 6.66 mmole) were mixed in benzene (ca. 70 ml) and the mixture was refluxed for about 2 h. The binary azeotrope (benzene–ethanol) thus formed was then fractionated very slowly from the reaction mixture. Excess of solvent was distilled out and the product upon vacuum distillation yielded a yellow liquid (ca. 43 %) b.p. 140–146°C/0.1 mm. (Weight of ethanol in azeotrope: found, 0.29 g; calcd., 0.30 g). (Found: N, 3.96; Sn, 34.1 mol. wt., 370. $C_{13}H_{31}NO_2Sn$ calcd.: N, 3.98; Sn, 33.7 %; mol. wt., 352)

(2) *Reaction of* $Bu_2Sn(OEt)_2$ *with* $HOCH_2CH_2CH_2NH_2$ *(1/2 molar ratio)*:

Using the above procedure, a mixture of $Bu_2Sn(OEt)_2$ (2.11 g, 6.50 mmole) and $HOCH_2CH_2CH_2NH_2$ (0.98 g, 13.1 mmole) upon vacuum distillation yielded a yellow liquid (ca. 45%) b.p. 155–160° C/0.1 mm. (Weight of ethanol in azeotrope: found 0.58; calcd., 0.60 g). (Found: N, 7.34; Sn, 30.6; mol. wt., 369. $C_{14}H_{34}N_2O_2Sn$ calcd.: N, 7.36; Sn, 31.2 %; mol. wt., 381.)

The products obtained by similar reactions of dibutyltin diethoxide with various alkanolamines in 1/1 and 1/2 molar ratios are summarised in Table 1.

(3) *Reaction of* $Et_2Sn(OEt)_2$ *with* $HOCH_2CH_2NH_2$ *(1/1 molar ratio)*

$Et_2Sn(OEt)_2$ (2.32 g, 8.69 mmole) and $HOCH_2CH_2NH_2$ (0.54 g, 8.86 mmole) were mixed with benzene (ca. 80 ml) and the mixture was refluxed for about 4–5 h. The azeotrope was very slowly fractionated out of the mixture followed by excess of solvent. Upon drying the product under reduced pressure a brown viscous liquid was obtained which decomposed on attempted vacuum distillation (yield, 2.01 g). (Weight of ethanol in azeotrope: found, 0.78 g; calcd., 0.80 g) (Found: N, 5.86; Sn, 49.6. $SnC_6H_{15}NO$ calcd.: N, 5.94; Sn, 50.3 %.)

Compounds obtained by the reactions of $Et_2Sn(OEt)_2$, $Et_2Sn(OBu\text{-}t)_2$ and $Pr_2Sn(OEt)_2$ with equimolar ratios of alkanolamines are summarised in Table 2.

(4) *Preparation of* $Et_2Sn(OBu\text{-}t)_2$

A mixture of $Et_2Sn(OEt)_2$ (9.94 g, 37.23 mmoles) and a large excess of t-butanol (ca. 200 g, 2.70 mole) in benzene was refluxed for ca. 18–20 h and the binary azeotrope (ethanol–benzene) was slowly fractionated out of the mixture till the temperature reached to 80°C. Excess of solvent was distilled out and the product was dried under reduced pressure. Upon vacuum distillation colourless liquid (ca. 76 %) was obtained, b.p. 57–60°C/0.2 mm. (Weight of ethanol in azeotrope: Found: 3.14 g; calcd., 3.34 g). (Found: Sn, 37.2; mol. wt., 324. $C_{12}H_{28}O_2Sn$ calcd.: Sn, 36.8 %; mol. wt., 323.)

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