



Action of Metal and Organometallic Halides and Pseudohalides Towards Stannoxanes

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Interactions of HgX_2 ($X = Cl, Br, I, SCN, CN, NCO$), $SbCl_3$, $TeCl_4$ and $PhTeCl_3$ with $(p-FC_6H_4)_3Sn-O-Sn(p-FC_6H_4)_3$ at room temperature have been found to proceed with the simultaneous cleavage of Sn-O and Sn-C bonds, invariably yielding $(p-FC_6H_4)_2SnO$, $(p-FC_6H_4)_3SnX$ and the corresponding organo-mercury, -antimony and -tellurium derivatives. The course of the reactions suggests the instability of the Sn-O-M ($M = Hg, Sb, Te$) system.

Key Words: Stannoxane, Interactions metallic, Organometallic-halides and pseudohalides.

INTRODUCTION

In sharp contrast to well-documented reactions of metallic and organometallic halides with tetraorganotin and hexaorganoditins, those involving $R_3Sn-O-SnR_3$ compounds have been studied to a limited extent^{1,2}. Action of silicon, tin and phosphorus-halides on organotin oxides has been reported to produce organotin halides³ whereas reaction of vinyl-magnesium chloride with $(Bu_3Sn)_2O$ yielded tributylvinyltin⁴. Reactions of organometallic halides with diorganotin oxides have also been studied³. Datta *et al.*⁵ reported the action of mercuric halides on *bis*(triphenyltin) oxides in an attempt to isolate $R_3Sn-OHgCl$ compounds parallel to earlier reported reactions of AlX_3 ($X = Cl, Br$) with $R_3Si-O-SiR_3$, which produced stable and isolable $R_3SiOAlX_2$ compounds⁶. Interaction of $(R_3Sn)_2O$ with thionylchloride, $SOCl_2$ to give organotinhalides has also been investigated⁷⁻⁹. Despite such a variety of reactions of *bis*(triorganotin)oxide, reactions of the type of compounds $R_3Sn-O-SnR_3$ where R is *p*-fluorophenyl and other fully substituted phenyl compounds system towards heavier metal and organometal halides and pseudohalides have not been reported to date probably due to the fact that halophenyl substituted *bis*-(triorganotin) oxide *viz.* $[(p-FC_6H_4)_3Sn]_2O$ and $[(p-ClC_6H_4)_3Sn]_2O$ are not easily accessible.

Thus, the present work deals with an investigation into the reactivity of metallic and organometallic halides, namely HgX_2 ($X = Cl, CN, SCN$), $SbCl_3$, $SbCl_5$ and $TeCl_4$ towards Sn-O-Sn bond in *bis*(triorganotin) oxides, $(R_3Sn)_2O$ (where $R = p-FC_6H_4$).

The author's interest in the present investigation has been two fold (i) to examine the stability of Sn-O-Sn system under

the given set of conditions and (ii) to study the pattern and ease of cleavage of $\geq Sn-O-Sn \leq$ and Sn-C bonds in halo-substituted phenyl tin oxides. Consequently these reactions could be found useful to produce organotellurium and organoantimony compounds in moderate yields which otherwise are obtained by conventional longer routes and in some cases with difficulty, especially in case of bulkier cyclohexyl or α -naphthyl groups containing organometallic compounds.

EXPERIMENTAL

All the solvents were distilled before use. Inorganic metallic salts (Aldrich) were used without further purification IR data were recorded in solid state using KBR pellets, on FTIR spectrophotometer (Schimadzu 8201 PC Shimadzu-corporation Kyoto, Japan over the spectra range $4000-400\text{ cm}^{-1}$).

¹⁹F spectra were recorded on a Bruker spectrometer using CF_3COOH as references. The stoichiometry of compounds was established by elemental analysis on a semimicroscale using an elemental analyzer (elemental varioEL III, carloerba 1108, Milan Italy).

Reactions of few typical *bis*(triaryltin)oxides with metallic halides and pseudohalides are described below. Further details are given in Table-1.

Reaction of *bis*[tri(*p*-fluorophenyl)tin]oxide with mercuric cyanide: To a stirring solution of *bis*[tri(*p*-fluorophenyl)tin]-oxide (4.11 g 0.005 mol) in diethyl ether (30 mL) was added slowly to a suspension of mercuric cyanide (1.25 g 0.005 mol) in the same solvent (100 mL). The white precipitate thus obtained was refluxed with benzene for 12 h and filtered to leave a insoluble residue. m.p. > 300 °C.

TABLE-1
REACTIONS OF STANNOXANE [(*p*-FC₆H₄)₃Sn]₂O WITH METALLIC-HALIDES AND PSEUDOHALIDES (1:1)

Reactants/solvents (mL) [(<i>p</i> -FC ₆ H ₄) ₃ Sn] ₂ O (4.11 g, 0.005 mol)/(100mL) + metal/organometals moiety g (mol) ^a	Reaction products ^{b,c}
HgCl ₂ , 1.35 g (0.005 mol)/(30 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnCl, (<i>p</i> -FC ₆ H ₄)HgCl
HgBr ₂ , 1.80 g (0.005 mol)/(30 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnBr, (<i>p</i> -FC ₆ H ₄)HgBr
HgI ₂ , 2.27 g (0.005 mol)/(30 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnI, (<i>p</i> -FC ₆ H ₄)HgI
Hg(SCN) ₂ , 1.58 g (0.005 mol)/(100 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnNCS, (<i>p</i> -FC ₆ H ₄)HgNCS
Hg(NCO) ₂ , 1.42 g (0.005 mol)/(100 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnNCO, (<i>p</i> -FC ₆ H ₄)HgNCO
Hg(CN) ₂ , 1.25 g (0.005 mol)/(100 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnCN, (<i>p</i> -FC ₆ H ₄)HgCN
SbCl ₃ , 1.45 g (0.005 mol)/(100 mL)	(<i>p</i> -FC ₆ H ₄) ₂ SnCl ₂ , (<i>p</i> -FC ₆ H ₄) ₂ SbCl ₃
SbCl ₃ , 1.10 g (0.005 mol)/(100 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnCl, (<i>p</i> -FC ₆ H ₄) ₂ SbCl ₂
TeCl ₄ , 1.34 g (0.005 mol)/(100 mL)	(<i>p</i> -FC ₆ H ₄) ₃ SnCl, (<i>p</i> -FC ₆ H ₄)TeCl ₃

^aAll reactions were carried out in diethyl ether except for No. 9 which was carried out in toluene. ^b(*p*-FC₆H₄)₃SnO (m.p. > 300 °C) was obtained in all the reactants. ^cSatisfactory analysis for C, H and N was obtained for all the compounds.

TABLE-2
ANALYTICAL DATA AND ELEMENTAL ANALYSIS OF METAL AND ORGANOMETAL-HALIDES/-PSEUDOHALIDES WITH BIS(TRIORGANOTIN)OXIDES

Compound	m.f.	m.w.	m.p. (°C)	Yield (%)	Elemental analysis (%) found (calcd.)		
					C	H	N
(<i>p</i> -FC ₆ H ₄) ₂ SnO	C ₁₂ H ₈ F ₂ OSn	324.9	>300	68	44.23(44.36)	2.23(2.48)	–
(<i>p</i> -FC ₆ H ₄) ₃ SnCl	C ₁₈ H ₁₂ F ₃ SnCl	439.45	115	45	49.89(49.20)	2.01(2.75)	–
(<i>p</i> -FC ₆ H ₄)HgCl	C ₆ H ₄ FHgCl	331.14	224	75	21.01(21.76)	1.98(1.22)	–
(<i>p</i> -FC ₆ H ₄) ₃ SnBr	C ₁₈ H ₁₂ F ₃ SnBr	483.9	145	46	44.90(44.68)	2.02(2.50)	–
(<i>p</i> -FC ₆ H ₄)HgBr	C ₆ H ₄ FHgBr	375.59	236	70	19.89(19.19)	1.87(1.07)	–
(<i>p</i> -FC ₆ H ₄) ₃ SnNCS	C ₁₉ H ₁₂ F ₃ SnNS	462.08	256	58	49.85(49.39)	2.03(2.62)	3.68(3.03)
(<i>p</i> -FC ₆ H ₄)HgNCS	C ₇ H ₄ FHgNS	353.77	178	78	23.32(23.77)	1.56(1.14)	3.56(3.96)
(<i>p</i> -FC ₆ H ₄) ₂ SbCl ₃	C ₁₂ H ₈ F ₂ SbCl ₃	418.31	156	56	34.04(34.46)	1.34(1.93)	–
(<i>p</i> -FC ₆ H ₄) ₃ SnCN	C ₁₉ H ₁₂ F ₃ SnN	430.01	150	35	53.01(53.07)	2.12(2.81)	3.78(3.26)
(<i>p</i> -FC ₆ H ₄) ₂ SbCl ₂	C ₆ H ₄ Cl ₂ FSb	287.71	118	59	25.90(25.01)	1.34(1.40)	–
(<i>p</i> -FC ₆ H ₄) ₂ SnCl ₂	C ₁₂ H ₈ Cl ₂ F ₂ Sn	379.08	125	68	37.01(37.95)	2.10(2.12)	–

Identified as di(*p*-fluorophenyl)tin oxide: The benzene and ether solution on work up as discussed above yield *p*-fluorophenyl mercuric cyanide, yield: 46 %, m.p. 190 °C. Tri(*p*-fluorophenyl)tin cyanide, yield: 35 %, m.p. 150 °C.

Reaction of bis[tri(*p*-fluorophenyl)tin]oxide with antimony trichloride: To a stirring solution of bis[tri(*p*-fluorophenyl)tin]oxide (4.11 g, 0.005 mol) in 100 mL solvent ether was slowly added a solution of SbCl₃ (1.10 g, 0.005 mol) in the same solvent. A white solid appeared instantly. The reactants were stirred for 6 h in the same solvent under anhydrous oxygen free conditions and the filtered hot. The white solid obtained was identified as polymeric di(*p*-fluorophenyl)tin oxide. Yield: 67 %, m.p. > 300 °C.

The filtrate was completely evaporated to give a viscous solid. It was then treated with pet. ether/hexane mixture (50 mL) concentrated and then cooled on fractional crystallisation the following compounds were formed and isolated.

p-Fluorophenylantimony dichloride: Yield: 59 %, m.p. 118 °C, tri(*p*-fluorophenyl)tin chloride, Yield: 45 %, m.p. 115 °C.

Reaction of bis[tri(*p*-fluorophenyl)tin] oxide with antimony pentachloride: Antimonypentachloride (1.45 g 0.005 mol) in solvent ether (100 mL) was added slowly to a stirring solution of bis[tri(*p*-fluorophenyl)tin] oxide (0.82 g, 1 mmol) in ether (30 mL). A white solid appeared immediately. The contents were stirred for 2 h at reflux temperature and then filtered hot. The white residue was characterised as polymeric di(*p*-fluorophenyl)tin oxide. Yield: 62 %, m.p. > 300 °C.

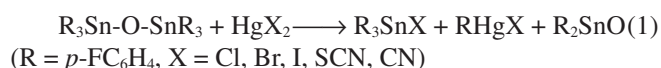
The filtrate was completely evaporated to give a viscous solid. It was then treated with pet. ether/hexane mixture 50 mL concentrated and then cooled on fractional crystallization yielded di(*p*-fluorophenyl) antimonytrichloride. Yield: 56 %, m.p. 156 °C and di(*p*-fluorophenyl)tin dichloride, yield: 68 %, m.p. 125 °C.

Reaction of bis[tri(*p*-fluorophenyl)tin]oxide with tellurium tetrachloride: To stirring solution of bis[tri(*p*-fluorophenyl)tin]oxide (0.3 g, 1 mmol) in diethylether was added slowly tellurium tetrachloride (0.27 g, 1 mmol) in the same solvent. A white precipitate appeared immediately. The mixture was stirred for 2 h and then filtered. The residue was digested with benzene for 10 h in a soxhlet extractor to leave off white residue which was identified as di(*p*-fluorophenyl)tin oxide. m.p. > 300 °C, yield: 68.5 %.

The benzene extract on evaporation yielded tri(*p*-fluorophenyl)tin chloride. m.p. 115 °C, yield: 45 %.

RESULTS AND DISCUSSION

Action of mercuric salts on (*p*-FC₆H₄)₃Sn-O-Sn(*p*-FC₆H₄)₃: The interaction of equimolar amount of mercuric halides and pseudohalides HgX₂ (X = Cl, Br, I, SCN, CN) with (*p*-FC₆H₄)₃Sn-O-Sn(*p*-FC₆H₄)₃ in diethyl ether at room temperature resulted in the formation of diparafluorophenyl oxides and the corresponding organotin and mercuric-halides or -pseudohalides. In each case polymeric diorganotin oxide as a white precipitate appeared immediately as shown in eqn. 1



The reaction of mercuric halides and pseudohalides with *bis*(triaryltin) oxide (aryl = *p*-FC₆H₄) also proceeded in the same fashion, yielded aryl mercuric halides, triaryltin halides and diaryltin oxide.

Action of antimony halides on *bis*(triorganotin) oxides:

Metallic halides *viz.*, antimonypentachloride has been used to cleave metal-carbon bonds to varying extent and in the process itself get arylated to give Ar₂SbCl₃ or ArSbCl₂, respectively SbCl₅ readily cleave two aryl groups from tetraaryltin even at room temperature. On the other hand SbCl₃ being mild electrophile is arylated to give ArSbCl₂ under ordinary condition although complete arylation of Sb has also been reported^{1,2,10}.

It is therefore, not surprising that the reaction of antimony pentachloride with (R₃Sn)₂O proceeded not only with the specific cleavage of $\text{>Sn-O-Sn<} \rightleftharpoons$ bond but also with the removal of organic group from the tin atom takes place simultaneously (eqn. 2)



where R = *p*-FC₆H₄.

Similarly the reaction of SbCl₃ with *bis*(triaryltin)oxide yielded RSbCl₂, R₂SnO and R₃SnCl (eqn. 3)



where R = *p*-FC₆H₄.

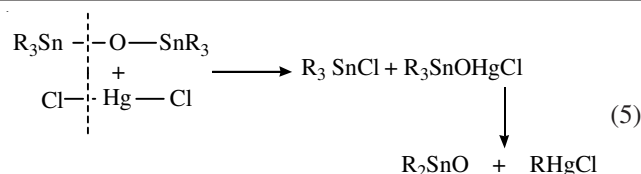
Action of tellurium tetrachloride with *bis*(triorganotin) oxides: Both tin-oxygen and tin-carbon bonds in *bis*(tri *p*-fluorophenyltin) oxide were found to be prone to attack by TeCl₄. Cleavage of tin-carbon bond from R_nSnR'_{4-n} compounds employing TeCl₄ is well established and has been used as convenient method for the preparation of organotellurium compounds in high yield and high purity^{11,12}. The reactions of *bis*(tri *p*-fluorophenyltin) oxide with TeCl₄ was conducted at room temperature and in refluxing toluene, respectively, with the immediate formation of white solid, R₂SnO, in both cases (eqn. 4):



where R = *p*-FC₆H₄.

The separation of organotin halides from organotellurium compounds does not pose much difficulty due to a significant difference in solubilities. Organotin chlorides are highly soluble in organic solvents, whereas organotellurium halides are insoluble at room temperature.

As has been reported earlier for the reactions of *bis*(tri *p*-fluorophenyltin) oxides with mercuric halides, the reactions of mercuric cyanide, proceeded in the same fashion. The intermediate R₃Sn-O-Hg- is unstable, rearranges and split itself to give diorganotin oxide and the corresponding organomercuric compounds as shown below (eqn. 5).



The mechanism of the reaction with tellurium and antimony derivatives may or may not be the same but on the basis of the nature of products obtained, it is most reasonable to assume that the reactions proceeded in the same manner as that of mercuric salts⁵.

Conclusion

Apart from an insight into the relative ease of cleavage of Sn-O and Sn-C bonds, these reaction are useful to afford organometallic derivatives of Hg, Sb, Sn and Te in excellent yield and excellent purity in a simple step process.

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