TRIORGANOTIN(IV) COMPLEXES DERIVED FROM INTERNALLY FUNCTIONALIZED OXIMES

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ABSTRACT

Reactions of triorganotin(IV) chlorides with sodium salt of internally functionallized oximes in 1:1 molar ratio in refluxing anhydrous benzene, gives $R_3Sn[ONC(Me)Ar]$ (where R = Me, Et, Bu and $Ar = 2-NC_5H_4-$, 2-OC₄H₃- or 2-SC₄H₃-). All these derivatives have been characterized by their elemental analysis, IR and NMR [^{1}H , $^{13}C\{^{1}H\}$ and ^{119}Sn] spectral studies. Molecular weight measurements show their monomeric behaviour in freezing benzene. On the basis of tin-hydrogen [$^{2}J(^{119}Sn,^{1}H)$] and tin-carbon [$^{1}J(^{119}Sn,^{13}C)$] coupling constants as well as ^{119}Sn NMR data, a tetrahedral geometry around the tin atom has been proposed through oxygen atom of the ligand moiety.

INTRODUCTION

Recently we have reported the synthesis of some diorganotin(IV) complexes containing internally functionallized oxime moieties and have shown that subtle change in the R group on tin results in different structural motifs as revealed by the X-ray diffraction studies of $[\{Et_2Sn(ONC(Me)Py)\}_2O]_2$ (I) and $[\{Bu^n_2Sn(ONC(Me)Py)\}_2O]_2$ (II)'. In the case of (I), the oxime nitrogen is coordinated to the endocyclic tin atom whereas in the case of (II) it is coordinated to the exocyclic tin atom.

Triorganotin(IV) complexes of the type R₃SnL (where L = anionic bidentate ligand) have received considerable attention due to their varied coordination chemistry and diversity in their structural patterns.²⁻¹⁰ Biocidal activities of several triorganotin(IV) compounds are now well documented and the toxicity is species specific.¹¹⁻¹³ In addition, some tri- and diorganotin(IV) compounds exhibit anti-tumor activities.¹⁴⁻¹⁹

Oximes are an important class of multidentate organic ligands capable of forming complexes with a remarkable diversity in coordination pattern.^{1, 20-22} They also show a variety of biological applications.^{23, 24}

In view of the above and pursuance of our interest on organotins we have synthesized triorganotin(IV) complexes derived from internally functionallized oximes and the results are reported herein.

MATERIALS AND METHODS

All chemicals were of reagent grade and dried before use. Me 3SnCl and Bu 3SnCl were used as supplied while Et₃SnCl was prepared according to the literature method.²⁵ Tin was estimated as tin-oxide and nitrogen was estimated as reported in the literature. ²⁶ For compounds of the type R₃Sn{ONC(Me)Py}, the nitrogen present in the aromatic ring does not decompose by this procedure. This fact is further corroborated by carrying out blank estimation of nitrogen in pyridine itself.

Molecular weight measurements were carried out by determining depression in freezing point of benzene, using Beckman's Thermometer (Einsteiithermometer n-Beckmann, Labortherm-N, Skalewert, 0.01 K, made in GDR) fitted in a glass assembly (Supplied by JSGW, India). Calculation was done according to the formula $M = 1000 \times K_f \times w / W \times \Delta T_f$, where M = molecular weight, w = weight of solute in gms, $K_f = \text{molar}$ Depression Constant, W = weight of solvent in gms and $\Delta T_f = \text{depression}$ of freezing point. IR spectra were recorded as neat liquid on a Bomen MB - 102 FT - IR spectrophotometer. 1H , $^{13}C\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded as CDCl₃ solutions on a Bruker DPX-300 NMR specrometer operating at 300, 75.5, 111.9 MHz, respectively. Chemical shifts are relative to internal chloroform peak for 'H and ^{13}C and external Me_4Sn in C_6D_6 .

Preparation of [Bu3Sn{ONC(Me)Py}]

To a methanolic solution of sodium salt of the ligand [prepared by the reaction of sodium (150 mg, 6.52 m mol) with 2-acetylpyridyl oxime (892 mg, 6.55 m mol) in refluxing methanol], a benzene solution of Bu₃SnCl (2.13 g, 6.54 m mol) was added and refluxed for 5 h. NaCl formed (378 mg, 6.46 m mol) during the reaction was filtered off and the filtrate was concentrated in vacuo to give a pinkish liquid which was distilled under vacuo (190°C, at 0.1 mm, 2.50 g, yield 90 %) as pink liquid.

All other complexes were prepared by the similar rout, their physical and NMR data are given in tables 1 and 2, respectively.

RESULTS AND DISCUSSION

Triorganotin(IV) complexes containing internally functionallized oximes were prepared by the reactions of the sodium salt of the ligands with trialkyltin chloride in refluxing anhydrous benzene:

$$R_3SnCl + Na[ONC(Me)Ar] \longrightarrow [R_3Sn\{ONC(Me)Ar\}] + NaCl$$

 $(R = Me, Et, Bu \text{ and } Ar = 2-NC_5H_4-, 2-OC_4H_3- \text{ or } 2-SC_4H_3-)$

TABLE-1 Synthetic and Analytical data of triorganotin(IV)oximates

INDEL	1 ADDE-1 Synthetic and Analytical data of thorganoting 1 your lates							
Complex	Colour	% yield	B. P.	% Analysis Found (Calcd.)		Molec-		
		(After	(°C/.1			ular		
	1	distillati	mm)			weight		
l	1	on)		N	Sn	Found		
						(Calcd.)		
Me ₃ Sn{ONC(Me)Py} (1)	Colourless	96	155°C	4.5	39.5	297		
				$(4.7)^{a}$	(39.7)	(298.9)		
Et ₃ Sn{ONC(Me)Py} (2)	Pink	90	160°C	3.9	34.6	342		
				$(4.1)^a$	(34.8)	(340.9)		
$Bu^{n}_{3}Sn\{ONC(Me)Py\}$ (3)	Pink	90	190°C	3.4	27.8	412		
				$(3.3)^{a}$	(27.9)	(425.0)		
Me ₃ Sn{ONC(Me)C ₄ H ₃ O}	Colourless	96	115°C	4.7	41.1	281		
(4)				(4.8)	(41.2)	(287.8)		
$Et_3Sn\{ONC(Me)C_4H_3O\}$	yellow	96	130°C	4.1	35.8	312		
(5)	1			(4.2)	(36.0)	(329.9)		
Bu ⁿ ₃ Sn{ONC(Me)C ₄ H ₃ O}	yellow	87	210°C	3.3	28.5	435		
(6)				(3.4)	(28.6)	(413.9)		
Me ₃ Sn{ONC(Me)C ₄ H ₃ S}	Colourless	96	135°C	4.5	38.8	291		
(7)		The Part of the Pa		(4.6)	(39.0)	(303.8)		

The ring nitrogen of the oxime could not be decomposed by the Kjeldahl method. Therefore, the calculated N% relates only to the oxime nitrogen.

Triorganotin(IV) oximates, [R₃Sn{ONC(Me)Ar}], are faint coloured liquids which can be distilled *in vacuo*. The boiling point of all these complexes increases with increasing the chain length of the alkyl group on tin atom. Molecular weight measurements in freezing benzene, demonstrate these complexes to be monomeric.

IR spectra of these compounds were interpreted by comparing with the spectra of free oximes as well as with other triorgaotin(IV) oximates. Hydroxy group absorption (appears in the region $3100-3300~\text{cm}^{-1}$ in the free oximes) is absent in the IR spectra of all these complexes indicating metal-ligand bond formation through oxygen atom. A medium intensity absorption of C=N bond in the region 1557-1666 cm⁻¹ and strong N-O absorption in the region $900-936~\text{cm}^{-1}$ for free oximes, are shifted to the lower wave numbers and on complexation are observed in the region $1522-1635~\text{cm}^{-1}$ and $892-931~\text{cm}^{-1}$, respectively. The appearance of a new medium to weak intensity band at $467-513~\text{cm}^{-1}$, may be assigned to $v_{\text{Sn-O}}$ mode. Strong absorption in the region $543-578~\text{cm}^{-1}$ may be assigned to $v_{\text{Sn-C}}$. For the trimethyltin(IV) derivatives,the presence of two bands at ~ 544 and $513~\text{cm}^{-1}$ assigned to sym(Sn-Me) and antisym(Sn-Me),suggest a tetrahedral orientation of the Sn-Me bonds.

¹H and ¹³C{¹H} NMR spectra of all these complexes exhibit characteristic signals and multiplicities for R-Sn and ligand protons^{1,21} and carbons. In the ¹H NMR spectra of all these compounds the hydroxyl proton resonances of free ligand are absent, indicating deprotonation of hydroxyl group of the oxime and concomitant formation of Sn-O bond. No appreciable shift has been observed for the ligand ring proton resonances, ruling-out the possibility of coordination through hetero atom present on the aromatic ring of ligand moiety,possibly due to the opposite orientation of the substituents. Similarly, in the ¹³C NMR spectra, a slight down-field shift (δ 0.2 – 2.4 ppm) has been observed for the C=N carbon signal. Since, no significant shift in the hetero-aryl ring carbon/proton resonances was observed, it may be inferred that tinhetero atom interactions are absent. The Me₃Sn complexes displayed a singlet with ²J(¹¹⁹Sn, ¹H) of 56 Hz. Similarly, the ¹³C{¹H} NMR spectra of these compounds exhibited characteristic peaks for R₃Sn carbons with ¹J(¹¹⁹Sn, ¹³C) of 351 – 393 Hz. The C-Sn-C angle may be calculated from these coupling constants using the following relationship²⁷:

 $^{1}J(^{119}Sn.^{13}C) = 11.4 \theta (C-Sn-C) - 875$

The above relationship give an average value of 109° for C-Sn-C angles, suggesting tetrahedral geometry around tin atom, which is further substantiated by 119 Sn NMR chemical shifts. The 119 Sn NMR spectra of all these compounds displayed a single resonance in the region δ 110-150 ppm, which is the absorption region for tetra-coordinated triorganotin(IV) atom.

TABLE-2 1H.	13C{1H} a	nd 119Sn{1H}	NMR data of	triorganotin(IV)	oximates in CDCl ₃
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Com-	¹H NMR δ	¹³ C{ ¹ H} NMR δ	¹¹⁹ Sn	Estimated
plex No.			{¹H} NMR δ	C-Sn-C ∠ in °
(1)	0.50 (s, ${}^{2}J({}^{119}Sn, {}^{1}H) = 56$ Hz, Sn- CH_3); 2.33 (s, oxime-Me); 7.14 (t, 5.7 Hz, H-4); 7.56 (t, 7.6 Hz, H-5); 7.85 (d, 7.8 Hz, H-3); 8.54 (s, H-6).	-3.7 [${}^{1}J({}^{119}Sn, {}^{13}C) = 387 Hz, Sn-CH_{3}$]; 9.9 (oxime-Me); 120.1 (C-5); 122.6 (C-3); 135.6 (C-4); 148.5 (C-6); 155.8 (C-2); 157.5 (C=N).	149.7	110.7
(2)	1.16 – 1.44 (m, Sn-CH ₂ CH ₃); 2.34 (s, oxime-Me); 7.17 (br, H-4); 7.60 (br, H-5); 7.88 (d, 7.8 Hz, H-3); 8.56 (s, H-6)	7.0 [${}^{1}J({}^{119}Sn, {}^{13}C) = 365 \text{ Hz}, Sn-CH_{2}$]; 9.7 (Sn-CCH ₃); 9.8 (oxime-Me); 120.0 (C-5); 122.5 (C-3); 135.6 (C-4); 148.6 (C-6); 156.4 (C-2); 157.8 (C=N).	111.7	108.7
(3)	0.89 (t, 7.2 Hz, Sn-CCCCH ₃); 1.23 - 1.38 (m, Sn-CCH ₂ CH ₂); 1.66 (m, Sn-CH ₂); 2.32 (s, Oxime-Me); 7.14 (t, 6.0 Hz, H-4); 7.57 (td, 8.4 Hz (t), 1.4 Hz (d), H-5); 7.88 (d, 8.0 Hz, H-3); 8.55 (d, 4.2 Hz, H-6).	9.6 (oxime-Me); 13.4 (Sn-CCC H_3); 15.7 [$^{1}J_{1}^{(119}Sn, ^{13}C) = 355$ Hz, Sn- CH_2]; 26.9 [$^{2}J_{1}^{(119}Sn, ^{13}C) = 56$ Hz, Sn- CCH_2]; 27.9 (Sn- $CCCH_2$); 119.9 (C-5); 122.3 (C-3); 135.4 (C-4); 148.5 (C-6); 156.4 (C-2); 157.7 (C=N).	115.9	107.9
(4)	0.52 [s, ${}^{2}J({}^{119}Sn, {}^{1}H) = 56$ Hz, Sn- CH_3]; 2.17 (oxime-Me); 6.40 (s, H-4); 6.54 (br, H-3); 7.42 (s, H-5).	-3.7 [${}^{1}J({}^{119}Sn, {}^{13}C) = 393 \text{ Hz}, Sn-CH_{3}$]; 10.7 (oxime-Me); 107.2 (C-4); 111.0 (C-3); 142.6 (C-5); 149.1 (C-2); 152.0 (C=N).	149.5	111.2
(5)	1.09 – 1.46 (m, Sn-CH ₂ CH ₃); 2.17 (s, oxime-Me); 6.38 (s, H-4); 6.51 (br s, H-3); 7.39 (s, H-5).	6.9 [${}^{1}J({}^{119}Sn, {}^{13}C) = 354 \text{ Hz, Sn-} CH_{2}$]; 9.6 (Sn-CCH ₃); 10.3 (oxime-Me); 106.6 (C-4); 111.0 (C-3); 142.2 (C-5); 149.3 (C-2); 152.5 (C=N).	110.9	107.8
(6)	0.91 (t, 7.2 Hz, Sn-CCCCH ₃); 1.23 - 1.42 (m, Sn-CCH ₂ CH ₂); 1.66 (m, Sn-CH ₂); 2.16 (s, oxime-Me); 6.38 (br s, H-4); 6.50 (br s, H-3); 7.39 (s, H-5).	10.3 (oxime-Me); 13.4 (Sn-CCC H_3); 16.0 ['J(¹¹⁹ Sn, ¹³ C) = 351 Hz, Sn- CH_2]; 26.9 [² J(¹¹⁹ Sn, ¹³ C) = 55 Hz, Sn-CC H_2]; 27.8 (Sn-CC H_2); 106.4 (C-4); 111.0 (C-3); 142.0 (C-5); 149.1 (C-2); 152.7 (C=N).	114.4	107.5
(7)	0.54 {s, ${}^{2}J({}^{119}Sn, {}^{1}H) = 56$ Hz, Sn- CH_3 }; 2.26 (s, oxime-Me); 6.99 (br, H-4); 7.15 (br, H-3 and H-5).	-3.9, $[{}^{1}J({}^{119}Sn, {}^{13}C) = 393 \text{ Hz}, Sn-CH_3]; 11.5 (s, oxime-Me); 124.2 (C-4); 125.3 (C-3); 126.6 (C-5); 142.6 (C-2); 152.0 (C=N).$	150.6	111.2

Conclusion

On the basis of the above data, the following structure (III) may be proposed for these triorganotin(IV) compounds derived from internally functionalized oximes

III (R = Me, Et, Bu and Ar = $2-NC_5H_4-$, $2-OC_4H_3-$ or $2-SC_4H_3-$)

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