# S U M M A R Y

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

Part-I

Part-I of this dissertation describes the nature of bonding and other related properties required to explain chemical behaviours 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 triorganotin carboxylates with mercuric halides, mercuric acetate, phenylmercuric acetate and cadmium iodide. The following triorganotin carboxylates have been used viz., triphenyltin formate, triphenyltin acetate, triphenyltin propionate, tribenzyltin acetate, tripropyltin acetate, tributyltin acetate and tricyclohexyltin acetate. All the reactions have been carried out at room temperature .

The action of mercuric halides on triphenyltin carboxylates offers an efficient method of preparation of phenylmercuric halides. In addition to phenylmercuric halides, the other products isolated are triphenyltin halides and organotin polymeric compounds. Three distinct types of organotin polymeric products are obtained during

these reactions. They include the following types viz., $[PhSn(OH)_2OCOR]_n$, $[PhSn(O)OH]_n$ and $[Sn(OH)_4]_n$ containing few phenyl/carboxylate/halogen groups occupying the terminal positions of the large molecule. In order to get an idea about the chain length some oxine derivatives (oxine = 8-hydroxy quinoline) of the polymers have also been prepared. Thus the polymer $Sn(OH)_4$ on treatment with oxine produces $PhSn(Cl)Ox_2$ and $(OH)_6Sn_2Ox_2$ as new oxinate. From the stoichiometry of the reaction products it has been observed that this polymer probably contain a chlorine atom in every fifth tin atom of the molecule. $[PhSn(OH)_2OCOR]_n$ type usually produces triphenyltin oxinate, $PhSnOx_3$. It is interesting to note that $[PhSn(OH)_2OCOH]_n$ decomposes either thermally or during long storage to polymeric $PhSn(O)OH$ .

The reactions of mercuric chloride with tripropyl and tributyltin acetate are comparatively slow, but produce respective alkylmercuric chloride, trialkyltin chloride and polymeric $[RSn(OH)_2OCOCH_3]_n$ (R = Pr, Bu) as observed in most of the reactions of phenyl derivatives. Tricyclohexyltin acetate, on the other hand, does not practically react with mercuric chloride in the same condition. The results of these experiments suggest the following sequence of migration of different organic groups from tin atom to mercury atom:

$$Ph \rangle Pr \approx Bu \rangle\rangle\rangle \text{ cyclohexyl}$$

Diphenyltin diacetate reacts with mercuric bromide to produce phenylmercuric bromide and polymeric $[PhSn(OH)_2OOCCH_3]_n$. The polymer $[PhSn(OH)_2OOCCH_3]_n$ reacts with mercuric chloride only when the reactants are refluxed in benzene to produce phenylmercuric chloride and polymeric $[Sn(OH)_4]_n$ containing a few phenyl/acetate/chlorine groups.

Reactions of mercuric acetate and phenylmercuric acetate with triphenyltin acetate are rather interesting. In the former case mercury is completely arylated to produce diphenyl mercury. In both of these reactions diphenyl mercury and polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$ are the products. By these reactions diphenylmercury may be prepared quite easily in quantitative yield. With oxine, the polymer $[PhSn(O)OAc]_n$ produces a new carboxylate oxinate, phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$. Tribenzyltin acetate reacts with mercuric acetate in a different way producing benzylmercuric acetate and a new 1,3 substituted distannoxane derivative viz., $BzOAc(OH)SnO(OH)OAcBz$.

Reactions of tripropyl, tributyl and tricyclohexyltin acetate with mercuric acetate have also been studied. In all of the cases practically no reactions take place in ordinary conditions.

On the basis of these results the following sequence of the ease with which organic groups migrate from tin atom to mercury atom may be suggested:

$$Ph \rangle Bz \rangle\rangle\rangle Pr \approx Bu \approx \text{cyclohexyl}$$

The action of cadmium iodide on triphenyltin formate and acetate yields tetraphenyltin and poly stannoxane of the type $Ph_2SnO$ 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.

Possible mechanisms for the different reactions have also been discussed.

Part-III

Part-III describes the interaction between hexaorgano distannoxane, $(R_3Sn)_2O$ (Where R = Ph, Bz, Pr, Bu) with mercuric acetate. Reactions of bis(triphenyltin) sulphide, $(Ph_3Sn)_2S$ with mercuric acetate and $Ph_2SnO$ with phenylmercuric acetate have also been included. These reactions have usually been carried out at ordinary temperature excepting for the reaction of $Ph_2SnO$ with PhHgOAc.

Hexaphenyldistannoxane, when it reacts with mercuric acetate in 1:1 molar proportion, triphenyltin acetate, diphenylmercury and polymeric phenylstannoic acetate are the products. Whereas two equivalent of mercuric acetate produces only diphenylmercury and polymeric phenyl stannoic acetate.

The reactions of hexa propyl and butyl distannoxane and bis (triphenyltin) sulphide with mercuric acetate produce the corresponding triorganotin carboxylate and mercuric oxide/mercuric sulphide. These quick and clearcut reactions may successfully be

utilised for the preparation of triorganotin carboxylates.

Hexa benzyl distannoxane, on the other hand, behaves quite differently towards mercuric acetate. In this case benzyl mercuric acetate and a substituted distannoxane viz., 1,3 dibenzyl 1,1,3,3 tetraacetoxy distannoxane, $Bz(OAc)_2SnOSn(OAc)_2Bz$ are produced.

Action of phenylmercuric acetate on $Ph_2SnO$ in refluxing benzene produces diphenyl mercury and polymeric phenyl stannoic acetate. No reaction does take place at ordinary temperature.

Tentative mechanism of the above reactions have also been proposed.

Part-IV

Part-IV deals with the preparation of some organotin complexes. Seven new oxinate complexes have been prepared. These include phenyltin acetate dioxinate; $PhSn(OCOCH_3)Ox_2$, phenyltin propionate dioxinate; $PhSn(OCOCH_2CH_3)Ox_2$, phenyltin monochloroacetate dioxinate; $PhSn(OCOCH_2Cl)Ox_2$ phenyltintrifluoroacetate dioxinate; $PhSn(OCOCF_3)Ox_2$, diacetate tin dioxinate; $(CH_3OCO)_2SnOx_2$, dipropionate tin dioxinate; $(CH_3CH_2OCO)_2SnOx_2$ and bis monochloroacetate tin dioxinate; $(ClCH_2OCO)_2SnOx_2$. Except for phenyltin trifluoroacetate dioxinate, $PhSn(OCOCF_3)Ox_2$ all the oxinate complexes are prepared by the reaction of phenyltin chlorodioxinate, $PhSn(Cl)Ox_2$/ dichlorotin dioxinate, $Cl_2SnOx_2$ with the corresponding silver salt of carboxylic acid. $PhSn(OCOCF_3)Ox_2$ and also $PhSn(OCOCH_3)Ox_2$ are prepared very conveniently by dearylating $Ph_2SnOx_2$ with the corres-

ponding phenyl mercuric carboxylate.

Attempts have been made to prepare another carboxylate oxinate viz., $Ph_2Sn(OAc)Ox_2$ by the reaction of $Ph_2Sn(Cl)Ox_2$ with KOAc. Instead of the formation of $Ph_2SnOAcOx_2$, this reaction produces $Ph_2SnOx_2$ and $Ph_2SnO$. The formation of these products have been explained by assuming the redistribution of the intermediate product $Ph_2Sn(OAc)Ox_2$.

Reactions of triphenyltin oxinate with mercuric acetate and phenylmercuric acetate produce phenyltin acetate dioxinate, polymeric phenylstannoic acetate and diphenyl mercury. The later reaction always proceeds in 1:2 molar proportions.

It is interesting to note that reaction of diphenyltin chlorooxinate, $Ph_2Sn(Cl)Ox$ with phenylmercuric acetate not only produces diphenyl mercury but also phenyl mercuric chloride. The other products are phenyltinacetate dioxinate and polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$ .

Dearylation of triphenyltin salicylaldehyde with mercuric chloride produces triphenyltin chloride, phenyl mercuric chloride and an organotin polymer; approximately $[Sn(OH)_4]_n$ containing a few chlorine/salicylaldehyde/phenyl groups. Tentative mechanisms for these reactions have also been suggested.

Triphenyltin hydroxide react with alizarin to produce a new complex compound together with other products. Quinalizarin, on the other hand, produces a new polymeric organotin complex along with

benzene. However, more detailed investigation is necessary to fina
establish these reactions.