SUMMARY

The present investigation carried out on organotin compounds, is divided into five parts:

Part-I

Part-I of this dissertation describes the nature of bonding and other related properties required to explain the chemical properties of organotin compounds in a general way. Specific classes of organotin compounds, related to the present investigation, have been reviewed in appropriate parts of this investigation.

Part-II

Part-II deals with the reaction of bis(triorganotin) oxides with some anhydrous covalent metal halides. The bis(triorganotin) oxides used in this investigation include bis(tripropyltin) oxide, bis(tribenzyltin) oxide and bis(triphenyltin) oxide, while the covalent halides include mercuric halides, zinc chloride, cadmium iodide and aluminium chloride. The bis(triphenyltin) oxide system has been studied in detail. All the bis(triorganotin) oxides react quite readily with the metal halides at room temperature, zinc chloride and aluminium chloride react with bis(triphenyltin) oxide to produce triphenyl tin chloride, zinc oxide and triphenyl tin chloride,

aluminium oxychloride respectively. These reactions are similar to the reactions of disiloxanes, $(R_3Si)_2O$ with the covalent metal halides. Cadmium iodide reacts with bis(triphenyltin) oxide in a different manner. The reaction products are polymeric diphenyl tin oxide, benzene, tetraphenyltin and cadmium iodide remains unchanged. The reaction proceeds even with small amounts of cadmium iodide. Cadmium iodide apparently acts as a catalyst without taking part in the overall reaction.

The action of mercuric halides on bis(triphenyltin) oxide offers a new and simple method of preparation of phenyl mercuric halides. In addition to phenyl mercuric halides, the other products isolated from the reaction include triphenyltin halides, polymeric diphenyl tin oxide and tetraphenyl tin. The action of mercuric chloride on bis(tripropyltin) oxide and bis(tribenzyltin) oxide have also been studied. In these cases also organo mercuric chlorides i.e. propyl mercuric chloride and benzyl mercuric chloride have been isolated. The reaction between bis(tripropyltin) oxide and mercuric chloride yields propyl mercuric chloride, tripropyl tin chloride and polymeric dipropyl tin oxide as observed in the case of corresponding phenyl derivative of tin but the action of mercuric chloride on bis(tribenzyltin) oxide proceeds in a different way. In this case a new compound tetrabenzyl 1-chloro 3-hydroxy distannoxane $ClBz_2SnOSnBz_2OH$ has been isolated in addition to benzyl mercuric chloride.

The action of mercuric oxide on triphenyl tin chloride yielded phenyl mercuric chloride and polymeric diphenyltin oxide where as the action of mercuric oxide on tribenzyltin chloride afforded benzyl mercuric chloride and tetrabenzyl 1-Chloro 3-hydroxy distannoxane. The products are thus identical with the products of the reaction of mercuric chloride with the appropriate bis(triorganotin) oxide.

The reactions of bis(triphenyltin) sulphide with aluminium chloride, zinc chloride, mercuric chloride and cadmium iodide have also been investigated to see whether or not the bis(triphenyltin) sulphide behaves similar to that of the bis(triphenyltin) oxide. In this case no arylation takes place and all the four metal halides investigated react in the same way. They yield corresponding triphenyltin halide and metal sulphide .

The reaction between the sodium salt of triphenyltin hydroxide and mercuric chloride has also been described in this part. Although $(Ph_3SnO)_2Hg$ or $Ph_3SnOHgPh$ would be the expected products of the reaction in view of the products obtained by MacDiarmid et al[a] from the reaction of sodium salt of triphenylsilyl hydroxide,

---

(a) A.K.Ghosh, C.E.Hansing, A.I.Stutz and A.G.MacDiarmid-J.Chem. Soc. 403 (1962).

(Ph_3SiONa) with mercuric chloride, no such products could be isolated. Instead diphenyl mercury and polymeric diphenyl tin oxide were isolated as major products. Varying amounts of triphenyl tin chloride, tetraphenyl tin and phenyl mercuric chloride have also been isolated from the reaction.

Possible mechanisms for the different reactions have also been discussed.

Part-III

Part-III describes the interaction between different organotin oxinates with mercuric halides and subsequent isolation of three new halotin oxinates viz. phenyl chloro tin dioxinate, $PhSn(Ox)_2Cl$; phenyl bromo tin dioxinate, $PhSn(Ox)_2Br$; phenyl iodo tin dioxinate, $PhSn(Ox)_2I$.

Since some organotin oxinates contain the Sn-O-moiety similar to bis(triorganotin) oxide, $R_3Sn\text{-}O\text{-}SnR_3$, it is expected that the action of mercuric halides on these compounds should proceed in a similar way as observed in the previous part. Results of the investigation have amply fullfilled this expectation. The organotin oxinates studied are penta-coordinated triphenyl tin oxinate, $Ph_3Sn(Ox)$, diphenyl chloro tin oxinate, $Ph_2Sn(Ox)Cl$ and hexa coordinated, diphenyl tindioxinate,

Ph_2SnOx_2. The action of mercuric halides on the penta-coordinated complex have been observed to occur readily at room temperature where as the hexa coordinated complex reacts with mercuric halides only when refluxed in ether or benzene.

From the reaction of triphenyl tin oxinate and mercuric chloride, triphenyl tin chloride, phenyl mercuric chloride and a compound phenyl chloro tin dioxinate, $PhSn(Ox)_2Cl$ have been isolated. Similarly the action of mercuric bromide and mercuric iodide on triphenyl tin oxinate produce two other compounds analogous to phenyl chloro tin oxinate, vis. phenyl bromo tin dioxinate, $PhSn(Ox)_2Br$ and phenyl iodo tin dioxinate, $PhSn(Ox)_2I$ together with triphenyl tin halides and phenyl mercuric halides.

The actions of mercuric halides on diphenyl tin dioxinate are rather simple and furnish phenyl mercuric halides and phenyl halo tin dioxinates, $PhSn(Ox)_2X$.

Mercuric chloride reacts with diphenyl chloro tin oxinate yielding the products dichloro tin dioxinate, $Sn(Ox)_2Cl_2$ together with phenyl mercuric chloride and diphenyl tin dichloride.

Tentative mechanisms of the above reactions have also been suggested.

Part-IV

Part-IV deals with spectro-photometric investigation on the solvolysis of triphenyl tin oxinate in methanol. While Roncucci et al[b] suggested a non-chelated four coordinated structure for this compound because of the close similarity of its electronic spectra in aqueous ethanol with that of oxine in the same solvent, a penta-coordinated chelated structure has been preferred by Okawara et al[c] on the basis of the similarity of the absorption spectra of triphenyl tin oxinate with that of the other metal oxinates in cyclohexane. Although the apparent contradiction has been attributed to the possible hydrolysis of triphenyl tin oxinate by Okawara et al[c], no detailed investigation was carried on this system so far. The present investigation carried in pure methanol and methanol-benzene mixtures not only confirms the solvolysis, but also affords evidence for the formation of an intermediate, $Ph_3SnOx.MeOH$. The results of this investigation can be quantitatively accounted for by the following simultaneous equilibria:

$$Ph_3SnOx + MeOH \xrightleftharpoons{K_1} Ph_3SnOx.MeOH \xrightleftharpoons{K_2} Ph_3SnOMe$$

The equilibrium constants K_1 and K_2 have also been determined.

(b) L.Roncucci, G.Faraglia and R.Barbieri- J.Organometal. Chem 1, 427 (1964).

(c) M.Wada, K.Kawakami and R.Okawara-J.Organometal.Chem. 4, 159 (1965).

Part-V

Part-V describes the action of triphenyl tin chloride on sodium-tetraphenyl ethylene adduct. The reaction has been carried out with a view to observe whether triphenyl tin (Ph_3Sn -) substituted reduced olefin could be prepared. Very small amount of tetraphenyl ethane, possibly due to hydrolysis of sodium-tetraphenyl ethylene adduct by moisture which could not be rigorously avoided in the present investigation, has, however been formed; and the reaction follows a different course to produce hexaphenyl di-tin, tetraphenyl tin, a diphenyl tin polymer. Major portion of the tetraphenyl ethylene has been recovered as such.

Probable mechanism for the formation of the above products has been suggested.