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THE REACTIONS OF DIALKYLTIN DIISOPROPOXIDES WITH 2-(DIMETHYLAMINO)- AND 2-(DIETHYLAMINO)ETHANOL

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SUMMARY

The reactions of dimethyltin, diethyltin and dibutyltin diisopropoxides with 2-(dimethylamino)- and 2-(diethylamino)ethanol have been studied.

INTRODUCTION

The reactivity of Sn–N compounds has been compared with Grignard reagent[1], and is due to the presence of a weak and highly polar $Sn^{\delta+}$–$N^{\delta-}$ bond. Jones and Lappert[2] predicted the following order for bond strengths, $SiN > CN \geqslant GeN > SnN > PbN$ and $SnN < SnP$[3,4], unlike $SiN > SiP$ and the basicity of nitrogen was predicted in the following series $CN > PbN > SnN > GeN > SiN$.

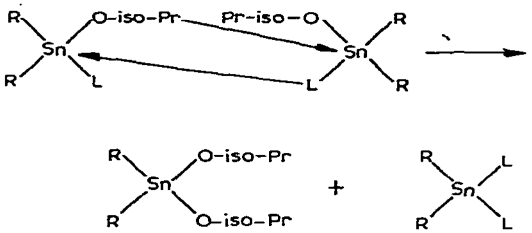
In the above group of compounds a monodentate nitrogen donor ligand is attached to the metal atom through a σ-bond. In order to examine the stability of the Sn–N bonds in a compound obtained by using bidentate chelating agent containing a N donor atom, an attempt has been made to study the reactions of dialkyltin(IV) diisopropoxides with bidentate chelating agents of the type 2-(dimethylamino)- and 2-(diethylamino)ethanol. Similar reactions with oxygen donor ligands have been recently studied[5–7].

The dialkyltin diisopropoxide was found to interchange its isopropoxy groups readily with substituted aminoethanols in dry benzene. The isopropanol/benzene azeotrope could be fractionated out and by determining the amount of isopropanol liberated, the progress of the reaction could be followed.

All the reactions were carried out in the required molar ratios and were found to be exothermic. The bis-compounds obtained were lemon yellow and remained unchanged *in vacuo*. Except the 2-(dimethylamino)ethanol derivative of dibutyltin monoisopropoxide, all the 1/1 products disproportionate during their attempted distillation as indicated below:

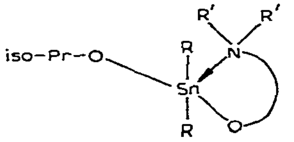
$$2\,R_2Sn(O\text{-iso-Pr})(L) \rightarrow R_2SnL_2 + R_2Sn(O\text{-iso-Pr})_2$$
$$(R = CH_3,\ C_2H_5 \text{ and } C_4H_9;\ L = (CH_3)_2NCH_2CH_2O \text{ and }$$
$$(C_2H_5)_2NCH_2CH_2O)$$

The mechanism for the disproportionation probably involves a four-centered interaction by two chelated molecules:



In dibutyltin monoisopropoxide 2-(dimethylamino)ethoxide the bulky dibutyl group hinders the bond formation between tin and the ligand, so that the four-centered interaction is prevented.

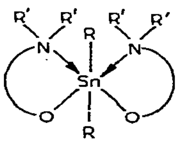
In the compounds of the type $R_2Sn(O\text{-iso-}Pr)(L)$ the tin atom appears to be penta-coordinated, as revealed by their monomeric nature in refluxing benzene:



($R = CH_3, C_2H_5$ and C_4H_9; $R' = CH_3$ and C_2H_5)

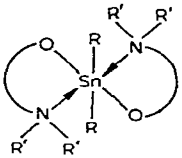
Penta-coordination in tin has been established in large number of cases[8-10] *e.g.*, the trialkyltin halides, hydroxides and carboxylates.

In compounds of the type R_2SnL_2, the tin atom appears to be hexa-coordinated; several examples of hexa-coordination in dialkyltin complexes have been established by IR and Raman studies[11,12] and it has been further shown that the alkyl groups attached to tin occupies *trans* rather than *cis* positions:



(*Trans* with respect to R but *cis* with respect to ligand.)

or



(*Trans* with respect to R and *trans* with respect to ligand)

However, Nelson *et al.*[13] have determined the dipole moment of various hexa-coordinated derivatives and shown that in most cases there is a distorted octahedron with the alkyl groups attached to tin occupying *cis* position.

These products are readily hydrolysed to form organotin oxides and substituted 2-aminoethanols, which indicates the weak and high polarity of the Sn–N bond.

EXPERIMENTAL

Moisture was rigorously excluded where appropriate. Molecular weights were determined with a semi-micro ebulliometer (Gallenkamp) with thermistor sensing. Solvents were dried by standard procedures. 2-(Dimethylamino)- and 2-(diethylamino)ethanol, with b.p. 135° and 163°, were dried by keeping them over BaO for two days and distilled at normal pressure. The IR spectra of the neat liquids were recorded on a Perkin–Elmer 337 spectrometer with KBr optics.

Tin and nitrogen in the above compounds were estimated by usual procedures. Isopropanol in the azeotrope was determined by oxidation with chromic acid[14,15].

(1). *Preparation of dibutyltin diisopropoxide by the sodium method*

The solution of dibutyltin dichloride (11.41 g) dissolved in benzene (50 g) was added dropwise to a solution of sodium isopropoxide (sodium 1.72 g) in isopropanol (16.0 g). Sodium chloride precipitated immediately. After the addition, refluxing was continued for three h and the mixture was kept overnight and filtered. Surplus isopropanol and benzene were removed by distillation, and the residue was distilled under reduced pressure to give a colourless viscous liquid (12.1 g, yield, 95%), b.p. 87°/1.5 mm. (Found: Sn, 34.94. $C_{14}H_{32}O_2Sn$ calcd.: Sn, 35.40%.)

(2). *Preparation of diethyltin diisopropoxide by the sodium method*

To a solution of sodium isopropoxide (sodium 5.92 g) in isopropanol (50 g) was added dropwise diethyltin dichloride (31.88 g) dissolved in benzene (60 g). The mixture was refluxed, filtered, and distilled to give a colourless viscous liquid b.p. 96–98°/10 mm, yield: 32.5 g, 85.6%. (Found: Sn, 40.20. $C_{10}H_{24}O_2Sn$ calcd.: Sn, 40.25%.)

(3). *Preparation of dimethyltin diisopropoxide by the sodium method.*

To a solution of sodium isopropoxide (sodium 2.22 g) in isopropanol (25 g) was added dropwise dimethyltin dichloride (10.64) g) dissolved in benzene (40 g). The mixture was refluxed, filtered, evaporated to a residue which was sublimed at 6 mm (80°) to give a white crystalline solid. Yield, 8.0 g, 62.2%. (Found: Sn, 43.98. $C_8H_{20}O_2Sn$ calcd.: Sn, 44.47%.)

(4). *Preparation of dialkyltin(IV) derivatives of 2-(dimethylamino)- and 2-(diethylamino)-ethanol*

To a solution of dialkyltin(IV) diisopropoxide in benzene a stoichiometric amount of ligand was added. In the initial stages a white turbidity appeared, but this vanished on refluxing. The benzene isopropanol azeotrope was collected and isopropanol was determined by oxidation with chromic acid[14,15]. The general reactions can be represented as below and the results are tabulated in Table 1.

$$R_2Sn(O\text{-iso-}Pr)_2 + R'_2NCH_2CH_2OH \rightarrow R_2Sn(O\text{-iso-}Pr)(OCH_2CH_2NR'_2) + \text{iso-}PrOH \quad (1)$$

$$R_2Sn(O\text{-iso-}Pr)_2 + 2\,R'_2NCH_2CH_2OH \rightarrow R_2Sn(OCH_2CH_2NR'_2)_2 + 2\ \text{iso-}PrOH \quad (2)$$

Products were dried *in vacuo* and analyzed for Sn and N.

RESULTS AND DISCUSSION

The IR spectra of dimethyltin(IV) derivatives of 2-(dimethylamino)- and 2-(diethylamino)ethanol are shown in Table 3, along with tentative band assign-

TABLE 1

PREPARATION AND ANALYSIS OF DIALKYLTIN DERIVATIVES OF SUBSTITUTED 2-AMINOETHANOLS

No.	Weight of alkoxide (g)	Weight of ligand (g)	Molar ratio	Yield (g)	Weight of isopropanol found (calcd.) (g)	Analysis found (calcd.) (%)	
						Sn	N
$(CH_3)_2Sn(O\text{-}iso\text{-}Pr)_2+(CH_3)_2NCH_2CH_2OH$							
1	2.77	1.85	1/2	3.20	1.237 (1.251)	35.96 (36.53)	8.59 (8.61)
2	2.59	0.86	1/1	2.50	0.558 (0.583)	39.64 (40.13)	4.65 (4.73)
$(C_2H_5)_2Sn(O\text{-}iso\text{-}Pr)_2+(CH_3)_2NCH_2CH_2OH$							
3	2.05	1.24	1/2	2.45	0.756 (0.835)	33.28 (33.63)	7.88 (7.93)
4	4.52	1.36	1/1	4.71	0.916 (0.922)	36.53 (36.64)	4.28 (4.32)
$(C_4H_9)_2Sn(O\text{-}iso\text{-}Pr)_2+(CH_3)_2NCH_2CH_2OH$							
5	1.90	0.97	1/2	2.27	0.632 (0.652)	28.92 (29.02)	6.75 (6.84)
6	1.58	0.40	1/1	1.50	0.266 (0.271)	30.90 (31.23)	3.44 (3.68)
$(CH_3)_2Sn(O\text{-}iso\text{-}Pr)_2+(C_2H_5)_2NCH_2CH_2OH$							
7	1.33	1.17	1/2	2.38	0.591 (0.600)	30.88 (31.15)	7.15 (7.35)
8	1.92	0.84	1/1	1.09	0.340 (0.345)	35.56 (36.64)	4.28 (4.32)
$(C_2H_5)_2Sn(O\text{-}iso\text{-}Pr)_2+(C_2H_5)_2NCH_2CH_2OH$							
9	5.78	4.60	1/2	6.82	2.306 (2.356)	28.97 (29.01)	6.80 (6.84)
10	9.58	3.81	1/1	11.14	1.765 (1.953)	36.55 (36.64)	3.90 (3.97)
$(C_4H_9)_2Sn(O\text{-}iso\text{-}Pr)_2+(C_2H_5)_2NCH_2CH_2OH$							
11	2.32	1.54	1/2	2.85	0.789 (0.792)	25.16 (25.51)	5.90 (6.02)
12	4.13	1.37	1/1	4.87	0.267 (0.272)	29.05 (29.08)	3.34 (3.43)

ments[16,17]. A few of the observed absorptions are discussed below to throw light on the nature of these derivatives.

3400–3000 cm^{-1} *region*

The unchelated ligands A and B show broad absorptions of high intensity, which indicates the presence of –OH group. The disappearance of these bands in this region is a pretty good indication that complex formation is taking place through OH group as revealed in the spectrum of C, D and E. There is, however, a very weak absorption in C, D and E, which is probably due to partial hydrolysis of these compounds by the atmospheric moisture, during the IR measurements.

TABLE 2

PROPERTIES OF DIALKYLTIN DERIVATIVES OF SUBSTITUTED 2-AMINOETHANOLS[a]

No.	Nature of the compounds	Mol. wt. in benzene		Sublimation or distillation temp.[b] [°C(mm)]
		Found	Calcd.	
1	$(CH_3)_2Sn[OCH_2CH_2N(CH_3)_2]_2$	327	325	105–107 (1)
2	$(CH_3)_2Sn[OCH_2CH_2N(CH_3)_2](O\text{-iso-Pr})$	346	295	(a) 60 (8.0) characterised as $(CH_3)_2Sn(O\text{-iso-Pr})_2$ (b) 106–107 (1) characterised as $(CH_3)_2Sn[OCH_2CH_2N(CH_3)_2]_2$
3	$(CH_3)_2Sn[OCH_2CH_2N(C_2H_5)_2]_2$	387	381	108–110 (2.5)
4	$(CH_3)_2Sn[OCH_2CH_2N(C_2H_5)_2](O\text{-iso-Pr})$	331	324	(a) 50 (3.0) characterised as $(CH_3)_2Sn(O\text{-iso-Pr})_2$ (b) 109–110 (2.5) characterised as $(CH_3)_2Sn[OCH_2CH_2\text{-}N(C_2H_5)_2]_2$
5	$(C_2H_5)_2Sn[OCH_2CH_2N(CH_3)_2]_2$	351	353	142 (3.0)
6	$(C_2H_5)_2Sn[OCH_2CH_2N(CH_3)_2]O\text{-iso-Pr}$	456	324	(a) 65–66 (1.0) characterised as $(C_2H_5)_2Sn(O\text{-iso-Pr})_2$ (b) 126 (1.0) characterised as $(C_2H_5)_2Sn[OCH_2CH_2N\text{-}(CH_3)_2]_2$
7	$(C_2H_5)_2Sn[OCH_2CH_2N(C_2H_5)_2O]_2$	398	409	162–164 (2.5)
8	$(C_2H_5)_2Sn[OCH_2CH_2N(C_2H_5)_2]O\text{-iso-Pr}$	400	352	(a) 65 (1.0) characterised as $(C_2H_5)_2Sn(O\text{-iso-Pr})_2$ (b) 162 (2.5) characterised as $(C_2H_5)_2Sn[OCH_2CH_2N\text{-}(C_2H_5)_2]_2$
9	$(C_4H_9)_2Sn[OCH_2CH_2N(CH_3)_2]_2$	515	409	145 (2.0)
10	$(C_4H_9)_2Sn[OCH_2CH_2N(CH_3)_2]O\text{-iso-Pr}$	569	380	128 (6.0)
11	$(C_4H_9)_2Sn[OCH_2CH_2N(C_2H_5)_2]_2$	436	465	174–178 (4.5)
12	$(C_4H_9)_2Sn[OCH_2CH_2N(C_2H_5)_2]O\text{-iso-Pr}$	392	408	(a) 128–130 (0.7) characterised as $(C_4H_9)_2Sn(O\text{-iso-Pr})_2$ (b) 158–162 (0.7) characterised as $(C_4H_9)_2Sn[OCH_2CH_2\text{-}N(C_2H_5)_2]_2$

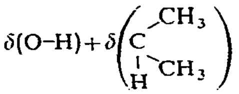
[a] All compounds are lemon yellow. [b] The compounds described under nos. 2, 4, 6, 8 and 12 disproportionates on distillation giving two fractions, in each case Sn and N analysis were done.

3000–2700 *cm*$^{-1}$ *region*

The bands in this region are due to asymmetric and symmetric stretching vibrations of C–H groups originating from CH_3 or CH_2 groups attached to carbon, tin and nitrogen. Hill and Meakins[18] have pointed out that in $(CH_3)_2N$ group, the position of the band is varied and found two bands at 2825–2810 and 2775–2765 cm^{-1}. Braunholtz *et al.*[19] and Wright[20] confirmed the above conclusions. Braunholtz *et al.* noted that the band was absent in amides, in complexes of amines with metals

TABLE 3

INFRARED SPECTRA OF DIALKYLTIN DERIVATIVES (cm^{-1})[a]

A	B	C	D	E	Assignment
3385 (b)	3437 (b)	3300–3200 w	3300–3200 w	3400–3200 w	ν(O–H)
2990 (sh)	2987 s	2970 (sh)	2970 vs	3115 w 2970 vs	ν(C–H)
2960 m		2950 s			$\nu[C\text{–}H(SnCH_3)]+\nu(C\text{–}H)$
	2937 (sh)			2930 (sh)	
2900 w			2900 w		
	2875 (sh)		2880 w		
2840 w		2820 m		2840 m	
	2812 w		2810 w	2800 (sh)	$\nu[C\text{–}H(NCH_3),(CH_2)]$
2770 w	2760 (sh)	2780 w		2775 (sh)	(CH_3) groups O–CH_3
1460 vs	1452 s	1450 s	1435 s	1445 vs	ν(C–H) of CH_2 or NCH_3 gr. CH_2CO
1400 (sh)	1390 (sh)				$\nu(CH_2OH)$ primary alcoholic group. δ(OH) in plane deformation vibration
1360 m	1362 m	1360 w	1365 s	1350 m	 $\delta(O\text{–}H)+\delta\left(\overset{CH_3}{\underset{H}{C}}\!\!\diagdown_{CH_3}\right)$
1315 w				1330 (sh)	
1267 s	1295 m	1270 w	1295 mw	1250 w	δ(O–H)
1193 m	1200 s	1185 m	1208 m 1185 w	1180 s[b]	
1174 m	1170 m				
1153 w		1155 w		1160 m[b]	
	1125 w	1100 s	1103 (sh)	1125 w	ν(C–O) and δ(O–H) of primary alcohol
1098 (sh)				1100 m	
1083 m	1045 s	1050 m	1060 s	1070 (sh)	
1033 s	992 (sh)		1000 (sh)	1035 m	
938 s		948 s	945 (sh)	978 s 948 m	
	908 (sh)		916 m		
888 (sh)	870 m	870 s	875 m	870 s	ρ(C–H)
871 s					
848 m	798 s			825 m	
791 (sh)					
768 s	760 (b)	770 m	770 s	770 (sh)	π(CH)
	725 m	758 w		758 m	
698 m		670 s	670 s	670 w	ν_{as} (Sn–O)
				620 (sh)	
		595 w	600 s	595 m	ν_s(Sn–O)
528 w	528 (b)	555 w	550 m	538 m	ν_{as}(Sn–C)
		515 w	510 w	515 m	
		450 vw	442 vw	410 vw	

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[a] A = $(CH_3)_2NCH_2CH_2OH$; B = $(C_2H_5)_2NCH_2CH_2OH$; C = $(CH_3)_2Sn[OCH_2CH_2N(CH_3)_2]_2$; D = $(CH_3)_2Sn[OCH_2CH_2N(C_2H_5)_2]_2$; E = $(CH_3)_2Sn[OCH_2CH_2N(CH_3)_2]$O-iso-Pr. [b] These absorptions are due to the isopropoxy group.

and in other compounds such as 1(H)-methyl quinol-4-one, in which there is a substantial degree of delocalisation of the lone pair electrons of the nitrogen atom. In compounds A and B, the bands at 2840 and 2770 cm^{-1} and 2760 and 2812 cm^{-1} are assigned to ν(CH) originating from $N(CH_3)_2$ and $N(C_2H_5)_2$ groups.

1460–1400 *cm^{-1} region*

The deformation mode of the CH_3 group attached to nitrogen atom could be expected to give a band in the range 1460–1430 cm^{-1}. In ligands A and B the strong intensity bands at 1460 and 1452 cm^{-1} are assigned to $\nu(N{-}CH_3)$ or $(N{-}C_2H_5)$, although it is indistinguishable from the main CH_2 deformation vibration and asymmetrical CH_3 deformations.

1365–1260 *cm^{-1} region*

One or two medium to strong intensity bands are observed in this region which are assigned to *gem*-dimethyl structure in A, C, D and E and *gem*-diethylstructure in B. In isopropoxides of transition metals, the doublet[21] occurs at 1375 and 1365 cm^{-1} and has been assigned to the *gem*-dimethyl structure. When the two methyl or ethyl groups are attached to nitrogen the doublet appears at lower wave numbers, *e.g.*, 1360 to 1295 cm^{-1}, this is due to the slight increase in the electronegativity of nitrogen atom as compared to carbon. In the lower region of the spectrum a weak to strong intensity band at 1267–1275 cm^{-1} is observed which is assigned to deformation vibrations of the −OH group in A and B.

1200–1000 *cm^{-1} region*

A number of bands of weak to strong intensities have been observed in all the compounds studied. They have been assigned to the stretching vibrations of C−N. Colthup[22] has identified these bands in aliphatic amines in the range 1220–1020 cm^{-1}, which are assigned to C−N stretching frequencies of non-conjugate links and the bands are of low intrinsic intensity. Because of this, and of wide frequency range in which they occur along with so many other skeletal vibrations, *i.e.*, those of isopropoxy groups, these bands are not of much direct value for identification. In E the bands 1180 s cm^{-1} and 1160 m cm^{-1} are due to the isopropoxy group as established by Mazdiyasni[21] and the band at 1070 cm^{-1} is assigned to the ν(C−O) stretching vibrations. Bradley and coworkers[23] have observed that the C−O stretch in metal alkoxides show a characteristic absorption around 1060 cm^{-1}. The region for ν(C−O) could vary from 950–1070 cm^{-1} depending upon the metal–oxygen link.

900–700 *cm^{-1} region*

Several bands with weak to strong intensities are obtained they have their origin due to out-of-plane deformation vibration of C−H as well as rocking of CH_3 or CH_2 groups attached to nitrogen and tin, respectively.

670–400 *cm^{-1} region*

In this spectroscopically significant region, most of the Sn−O and Sn−C stretching vibrations occur and five bands of weak to strong intensities are observed. The bands at 670 cm^{-1} and 595–600 cm^{-1} have been assigned to the asymmetric and symmetric Sn−O vibrations. In the spectrum of dimethyltin diisopropoxide two bands are observed at 650 vs cm^{-1} and 593 w cm^{-1} respectively[24], which are assigned to Sn–O stretching vibrations and these appear to be slightly shifted from 644 and 609 cm^{-1} observed in case of dimethyltin dimethoxide[25,26]. However, marked lowering in the stretching vibrations are observed in hexacoordinated compounds such as acetylacetonatotin dihalides (460–440 cm^{-1})[27]. Although a number of authors[28,29,30] have used ν(Sn–C) for elucidating the structure of dialkyltin derivatives, it is difficult to make a similar deduction from our studies as along with bands at 555, 550 and 538 cm^{-1} [assigned to ν_{as}(Sn–C) in C, D and E] a number of other weak bands at 515 and 510 cm^{-1} appear to be originating from skeletal vibrations of the ligand.

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