

## Reactivity of diorganotin(IV) and triorganotin(IV) phenoxides

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**Abstract:** The reactivity of diorganotin(IV) diphenoxides toward acetylacetone and salicylaldehyde; diorganotin(IV) chlorophenoxides towards potassium salts of benzohydroxamic acids, aluminium(III) chloride and iron(III) chloride and triorganotin(IV) phenoxides towards Hg(II) salts has been examined. The products were authenticated by physico-chemical and spectral studies. This article deals with study of cleavage of Sn-O, Sn-C bond and behaviour of the organotin(IV) phenoxides as chloride ion donors under different conditions. These reactions can be utilized as the course for the synthesis of the reaction products as these are obtained in quantitative yields.

**Keywords:** Reactivity of organotin phenoxides; acetylacetone; salicylaldehyde; benzohydroxamates; aluminium trichloride and iron trichloride.

### Introduction

The organotin chemistry has developed into one of the significant domains of research in organometallic chemistry ascribing to their numerous applications<sup>1-10</sup>. The full scope of usage of organotin compounds, have fascinated many researchers to look into different aspects of organotin chemistry. Among several classes of extensively studied organotin(IV) compounds, organotin(IV) phenoxides represent a category of compounds which has not been analysed considerably. The bulk of the reports available in literature focus on the synthesis and characterization of organotin phenoxides<sup>11-18</sup> and merely a few publications on the reactions of organotin(IV) phenoxides with ethylpropiolate<sup>19</sup>, diethylacetylenedicarboxylate<sup>20</sup>, bis 2,2,2-trichloroethyl azodicarboxylate<sup>21</sup>, diethyl azo dicarboxylate<sup>22</sup>, carbon dioxide and isocyanate<sup>23</sup> etc have been described.

As a part of our ongoing work and our pursuit to look into different aspects of organotin phenoxides chemistry, we report herein the synthesis and characterization of reaction products of organotin(IV) phenoxides towards various ligands viz. acetylacetone, salicylaldehyde, *p*-chloro-, *p*-nitro-benzohydroxamic acid, iron(III) chloride and aluminium(III) chloride in order to have an insight into the stability of various bonds present in organotin(IV) phenoxides. We have already reported the synthesis and characterization of parent organotin phenoxides<sup>17,18</sup>.

### Experimental Section

#### Materials and Methods

Acetylacetone (Sisco) was firstly dried by refluxing over P<sub>2</sub>O<sub>5</sub> (5-6 hours) and was then distilled under reduced pressure and salicylaldehyde (Reidel) was purified by distillation. *p*-

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chlorobenzoic acid (Merck), *p*-nitrobenzoic acid (Merck), Iron(III) chloride (AR), Mercuric(II) chloride (Ranbaxy), Mercuric(II) bromide (Merck) and Mercuric(II) acetate (Merck) were used as received without further purification. Anhydrous aluminium(III) chloride (BDH) was purified by subliming in an atmosphere of chlorine. All solvents are purified according to methods described in literature. *p*-chloro, *p*-nitro benzohydroxamic acids were prepared via the ethyl esters of *p*-chlorobenzoic acid, *p*-nitrobenzoic acid by a literature method<sup>24</sup>.

Tin was evaluated as SnO<sub>2</sub> by utilizing a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> in 2:3 ratios (by vol.) and chlorine content was approximated by the Volhard's method. Analysis for carbon and hydrogen elements was carried out on Elemental Vario EL III Carlo Erba 1108 analyzer. The melting points were recorded in capillary tubes using melting point apparatus. Molar conductance values of 10<sup>-3</sup> mol L<sup>-1</sup> solutions of compounds in nitrobenzene were taken at 25±0.1°C on an Elico Conductivity Bridge (type CM-82T). Rast's camphor method was used to find the molecular weights of the complexes. FTIR spectra of the complexes were collected with Nicolet 5700 spectrophotometer.

### Synthesis

#### Reactions of R<sub>2</sub>Sn(OAr)<sub>2</sub> {where OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2 and C<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4} with chelating ligands viz. acetylacetone and salicylaldehyde.

In a representative reaction, to a solution of parent organotin(IV) phenoxides of composition R<sub>2</sub>Sn(OAr)<sub>2</sub> in dry benzene was added bimolar number of chelating ligands under anhydrous conditions, in separate experiments. The reaction components furnished a clear solution upon mixing followed by refluxing for 8-10 hours. The solids separated during the course of reaction were filtered and dried under vacuum. The filtrate upon keeping undisturbed for 3-4 days gave phenolic crystals in case of a reaction with organotin(IV) 2-tert-butyl-4-methyl phenol. Solids were recrystallized from benzene.

#### Reactions of R<sub>2</sub>SnCl(OAr) (where R = n-Bu, Me: OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2 and OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4) with Potassium salts of *p*-chloro and *p*-nitro benzhydroxamic acids:

To the solutions of parent organotin(IV) chloro phenoxides in methanol (30 mL) were added equimolar solutions of potassium salts of *p*-chloro and *p*-nitro benzhydroxamic acids in dry methanol (20 mL) in different experiments. The reaction mixtures were stirred for 2-3 hours at room temperature and were then refluxed for 8-10 hours. White solids separated in the course of refluxing were filtered and filtrates were vacuum concentrated. The filtrates were then kept for 3-4 days undisturbed whereupon crystalline solids separated out. These were then dried under vacuum. The solids were recrystallized from methanol.

#### Reactions of R<sub>2</sub>SnCl(OAr) (where R = n-Bu, Me: OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2 and OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4) with Lewis acids (Lewis acids = FeCl<sub>3</sub> and AlCl<sub>3</sub>)

In a typical preparative scheme, to a suspension of organotin(IV) phenoxides in THF (20 mL), an equimolar quantity of FeCl<sub>3</sub> dissolved in the same solvent, was added. The reaction mixture was firstly stirred, followed by refluxing for 4-5 hours. It was then filtered and the filtrate was distilled off to eliminate excess of solvent. The concentrate was then treated with diethyl ether and the solid, hence attained was dried in vacuum. The resultant solids were recrystallized from THF.

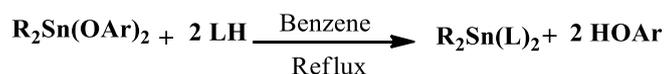
### Reactions of triphenyltin(IV) phenoxides with mercuric(II) salts viz. HgCl<sub>2</sub>, HgBr<sub>2</sub> and Hg(ac)<sub>2</sub>.

In a standard reaction run, to a solution of triphenyltin(IV) phenoxides in THF (25 mL), a solution of mercuric(II) salts in 1:1 molar ratios in THF, were added drop wise with continuous stirring for 5-8 hours at room temperature. The reaction mixture was concentrated under vacuum and the concentrate was treated with petroleum ether, upon which a white solid (I) resulted. The solid was removed by filtration and washed with petroleum ether. It was then treated with hot benzene and the solution was set aside overnight, which left a white crusty solid (II). The crusty white solids were recrystallized from THF.

## Results and Discussion

### Reactions of diorganotin(IV) phenoxides with acetylacetone and salicylaldehyde

The reactions of parent diorganotin(IV) complexes of composition R<sub>2</sub>Sn(OAr)<sub>2</sub> (where R = n-Bu and Me; OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2 and OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4) have been undertaken with the acetylacetone and salicylaldehyde in accordance with the following reaction:



{Where R = n-Bu, Me; OAr = OC<sub>6</sub>H<sub>4</sub>But-2, OC<sub>6</sub>H<sub>3</sub>But-2-Me-4; LH = acetylacetone and salicylaldehyde}

Interestingly, on varying the molar ratios of reactants, only bis-chelated diorganotin(IV) complexes have been obtained. The elemental analyses of the isolated complexes agreed well with their expected stoichiometric compositions. The complexes obtained were sharp melting, non-electrolytic and monomeric solids. The physico-chemical and IR spectral data has been presented in Table 1.

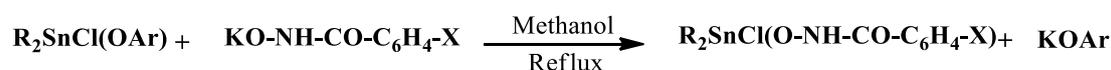
**Table 1.** Analytical data and principal IR bands of chelate complexes of dibutyltin(IV) and dimethyltin(IV) with acetylacetone and salicylaldehyde

Parent Complex	Ligand	Main Product	Side Product	Colour	M.Pt (°C)	Elemental analysis	IR Bands (cm <sup>-1</sup> )			
						% Found (calc.) Sn	ν(C=O)	ν(C-C)	ν(Sn-O)	ν(-OH)
-	acac	-	-	-	-	-	1600-1580 1370-1350	1525	-	3333
Bu <sub>2</sub> Sn (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>2</sub>	acac	Bu <sub>2</sub> Sn (acac) <sub>2</sub>	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Light Yellow	33	27.4 (27.6)	1560 1330	1532	490	-
Me <sub>2</sub> Sn (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>2</sub>	acac	Me <sub>2</sub> Sn (acac) <sub>2</sub>	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Yellow	77	34.4 (34.2)	1565 1325	1530	462	-
Bu <sub>2</sub> Sn (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>2</sub>	acac	Bu <sub>2</sub> Sn (acac) <sub>2</sub>	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Light Yellow	33	27.4 (27.6)	1561 1335	1532	488	-
Me <sub>2</sub> Sn (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>2</sub>	acac	Me <sub>2</sub> Sn (acac) <sub>2</sub>	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Yellow	77	34.5 (34.2)	1565 1328	1535	460	-
-	Sal	-	-	-	-	-	1660	1200	-	3180
Bu <sub>2</sub> Sn (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>2</sub>	Sal	Bu <sub>2</sub> Sn (sal) <sub>2</sub>	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Light Yellow	142	27.7 (27.6)	1628	1218	480	-
Me <sub>2</sub> Sn (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>2</sub>	Sal	Me <sub>2</sub> Sn (sal) <sub>2</sub>	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Light Yellow	126	33.9 (34.2)	1625	1215	476	-
Bu <sub>2</sub> Sn (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>2</sub>	Sal	Bu <sub>2</sub> Sn (sal) <sub>2</sub>	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Light Yellow	142	27.8 (27.6)	1628	1218	481	-
Me <sub>2</sub> Sn (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>2</sub>	Sal	Me <sub>2</sub> Sn (sal) <sub>2</sub>	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Light Yellow	126	33.9 (34.2)	1625	1215	476	-

The IR spectra of the complexes scanned in the 4000-200  $\text{cm}^{-1}$  region and have provided useful information for the formation of the complexes. The absence of bands at 3333  $\text{cm}^{-1}$  and 3180  $\text{cm}^{-1}$  due to simple hydrogen bonded OH group in case of acetylacetone and salicylaldehyde respectively has indicated deprotonation and is further affirmed by the separation of respective phenols during the course of the reactions. The sharp bands known to occur in 1600-1580  $\text{cm}^{-1}$  and 1370-1350  $\text{cm}^{-1}$  regions due to  $\nu_{\text{as}}(\text{C}=\text{O})$  and  $\nu_{\text{s}}(\text{C}=\text{O})$  stretching frequencies in the enolic form of acetylacetone and at 1660  $\text{cm}^{-1}$  in case of the free salicylaldehyde ligand have been found to move to lower wave numbers by 20-30  $\text{cm}^{-1}$  in the complexes suggesting thereby the coordination of carbonyl oxygen to tin metal. In addition, sharp bands observed at 1535-1530  $\text{cm}^{-1}$  and at 1200  $\text{cm}^{-1}$  in uncoordinated acetylacetone and salicylaldehyde respectively assignable to  $\nu(\text{C}=\text{C})$  mode have been found to move to higher wave numbers on complexation. The complete absence of important bands that could be attributed to the coordinated phenoxide anion has confirmed the formation of the complex by the substitution of phenoxide ligand by salicylaldehyde ligand in accordance with the reaction mentioned above. The coordination through oxygen of the ligand to tin has been further confirmed by the appearance of new bands in 490-460  $\text{cm}^{-1}$  region has been assigned to  $\nu(\text{Sn}-\text{O})$  mode<sup>15</sup>.

#### Reactions of diorganotin(IV) chloro phenoxides with benzohydroxamic acids

The reactivity of complexes of composition  $\text{R}_2\text{SnCl}(\text{OAr})$  (where R = n-Bu, and Me; OAr =  $\text{OC}_6\text{H}_4\text{Bu}^t\text{-2}$  and  $\text{OC}_6\text{H}_3\text{Bu}^t\text{-2-Me-4}$ ) has been studied towards potassium salts of hydroxamic acids with an aim to achieve the replacement of chloride ion by hydroxamate ion. These reactions may be represented as:



{Where R = n-Bu, Me; OAr =  $\text{OC}_6\text{H}_4\text{Bu}^t\text{-2}$ ,  $\text{OC}_6\text{H}_3\text{Bu}^t\text{-2-Me-4}$ ; X = Cl,  $\text{NO}_2$ }

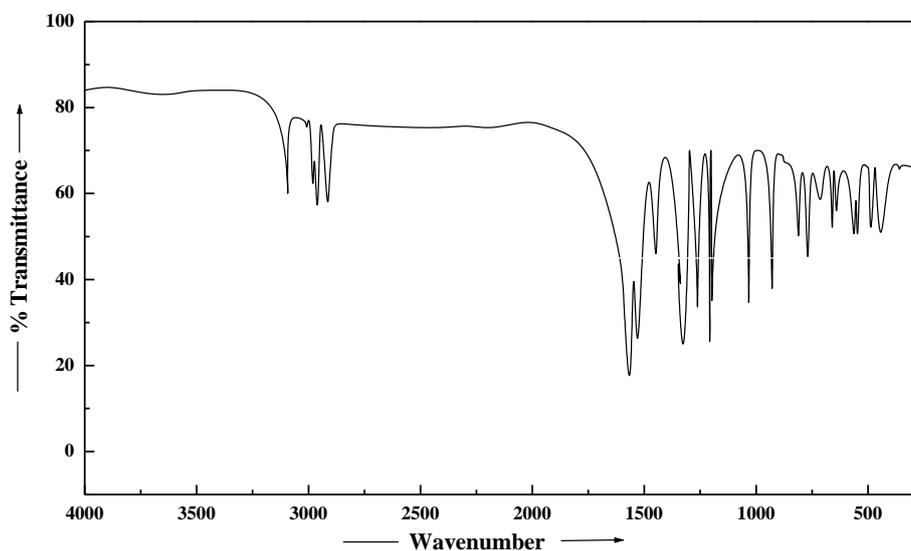
Surprisingly, formation of KCl was not observed in these reactions instead a quantitative amount of respective potassium salt of the respective phenols separated out. More interestingly, the potassium salt of *p*-nitro benzohydroxamic acid has been found to be more responsive than the *p*-chloro benzohydroxamic acid towards parent phenoxides, as apparent from the separation of white solid (identified as KOAr) during the stirring of reactants. Nevertheless, the separation of white solid resulted only after refluxing in case of reaction with potassium salt of *p*-chloro benzohydroxamic acid. The organotin(IV) hydroxamic acid complexes are moisture sensitive, sharp melting, non-electrolytic, mono-meric solids and are soluble in common organic solvents. The physico-chemical data and IR spectral data has been presented in Table 2.

IR spectra of the complexes scanned in the 4000-200  $\text{cm}^{-1}$  region and IR spectra of  $\text{Bu}_2\text{SnCl}(\text{O-NH-CO-C}_6\text{H}_4\text{-Cl})$  is given in Figure 1.

In the IR spectra, important ligation frequencies of the hydroxamate ion are due to  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}-\text{N})$ ,  $\nu(\text{N}-\text{O})$  and  $\nu(\text{N}-\text{H})$  modes undergo shifts on complexation. The absorption bands due to  $\nu(\text{C}=\text{O})$  vibration in potassium salts of *p*-chloro and *p*-nitro benzohydroxamic acids are known to occur at 1590 and 1600  $\text{cm}^{-1}$  respectively.

**Table 2.** Analytical and IR spectral data of reaction products of dibutyltin(IV) and dimethyltin(IV) phenoxides with benzohydroxamates

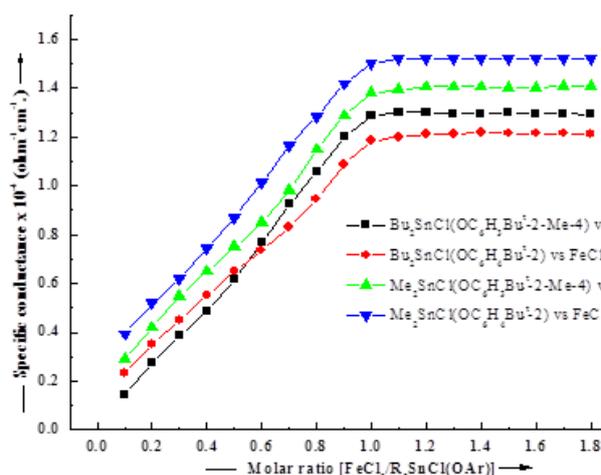
Parent Complexes	Ligand	Product	By Product	Colour	Elemental analysis % found (calc.)		Molar conductance in PhNO <sub>2</sub> (Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	IR bands (cm <sup>-1</sup> )					
					Sn	Cl		$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{O})$	$\nu(\text{N}-\text{H})$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{Cl})$
-	<i>p</i> -Clbenzohydroxamic acids	-	-	-	-	-	-	1590	1320	945-910	3250	-	-
Bu <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	<i>p</i> -Clbenzohydroxamic acids	Bu <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -Cl)	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Yellowish orange	27.3 (27.1)	7.8 (8.0)	0.87	1590	1382	1012	3251	470	360
Me <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	<i>p</i> -Clbenzohydroxamic acids	Me <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -Cl)	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Yellowish orange	33.3 (33.5)	9.8 (10.1)	0.43	1589	1395	996	3250	448	366
Bu <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	<i>p</i> -Clbenzohydroxamic acids	Bu <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -Cl)	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Yellowish orange	26.7 (26.5)	6.9 (7.1)	0.60	1590	1383	1014	3250	468	360
Me <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	<i>p</i> -Clbenzohydroxamic acids	Me <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -Cl)	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Yellow	32.5 (32.6)	9.9 (9.7)	0.75	1589	1395	995	3250	448	366
-	<i>p</i> -NO <sub>2</sub> benzohydroxamic acids	-	-	-	-	-	-	1600	1315	945-910	3250	-	-
Bu <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	<i>p</i> -NO <sub>2</sub> benzohydroxamic acids	Bu <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> )	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Yellowish orange	26.9 (27.1)	8.3 (8.0)	0.82	1601	1343	967		462	362
Me <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	<i>p</i> -NO <sub>2</sub> benzohydroxamic acids	Me <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> )	HOC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2	Yellowish orange	33.8 (33.5)	9.8 (10.1)	0.46	1600	1367	980		491	368
Bu <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	<i>p</i> -NO <sub>2</sub> benzohydroxamic acids	Bu <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> )	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Yellowish orange	26.2 (26.5)	6.9 (7.1)	0.58	1601	1341	963		460	362
Me <sub>2</sub> SnCl (OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	<i>p</i> -NO <sub>2</sub> benzohydroxamic acids	Me <sub>2</sub> SnCl (O-NH-CO-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> )	HOC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4	Yellow	32.5 (32.6)	9.5 (9.7)	0.71	1600	1365	980		490	366

**Figure 1.** IR Spectra of Me<sub>2</sub>Sn(acac)<sub>2</sub>

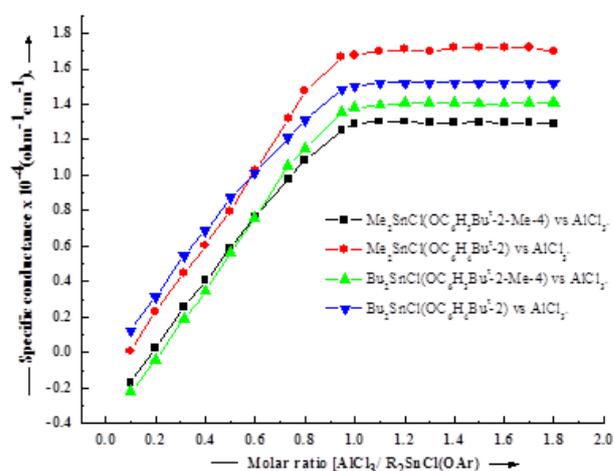
The occurrence of these bands at almost same wave numbers in the IR spectra of complexes studied herein has suggested the non-participation of carbonyl oxygen in coordination. The  $\nu(\text{C}-\text{N})$  mode which appears at 1320 and 1315 cm<sup>-1</sup> in case of respective potassium salts of *p*-chloro and *p*-nitro benzohydroxamic acids, has been found to shift to higher wave numbers (1395-1345 cm<sup>-1</sup>) upon complexation.

The absorption band due to  $\nu(\text{N-O})$ , known to occur in  $945\text{-}910\text{ cm}^{-1}$  region in potassium salts of *p*-chloro and *p*-nitro benzohydroxamic acids, appeared in  $1015\text{-}960\text{ cm}^{-1}$  region in organotin(IV) hydroxamates. These positive shifts in  $\nu(\text{C-N})$  and  $\nu(\text{N-O})$  modes are suggestive of coordination through hydroxylamine oxygen with tin metal, indicating bonding of the type N-O-Sn.

The separation of the KOAr during the course of these reactions supplemented the IR spectral observations. A strong and distinct band at  $\sim 3250\text{ cm}^{-1}$  due to  $\nu(\text{N-H})$  mode in potassium salts of benzohydroxamates has remained nearly unchanged in organotin(IV) derivatives except for a slight reduction in the intensity of this band, indicative of the fact that in present study hydroxamate ligand is coordinating as monodentate ligand. The appearance of new and important  $\nu(\text{Sn-O})$  mode in  $490\text{-}448\text{ cm}^{-1}$  region has further supported bonding through hydroxylamine oxygen<sup>15</sup>. The  $\nu(\text{Sn-O})$  mode depends on the precise environment of the  $\nu(\text{Sn-O})$  in the molecule. The  $\nu(\text{Sn-Cl})$  mode in these complexes has been observed at  $366\text{-}360\text{ cm}^{-1}$  region<sup>11</sup>.



**Figure 2.** Conductance composition curves of  $\text{Bu}_2\text{SnCl}(\text{OAr})$  and  $\text{Me}_2\text{SnCl}(\text{OAr})$  vs.  $\text{FeCl}_3$



**Figure 3.** Conductance composition curves of  $\text{Bu}_2\text{SnCl}(\text{OAr})$  and  $\text{Me}_2\text{SnCl}(\text{OAr})$  vs.  $\text{AlCl}_3$

### Reactions of diorganotin(IV)chlorophenoxides with Lewis acids ( $\text{FeCl}_3$ and $\text{AlCl}_3$ )

The reactivity of diorganotin(IV) phenoxides of composition  $\text{R}_2\text{SnCl}(\text{OAr})$  (where  $\text{R} = n\text{-Bu}$ , and  $\text{Me}$ ;  $\text{OAr} = \text{OC}_6\text{H}_4\text{Bu}^1\text{-2}$  and  $\text{OC}_6\text{H}_3\text{Bu}^1\text{-2-Me-4}$ ) towards Lewis acids such as  $\text{FeCl}_3$  and  $\text{AlCl}_3$  has been studied. The conductometric titrations between parent diorganotin(IV) chloro phenoxides and Lewis acids have been carried out in dry nitrobenzene at  $25 \pm 0.1^\circ\text{C}$ . The conductance values of parent diorganotin(IV) chloro phenoxides in nitrobenzene are very low. However, the addition of solutions of  $\text{FeCl}_3$  and  $\text{AlCl}_3$  in nitrobenzene results in a significant rise in the conductance of the parent organotin(IV) phenoxides. The conductance composition (acid/base) curves (Figure 2 and 3) have revealed sharp breaks at 1:1 molar ratios {Lewis acid/ $\text{R}_2\text{SnCl}(\text{OAr})$ }; suggesting thereby the possibility of formation of compounds with 1:1 stoichiometry (Table 3).

**Table 3.** Analytical data and principal IR bands of organotin(IV) chloro phenoxides and AlCl<sub>3</sub> and FeCl<sub>3</sub>

Parent Complex	Ligand	Reaction product	Colour	Elemental analysis % found (calc.)		Molar conductance in PhNO <sub>2</sub> (Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	IR data (cm <sup>-1</sup> ) FeCl <sub>4</sub> <sup>-</sup> /AlCl <sub>4</sub> <sup>-</sup>
				Sn	Cl		
Bu <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	FeCl <sub>3</sub>	Bu <sub>2</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sup>+</sup> . FeCl <sub>4</sub> <sup>-</sup>	Brownish yellow	20.2 (20.5)	24.7 (24.5)	12.1	377
Me <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	FeCl <sub>3</sub>	Me <sub>2</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sup>+</sup> . FeCl <sub>4</sub> <sup>-</sup>	Dark brown	21.2 (21.6)	26.0 (25.8)	11.2	379
Bu <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	FeCl <sub>3</sub>	Bu <sub>2</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sup>+</sup> . FeCl <sub>4</sub> <sup>-</sup>	Brown	23.9 (24.0)	28.4 (28.6)	13.0	381
Me <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	FeCl <sub>3</sub>	Me <sub>2</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sup>+</sup> . FeCl <sub>4</sub> <sup>-</sup>	Brownish yellow	25.5 (25.5)	30.1 (30.4)	10.4	383
Bu <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	AlCl <sub>3</sub>	Bu <sub>2</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sup>+</sup> . AlCl <sub>4</sub> <sup>-</sup>	Brown	19.7 (20.0)	23.9 (23.9)	11.7	482
Me <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	AlCl <sub>3</sub>	Me <sub>2</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sup>+</sup> . AlCl <sub>4</sub> <sup>-</sup>	Brownish yellow	20.8 (21.0)	24.8 (25.1)	12.9	486
Bu <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	AlCl <sub>3</sub>	Bu <sub>2</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sup>+</sup> . AlCl <sub>4</sub> <sup>-</sup>	Brown	23.4 (23.3)	27.8 (27.8)	10.6	480
Me <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	AlCl <sub>3</sub>	Me <sub>2</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sup>+</sup> . AlCl <sub>4</sub> <sup>-</sup>	Brown	24.7 (24.7)	29.6 (29.5)	12.5	485

The observed continuous increase in the conductance of the solutions may be ascribed to the formation of ions in solutions as:



{Where R = n-Bu, Me; OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4; M = Fe(III), Al(III)}

Substantiated from the conductance-composition curves, the compounds have actually been isolated in separate experiments by reacting the parent organotin(V) chloro phenoxides with FeCl<sub>3</sub> and AlCl<sub>3</sub> in predetermined 1:1 molar ratios in benzene. The elemental analyses of the isolated complexes supported their stoichiometric formulations as the compounds of composition {R<sub>2</sub>Sn(OAr)}<sup>+</sup>MCl<sub>4</sub><sup>-</sup>. The molar conductance values of milli-molar solutions of these complexes in dry nitrobenzene have been found to close to 1:1 electrolytes suggesting their electrolytic nature in nitrobenzene. The IR spectra of the compounds scanned in the 4000-200 cm<sup>-1</sup> have further substantiated their formation. Interestingly, the bands at ~360 cm<sup>-1</sup> due to ν(Sn-Cl) modes in parent phenoxides have been found to be missing in these compounds. The appearance of very sharp bands at 380 cm<sup>-1</sup> and ~485 cm<sup>-1</sup> may be assigned to ν(Fe-Cl) and ν(Al-Cl) modes respectively in tetrahedral anions in these complexes. It has thus been inferred that organotin(IV) chloro phenoxides behave as chloride ion donors in the presence of strong chloride ion acceptors resulting in the formation of stable ionic complexes of the type [R<sub>2</sub>Sn(OAr)]<sup>+</sup>FeCl<sub>4</sub><sup>-</sup> and [R<sub>2</sub>Sn(OAr)]<sup>+</sup>AlCl<sub>4</sub><sup>-</sup> in accordance with earlier reports<sup>25,26</sup>.

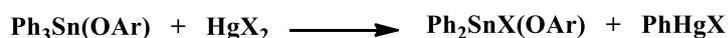
### Reactions of triphenyltin(IV) phenoxides with Hg(II) salts such as chloride, bromide and acetate

The reactivity of triphenyltin(IV) phenoxides of composition Ph<sub>3</sub>Sn(OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2) and Ph<sub>3</sub>Sn(OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4) with mercuric(II) salts such as chloride, bromide and acetate, has been attempted, in order to investigate, the nature of the ultimate reaction product formed. The products thus obtained have been evaluated for their stoichiometric formulations (Table 4).

**Table 4.** Analytical and IR data of reaction products of triphenyltin(IV) phenoxides with HgCl<sub>2</sub>/HgBr<sub>2</sub>/Hg(ac)<sub>2</sub>

Parent complex	Hg(II) Salts	Product	Color	Elemental Analysis % found (Calcd)			
				Sn	Cl	C	H
Ph <sub>3</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	HgCl <sub>2</sub>	Ph <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	White	26.2 (26.0)	7.6 (7.8)	57.9 (57.8)	4.8 (5.0)
		PhSn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>3</sub>	Shining white	18.2 (18.5)	-	67.5 (67.2)	6.7 (6.8)
Ph <sub>3</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	HgBr <sub>2</sub>	Ph <sub>2</sub> SnBr(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	White	23.7 (23.7)	-	52.8 (52.6)	4.3(4.6)
		PhSn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>3</sub>	Shining white	18.3 (18.5)	-	67.1 (67.2)	6.6 (6.8)
Ph <sub>3</sub> Sn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	Hg(ac) <sub>2</sub>	Ph <sub>2</sub> Sn(ac)(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2)	Off-White	24.5 (24.7)	-	60.1 (59.9)	5.2 (5.4)
		PhSn(OC <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> -2) <sub>3</sub>	Shining white	18.2 (18.5)	-	66.5 (67.2)	6.7 (6.8)
Ph <sub>3</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	HgCl <sub>2</sub>	Ph <sub>2</sub> SnCl(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	White	25.4 (25.2)	6.9 (7.2)	58.7 (58.5)	5.3 (5.3)
		PhSn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>3</sub>	Shining white	17.5 (17.4)	-	63.4 (63.1)	7.1 (7.3)
Ph <sub>3</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	HgBr <sub>2</sub>	Ph <sub>2</sub> SnBr(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	White	23.2 (23.1)	-	53.4 (53.5)	4.5 (4.8)
		PhSn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>3</sub>	Shining white	17.6 (17.4)	-	63.3 (63.1)	7.1 (7.3)
Ph <sub>3</sub> Sn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	Hg(ac) <sub>2</sub>	Ph <sub>2</sub> Sn(ac)(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4)	Off-White	24.2 (24.0)	-	60.4 (60.6)	5.5 (5.6)
		PhSn(OC <sub>6</sub> H <sub>3</sub> Bu <sup>t</sup> -2-Me-4) <sub>3</sub>	Shining white	17.6 (17.4)	-	63.3 (63.1)	7.1 (7.3)

The elemental analyses of the two isolated compounds from each reaction substantiated the compositions as Ph<sub>2</sub>SnX(OAr) (I) and PhSn(OAr)<sub>3</sub> (II) (X = Cl, Br, ac; OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2 and OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4). The following sequence of reactions may be suggested to account for the reactions products.



{Where OAr = OC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-2, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2-Me-4; X = Cl, Br, OCOCH<sub>3</sub>}

These reactions indicate an electrophilic substitution at carbon atom bonded to tin. The nucleophilic assistance either by chlorine or phenoxy groups cannot be ruled out. The isolated products are high melting (> 250 °C) solids. The IR spectra of the compounds scanned in

4000-200  $\text{cm}^{-1}$  region have shown the characteristic absorption bands due to phenoxide ion, tin-chlorine, tin-oxygen and tin-carbon modes. In case of compounds of composition  $\text{Ph}_2\text{Sn}(\text{ac})(\text{OAr})$ , the appearance of bands at  $\sim 1575 \text{ cm}^{-1}$  has been ascribed to the chelated  $\nu(\text{OCO})$  mode. It can be resolved from the present studies, that the reactions of triphenyltin(IV) phenoxides with mercuric(II) salts under present experimental conditions have led to the replacement of two phenyl groups only, thereby suggesting incomplete demetallation.

## Conclusion

The reactivity of organotin(IV) phenoxides has been illustrated in this report. The reactions with different ligands have signified polarity of different bonds. Reactions of parent complexes with chelating ligands like acetylacetone / salicylaldehyde and potassium salts of benzohydroxamic acids have demonstrated substitution of phenoxides ion from the parent complexes. In the reactions with Lewis acids, the organotin(IV) complexes have revealed chloride ion acceptor behaviour. In contrast, reactions of organotin(IV) phenoxides with Hg(II) salts have preferentially cleaved Sn-C bond. Such studies are required to elucidate the stability of different bonds of organotin(IV) phenoxides.

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