STUDIES ON THE MIGRATION OF ORGANIC GROUPS FROM ORGANOTIN COMPOUNDS CONTAINING TIN-OXYGEN LINKAGES

On Preparation and Properties of Some Organotin Carboxylates, Stannoxanes and Related Organotin Compounds.

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SUMMARY

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, Ph_3SnOx_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:

$$Ph > Pr \geq Bu \ggg \text{cyclohexyl}$$

Diphenyltin diacetate reacts with mercuric bromide to produce phenylmercuric bromide and polymeric $[PhSn(OH)_2OCOCH_3]_n$. The polymer $[PhSn(OH)_2OCOCH_3]_n$ 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:

$$\mathrm{Ph} > \mathrm{Bz} \ggg \mathrm{Pr} \simeq \mathrm{Bu} \simeq \text{cyclohexyl}$$

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 corresponding 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.

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EXPERIMENTAL

PART - I

A SHORT REVIEW ON THE NATURE OF BONDING AND OTHER RELATED PROPERTIES OF ORGANOTIN COMPOUNDS.

1.A. Introduction:

Organotin compounds are substances in which at least one tin-carbon bond is present. The first chemist to report an organotin compound seems to have been E.Frankland (1,2). But his work appears to have remained unknown to most of his contemporaries as well as to later authors. The work of C.Lowig (3) in 1852 has usually been considered to represent the beginning of organotin chemistry. Apart from the compounds described by Lowig , many significant contributions were made in this field during the next few decades. By studying the alkyl derivatives of group IVA metals, the accurate atomic weights of these elements were determined. A comparison of the organometallic derivatives of silicon, tin and lead formed part of the basis of Mendeleeff's famous prediction of new element, eka- silicon (germanium). The discovery of industrial applications of organotin compounds e.g. as stabilisers of polyvinyl chloride plastics, as rubber antioxidants, Ziegler type catalysts in the polymerisation of olefins, agricultural fungicides, as active ingredients in certain veterinary medicians (4) and an increased general interest have produced a striking renaissance of organotin chemistry starting about 1949 and continuing to the present day.

1.B. Bonding in organotin compounds:

Before going to describe the organotin compounds in detail, it would be useful to discuss briefly the nature of bonding in these compounds.

Tin is a member of group IVA of periodic table. The fifty electrons of the tin atom are arranged as follows: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$, the ground state of which is a $3P$ state derived from s^2p^2 configuration (5). The common tetra-covalent state is derived from the sp^3 hybridisation by promoting one of the paired s electrons to the next higher p level. The tetra-covalent state occours much more frequently than divalent state and a great number of organotin compounds contain tetra valent tin atom. The stable nature and relative low reactivity of the organo derivatives of group IVA metals may be attributed to the sp^3 hybridisation they possess. Thus, tetramethyltin is unreactive towards air and water but trimethylindium and trimethylantimony have a strong affinity towards those reagents. The marked increase in stabilities of R_4Sn compounds over R_2Sn types also demonstrate the effect of increased hybridisation.

1.C. Catenation properties of tin in organotin compounds:

Some excellent reviews on tin-tin compounds are made by various authors in recent years (31-35).

The ditin compounds may be prepared by a number of routes (33), the alkyl derivatives are generally liquid whereas aryl compounds tend to be solid at room temperature. A good number of compounds with chain length varying from 2-6 have been described (33).

Reactions of Me_2SnCl_2 with sodium in liquid ammonia produces linear molecules $\left[Me_2Sn \right]_n$ with chain length n = 12-20 and may be more, as well as at least one cyclic compound, $\left[Me_2Sn \right]_6$. There is no evidence for branching in chains in these compounds (78). Williamsens and Van der Kerk (36,37) have reported the formation of a branched chain compound, $(Ph_3Sn)_4Sn$ by the reaction of Ph_3SnLi with $SnCl_4$. Many a coloured products reported in the synthesis of dialkyltin compounds is due to the partially branched tin chains (38). N.M.R studies indicate the formation of polytin hydrides during the thermal decomposition of butyltin trihydride (33).

Carboxylate and halide derivatives of di and polytin compounds have also been reported (39,40).

Comparison of catenation properties among group IVA elements have shown that there is a decrease in the tendency to catenation in the order $C \ggg Si > Ge \approx Sn \ggg Pb$. This general, if not smooth, decrease in the tendency to catenation may be ascribed to diminished strength of the C-C, Si-Si, Ge-Ge, Sn-Sn and Pb-Pb bonds, which are approximately 83, 42, 40 and 37 K.Cal/mole for C-C, Si-Si, Ge-Ge and Sn-Sn bonds respectively (6).

1.D. The ionic nature of organotin compounds and the effect of bond polarity upon reactions:

The general feature that the electropositivity character increases with atomic number in a group, is also strikingly pronounced among the metals of group IVA. Some properties of the elements are given in table -I (6).

Table -I

Element	Electronic structure	Ionisation potentials in e.v.		Electro-negativities(a)	Covalent Radius(b) in ^{o}A
		First	Second		
C	$[He]2s^{2}2p^{2}$	11.3	24.4	2.50	0.77
Si	$[Ne]3s^{2}3p^{2}$	8.1	16.3	1.74	1.17
Ge	$[Ar]3d^{10}4s^{2}4p^{2}$	7.9	15.9	2.02	1.22
Sn	$[Kr]4d^{10}5s^{2}5p^{2}$	7.3	14.6	1.72	1.40
Pb	$[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$	7.4	15.0	1.55	1.54

a- According to Allred and Rochow; b- tetrahedral i.e. sp^{3} radii.

As evidenced from table-1, as because there is a considerable difference in electronegativities between carbon and other elements of group IVA, the metal-carbon bonds should be expected to be quite polar. In fact, Pauling (9) has calculated ionic character of C-Si and C-Sn bonds to be 12% and 15% respectively. Use of Allred and

Rochow's electronegativity values would make these values 14.2% and 14.6% almost identical. Since the electronegativity of carbon varies with the nature and number of attached atoms and groups, the ionic character of tin-carbon bond will also vary.

The physical as well as chemical properties of the compounds depend on the bond polarity. In general, bond partners that carry an appreciable difference of electrical charge relative to each other will serve as an electric dipole that attracts and orients neighbouring reagents. Since tin is positive with respect to carbon, the relative polarity of the C-Sn bond may be formally represented as

$$\overset{\delta-}{C} — \overset{\delta+}{Sn}$$

Therefore, when an organotin compound is exposed to water, the H-O dipole, as expected, would be attracted to C-Sn dipole and would orient in the appropriate direction.

$$\overset{\delta-}{C} - \overset{\delta+}{Sn}$$

$$\overset{\delta+}{H} - \overset{\delta-}{O}$$

The approach of dipoles will continue, with corresponding loss of potential energy, until the repulsion of the electron shells is balanced by the attraction. In these circumstances, the formed active intermediate may either break apart into the original components or reallign its bonds to form new substances. If the change in free energy favours the latter possibility, the products will be:

$$C-H \qquad Sn-OH$$

But due to low polarity of C-Sn bonds as in the tetraalkyls and aryl derivatives of tin are not actually hydrolysed by water. Hydrolysis, however, may be brought about by increasing pressure and temperature and using catalysts such as acids or alkalies which attacks the carbon or tin. A rather unusual feature of the organotin compounds is the ionisation of some of the R_3SnX and R_2SnX_2 compounds in water (6). The strength of single covalent bonds between group IVA and other atoms generally decrease in going down the group, as can be seen from table -II(6).

Table -II

Elements(a)	Energy of bonds, K Cal/mole with						
	H	C	F	Cl	Br	I	O
C	99	83	116	79	66	67	82
Si	70	69	129	86	69	51	88

Contd...

Table - II (Contd.)

Element (a)	Energy of bonds, K Cal/mole with						
	H	C	F	Cl	Br	I	O
Ge	74	71		86	68	50	
Sn	71	68		82	65	47	

a - data derived mainly from MX_4 type compounds which are unstable and or non-existent when M = Pb.

The polarity of the metal carbon bond increases with increasing atomic number within the group and the bond becomes more sensitive to attack by polar reagents. This is also evident from the increase in the polar character of the halogens in compounds such as R_3MX (4).

1.E. Multiple bonding and the effect of availability of d-orbitals of tin in organotin compounds.

Multiple bonds involving pπ orbitals among the metals or to other elements is not known with Silicon, germanium, tin or lead whereas carbon has a great tendency to do so. However, there is good evidence that the d orbitals of the elements, other than carbon are used in dπ - pπ bonding (6). Thus, the consideration of acid strength of the four acids of the type p-$R_3MC_6H_4COOH$ reveals that the carbon compound which would be expected to have the greatest acid strength because of its most electronegative character, shows the lowest acid strength. This indicates that dπ - pπ bonding is operative in the other three compounds (10). However, it seems that the tendency to use d orbitals in π bonding decreases from Si to Sn, since in $(GeH_3)_2S$ and $(GeH_3)_2O$, the Ge-S-Ge and Ge-O-Ge appear to be highly bent (11) where as in $(SiH_3)_2O$ the Si-O-Si angle is around 150° (12). Relative to the bond lengths of Si-X, Ge-X bond lengths are less shortened as computed from the sum of covalent radii of the bond partners (13). Further evidence of the lowering, or non existence of dπ - pπ bonding in the elements below silicon comes from the relative base strengths of the amines viz. $(SiMe_3)_3N$, $(GeMe_3)_3N$ and $(SnMe_3)_3N$ due to hydrogen bonding. The silicon compound is virtually non-basic, but the germanium compound is as basic as an organic amine, whereas the tin compound is more basic than any organic amine (6). However, the possibility of dπ - pπ bonding in tin cannot be completely ignored, at least with elements of higher atomic numbers e.g., Cl, Br, I etc. In fact, dπ - pπ bonding is partly responsible for higher values of Sn-Cl stretching frequency in certain tin compounds (14) and Sn-O frequency in $(Ph_3Sn)_2O$ (15). Although, later on, from IR and Raman studies of compounds $R_3SnXSnR_3$ (X = O, S) it was concluded that there was no

π-contribution to the Sn-O and Sn-S bonds (41), similar ideas regarding Sn-O and Sn-S bonds in other compounds were reached by other workers (43 - 45).

Due to the availability of d orbitals, tin can extend its coordination number from 2 to 8 and so organotin compounds can form various types of complexes with ligands. Thus the most interesting example is afforded by R_3SnX type compounds which forms various types of adducts with Lewis bases (4). These compounds are generally penta coordinated (16, 17). When X is Cl, Br or I in Me_3SnX, they are usually tetrahedral. But for X = ClO_4^- , F^-, CO_3^{-2} , BF_4^- , NO_3^- , AsF_6^- , $OCOR^-$ the compounds are five coordinate about tin, where the anions are probably either bridging or chelate types (18,19). The aquo- ion $\left[Me_2Sn(H_2O)_4\right]^{+2}$ has a linear C-Sn-C group, there are presumably four water molecules weakly coordinated in the equitorial plane (20). In alkaline solution of Me_2SnCl_2, there exists trans $\left[Me_2Sn(OH)_4\right]^{-2}$ ion (20). Similarly R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents such as 8-hydroxy quinoline (21,22,41) acetyl acetone (23,24), 1,10 phenanthroline (22,24) etc. which are generally five or six and sometimes seven and eight coordinated compounds.

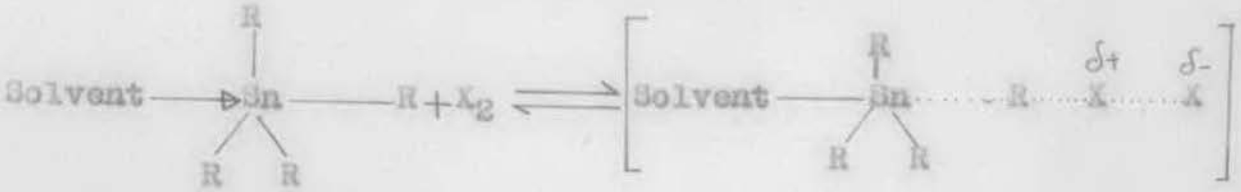
A penta coordinated intermediate of the type $\geqslant SnX.N$ may be formed when a neucleophilic substitution at tin takes place as follows (26)

$$\geqslant SnX + N \longrightarrow \geqslant SnN + X$$

Eaborn (27) has pointed out that in case of silicon atom such type of intermediate complex formation may decrease substantially the free energy of the transition state. Since complex formation is much more marked with tin than with silicon the facilitation of neucleophilic substitution reactions by this means is correspondingly more important. This facilitation may be pronounced even if the intermediate is very weak to be detected (27).

Neucleophilic assistance influences the cleavage of tin carbon bond by electrophilic attack at carbon atom (28-30). Thus in the halogen cleavage of Sn-C bond the presence of a donor solvent, such as an alcohol or acetic acid, even though it cannot form stable adduct with the tin compound can affect the rate of halogen cleavage by rendering neucleophilic assistance.

$$R_4Sn + \text{Solvent} \rightleftharpoons \text{Solvent} \rightarrow SnR_4$$



$$\text{Solvent} \rightarrow SnR_3{-}R + X_2 \rightleftharpoons \left[\text{Solvent}{-}SnR_3 \cdots R \cdots \overset{\delta+}{X} \cdots \overset{\delta-}{X}\right]$$

$$\rightleftharpoons R_3SnX.\text{solvent} + RX \text{ (where } X = Br, I).$$

The polarity of Sn-C bond together with the tendency of tin atom to form adducts with Lewis bases (donors) may be successfully utilised to explain a number of reactions, e.g., the cleavage of Sn-C bonds by some chelating agents studied by Nelson and Martin (25) and the reactions of $R_3SnOCOR'$, $(R_3Sn)_2O$ and some organotin oxinates with mercury salts etc.

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PART - II

ACTION OF MERCURIC HALIDES, MERCURIC ACETATE, PHENYLMERCURIC ACETATE AND CADMIUM IODIDE ON TRIORGANOTIN CARBOXYLATES AND RELATED COMPOUNDS.

Introduction:

During recent years interest in the field of organotin compounds is growing in a very rapid rate. The progress in this area is reflected by growing number of contributions in different journals and from the publication of several books and review articles by a number of authors (1-5). Organotin carboxylates, oxides and hydroxides constitute some major areas in the study of organotin compounds. Apart from the theoretical interest involved in such investigations, the compounds containing $\equiv Sn-O$ bonds could furnish potential areas of important polymers, insecticides, pesticides and other commercial products.

The carboxylates are of the following general types which may either be monomeric or polymeric: $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$ where R and R' may be same or different organic groups.

A brief review on the preparations, properties and structures of organotin carboxylates is presented here.

Preparation of organotin carboxylates:

A variety of methods have been applied for the preparation of organotin carboxylates. These are generally prepared by the reactions between organotin oxides (hydroxides) and carboxylic acids or their anhydrides (6-15).

$$R_3SnOSnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O$$

$$R_3SnOSnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR'$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O$$

The water produced in these reactions is removed usually by aseotropic distillation or alternatively be removed by refluxing the reaction at higher temperatures (16).

$$Bu_3SnOSnBu_3 + 2o\text{-}HOC_6H_4COOH \xrightarrow{100-110^\circ} 2Bu_3SnOCOC_6H_4OH\text{-}o + H_2O$$

A.Zilkha and his co workers (17) and [illegible] Sams et al (14, 18) have prepared organotin carboxylates by the reactions of triorganotin halides with alkali metal or silver (17) salts of carboxylic acids either by shaking or stirring the reactants in mixtures of organic/aqueous medium at room temperature. This method is used frequently for its simplicity.

$$R_3SnX + R'COOM \longrightarrow R_3SnOCOR' + MX$$

Where M = Na, K, Ag; X = halogen

It has been reported that acylation of R_3SnH, R_2SnH_2, $(R_3Sn)_2$, R_4Sn and $(R_3Sn)_2O$ [where $R = C_2H_5$] may be achieved with lead tetracetate, Pb $(OAc)_4$ (19).

The ability of carboxylic acids to cleave metal carbon bonds can be used for the preparation of organotin carboxylates (20, 21).

$$R_4Sn + R'COOH \longrightarrow R_3SnOCOR' + RH$$

The cleavage of organic groups depends on the acid strength, nature of groups R and R' and also on temperature (22-24). Vinyl groups are cleaved more readily than normal alkyl groups but less readily than phenyl groups.

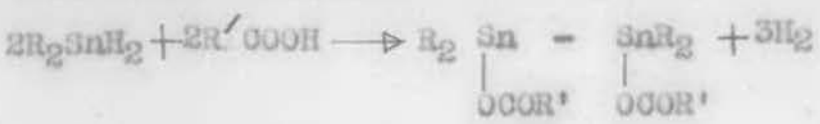
H.G.Kuivila (25) showed that the reaction of organotin hydrides with carboxylic acids produces carboxylates, the dihydrides yield hydride carboxylates.

$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2$$

$$R_2SnH_2 + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2H_2$$

$$R_2Sn(OCOR')_2 + R_2SnH_2 \longrightarrow 2R_2SnH(OCOR')$$

By using similar methods 1,2, dicarboxylates are also prepared (26-28). The nature of the products, however, sometimes depends on the acid present.



$$2R_2SnH_2 + 2R'COOH \longrightarrow R_2\underset{\displaystyle OCOR'}{\underset{|}{Sn}} - \underset{\displaystyle OCOR'}{\underset{|}{SnR_2}} + 3H_2$$

With di n-butyltin dihydride, the intermediate hydride carboxylate decomposes to tetra n-butyl 1,2 diacetate.

$$2Bu_2SnH_2 + 2CH_3COOH \longrightarrow 2Bu_2SnH(OAc) + 2\ H_2$$

$$2Bu_2SnH(OAc) \longrightarrow \underset{OAc}{\underset{|}{Bu_2Sn}} - \underset{OAc}{\underset{|}{SnBu_2}}$$

Action of benzoyl peroxide on di n-butyltin dihydride produces the 1,2, dibenzoate (29).

$$2Bu_2SnH_2 + (C_6H_5COO)_2 \longrightarrow \underset{C_6H_5COO}{Bu_2Sn} - \underset{OOCC_6H_5}{\underset{|}{SnBu_2}} + 2H_2$$

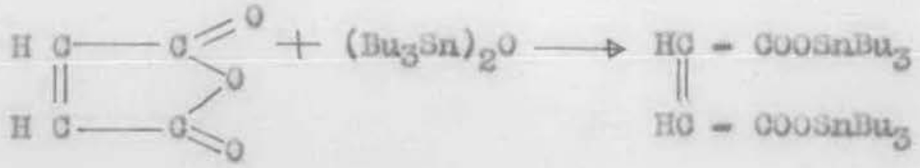
Halo carboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular propertion of dihalide and a dicarboxylate in an inert solvent (30, 31)

$$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \longrightarrow 2Bu_2SnBr(OAc)$$

These are also be prepared by the reaction between a dihalide and a metal carboxylate (32, 33).

$$Bu_2SnCl_2 + KOOCR' \longrightarrow Bu_2SnCl(OCOR') + KCl$$

Anhydride of an unsaturated acid viz. maleic anhydride forms a disubstituted organotin ester when reacted with hexabutyl distannoxane (34).



A novel method of preparation of trialkyltin acetate by electrochemical method using R_4Sn (where R = Me, Et, Pr, Bu) and Hg(1) acetate have been described very recently by G.Tagliavini and his co workers (35).

Tricarboxylates of n-butyl and phenyltins are usually prepared from the corresponding trichloride by the action of silver salts of carboxylic acids (36).

$$BuSnCl_3 + 3AgOAc \longrightarrow BuSn(OAc)_3 + 3AgCl$$

Physical properties of organotin carboxylates:

In organotin carboxylates the Sn-O bond is essentially covalent but mainly undergoes polar reactions depending on the solvents and the attacking groups. This is why the carboxylates with small organic groups are more soluble in alcohol, ether etc. than in water (2). Many of the carboxylates have low melting points.

The polymeric stannoic acids are colourless, infusible, few of them are soluble in chloroform, carbon tetrachloride and reasonably stable to hydrolysis.

Some of the physical properties of few representative carboxylates are given in table 1 (1-3,5).

Table - 1

Compound	Type	B.P.(^{o}C/mm)	M.P.(^{o}C)
Trimethyltin acetate	$R_3SnOCOR'$	-	196.5 -197.5
Triphenyltin formate	"	-	202-203
Tricyclohexyltin acetate	"	-	62-63
Tripropyltin trifluoroacetate	"	88-90/1	-
Dibutyltin diacetate	$R_2Sn(OCOR')_2$	142-145/10	-
Diphenyltin diacetate	"	-	116-117
Diethyl chlorotin acetate	$R_2SnX(OCOR')$	-	94
Dibutylbromotin acetate	"	-	67-68.5
Butyltin triacetate	$RSn(OCOR')_3$	117-119/1	-
Ethyltin tribenzoate	"	171-173/1	-

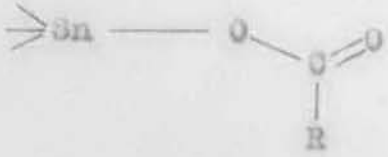
Some of the organotin carboxylates have been used as stabiliser of poly (vinyl chloride), fungicides, insecticides and bactericides which have been discussed in great detail by J.G.A. Luijten (3) and R.C.Poller (1).

Structure of organotin carboxylates:

The structure of organotin carboxylates have been studied extensively by Okawara and Wada (44). The possibility of chelation or bridging through weak co-ordination of oxygen atoms of carboxylate groups to tin atoms was pointed out by Beattie and Gilson (45) against the postulation of ionic nature of bonding by Freeman (46) and the ionic structure with a planar trimethyltin cation and a formate anion in trimethyltin formate as proposed by Okawara and his co workers (47).

Studying various features of infra red spectra of trialkyltin carboxylates in the solid as well as in the solution phase, Janssen et al (48) and Cummins and Dunn (49) have concluded that trialkyltin carboxylates are polymeric in the solid state with planar trialkyltin groups and bridging carboxylate groups and are move like monomeric esters in non polar solvents (fig. I). .... Sams et al (14,18,50,51) have provided significant data to establish this view.

In solid phase (A)



In solution phase (B)

<u>Fig. I</u>

Infrared spectra of trimethyltin carboxylates, $Me_3SnOCOR'$ (52) showed in the solid state two C-O stretching bands at about $\sim 1570\ cm^{-1}$ and $\sim 1410\ cm^{-1}$ indicating a symmetrical OCO group. The absence of a $510\ cm^{-1}$ band for $Me_3SnOCOMe$ indicated a planar trimethyltin group. In carbon tetrachloride solution the carboxylate absorption bands shifted to $\sim 1650\ cm^{-1}$ and $\sim 1300\ cm^{-1}$ respectively. Moreover the νas (Sn-C) and νs (Sn-C) bands were observed, indicating that in solution the polymeric structure (A) [Fig. I] is splitted to give ester type carboxyl groups and pyramidal units as shown in (B) [Fig. I]. This has been supported by R.E.Hester (26) and G.Tagliavini (53).

Okawara and Ohara (54, 55) from spectroscopic studies and molecular weight determinations in cyclohexane by cryoscopic method concluded that trialkyltin formates formed infinite linear polymer through bridging formoxy groups i.e., by co-ordination of oxygen to tin atoms in solid or liquid state. In liquid, however, the infinite polymer broke down to lower polymers having both bridging and terminal formoxy groups (Fig. II).

In the solid state or in neat liquid

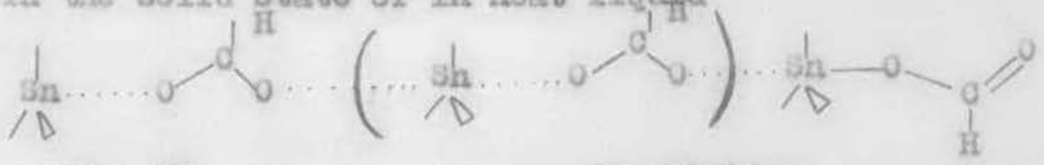


Fig. II

In solution

Tricyclohexyltin acetate, trineophyltin formate and acetate, tribenzyltin acetate have been suggested to be tetra co-ordinated monomers probably due to steric hindrance arising from the bulky organic groups (56-58).

Sams et al (18) have pointed out that the branching at ∝-carbon atom in the carboxylates prevented polymerisation.

Trialkyl and aryltin carboxylates (14,59-61) have been shown to have monomeric structures and they become more like organic esters as the number of substituted halogen atom increased in the carboxylic acid.

Okawara et al (47) investigated dimethyltin diformate spectroscopically and proposed a structure with a linear dimethyltin cation and a formate anion.

Symmetrical structure of dimethyltin diformate (fig. III) was proposed on the basis of infrafed spectral studies by H.Sato and R.Okawara (62). From infrared spectra and molecular weight determinations in benzene (63,64) dialkyltin diacetate was shown to have a non symmetrical chelated configuration (fig. IV). However,

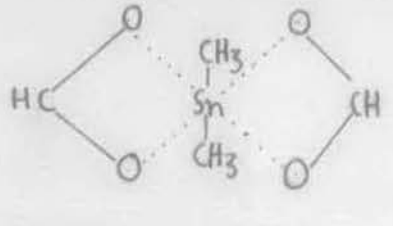


fig. III

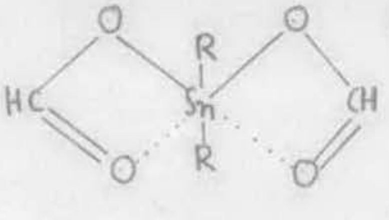


fig. IV

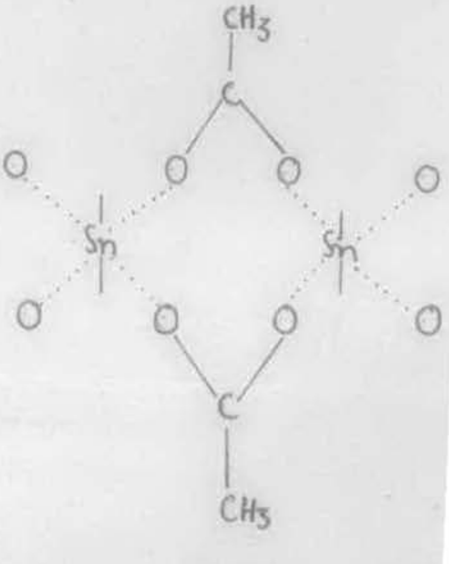


fig. V

due to the presence of an additional band at $\sim 1560\ \mathrm{cm}^{-1}$ and as the intensity of the band at 1400-1440 cm^{-1} increased in neat liquid or in the crystalline state, the structure (fig. V) having the partial bridging acetoxy groups have also been proposed.

A monomeric penta coordinated structure (fig. VI) had been proposed for dialkyl chlorotin formates and acetates by Okawara et al (65).

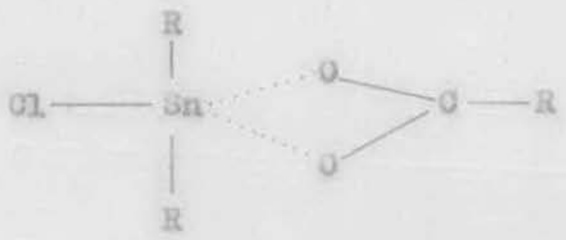


fig. VI

Allock and Timms (53) have studied the structure of tribenzyl and tricyclohexyltin acetate through X-ray defraction. On the basis of this study there is no doubt that the majority of organotin carboxylates have polymeric structure in the solid state. But with larger organic groups, the structure may become less polymeric and ultimately become monomeric.

The structure of polymeric monoorgano stannoic acids (43) and their carboxylate derivatives (14,15,18) have recently been studied through elemental analysis, IR and mossbauer spectroscopy. Herber and his co workers (66) have shown that polymerictin compounds are most likely to show a mossbauer effect at ambient temperature.

The stannoic acids are infusible powders for which a polymeric structure (fig. VII) have been proposed (67,68). And for a partially dehydrated material a structure as in fig. VIII was suggested by Pshiyalkovaskaya and his co workers (69).

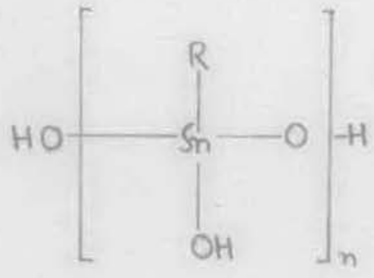


fig. VII

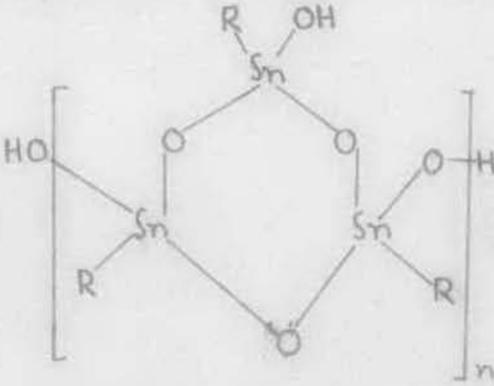


fig. VIII

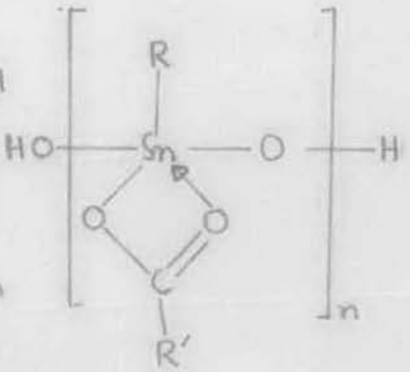


fig. IX

In both of the structures, tin atoms are tetra coordinated in a tetrahedral environment of the $RSnX_3$ [X = O].

A.G.Davies et al (43) suggested from the low observed quadrupole splitting[ΔE_Q = 1.29 - 1.83 mm/sec, table II (43)] of organostannoic acids, that the tin atom had a tetrahedral geometry, though they have not excluded the possibility of association. The isomer shift values (δ = 0.40 - 0.78 mm/sec) are very small because of the very low 's' electron density at the tin atom resulting from electron attraction by the surrounding oxygens.

The carboxylic acid derivatives $[RSn(O)OCOR']_n$ of the stannoic acids $[RSn(O)OH]_n$ showed larger quadrupole splitting values (ΔE_Q = 2.00 - 2.64 mm/sec) (15,18) which indicated a structure where the tin atoms occupy a trigonal bipyramidal configuration such as fig.IX and which would be expected to show a quadrupole splitting of about ΔE_Q = 2.25 mm/sec (69).

Table-II

Mossbauer parameters for organostannoic acids:

Compound	δ mm/sec	ΔE_Q mm/sec
$[MeSn(O)OH]_n$	0.40	1.29
$[EtSn(O)OH]_n$	0.76 - 0.70	1.61 - 1.70
$[BuSn(O)OH]_n$	0.65 - 0.70	1.52 - 1.71
$[C_8H_{17}Sn(O)OH]_n$	0.66	1.62
$[PhSn(O)OH]_n$	0.78	1.83

(where ΔE_Q = Quadrupole splitting, δ = isomer shift)

Sams et al (18) and R.C.Poller and his co workers (15) have studied some of the carboxylic acid derivatives of organostannoic acids by IR and mossbauer spectroscopy. The mossbauer parameters have been tabulated in table-III (18,43).

Table-III

Mossbauer parameters for organostannoic carboxylates.

Compound	δ mm/sec	ΔE_Q mm/sec
$PhSn(O)[OCO(CH_2)_8CH = CH_2]$	0.57	2.31
$PhSn(O)[OCO(CH_2)_{16}Me]$	0.56	2.32
$PhSn(O)[OCOC(CH_3)_3]$	0.59	2.00
$PhSn(O)[OCOCCl_3]$	0.72	2.33
$PhSn(O)[OCOCF_3]$	0.66	2.64
$BuSn(O)[OCOMe]$	0.70	2.26
$BuSn(O)OH$	0.65	1.71

(ΔE_Q and δ have their usual significance)

The quadrupole splitting for BuSn(O)OAc is essentially the same as those for phenyl stannoic carboxylates but that for BuSn(O)OH is appreciably lower. As because BuSn(O)OH is known to have a tetra coordinated tin atom, the increased large splitting may be attributed to penta coordination about tin atom for the carboxylate derivatives.

On the basis of mossbauer data J.R.Sams and his co workers (18) suggested a cyclic trimeric structure as in fig. VIII, but they have not excluded the probability of linear polymeric structure involving bridging oxygen atoms. [illegible].Poller et al (15), however, from general physical characterestics and room temperature mossbauer effect as shown by these compounds preferred to suggest a linear polymeric structure with bridging oxygen atoms.

Infrared absorption of impure phenyltin undecenoate and pure phenyltin stearate have been studied in detail by [illegible].Sams et al (18). They have assigned ~ 1536 cm^{-1} and ~1412 cm^{-1} bands to carboxylate group vibrations and have inferred that the carboxylate group to be either chelating or ionic. The positions of the bands, however, have not been shifted in solutions. Interpretation of absorptions at 560 -550 cm^{-1} to be due to asymmetric stretching of Sn-O-Sn bond accords well with the √as (Sn-O-Sn) stretching in mono and dialkyl poly stannoxanes (70-72). Assignment of the √as (Sn-O-Sn) band virtually led them to propose a structure as suggested in fig. VIII although possibility of a linear polymeric structure was not excluded.

Chemical properties of organotin carboxylates:

The most widely studied reactions of organotin carboxylates are decarboxylation and disproportionation. An interesting cyanomethyl derivative (yield 50%) is formed when triphenyltin cyanoacetate is heated under vacuum (73).

$$(C_6H_5)_3SnOCOCH_2CN \xrightarrow{\Delta} (C_6H_5)_3SnCH_2CN + CO_2$$

But in case of aliphatic series, this type of conversion is less pronounced, the organotin cyanomethyl compound is produced in low yield.

Trialkyltin carboxylates of unsaturated acids give tetra substituted organotin compounds after decarboxylation (74,75).

$$R_3SnOCOC\equiv CR' \xrightarrow{\Delta} R_3SnC\equiv CR' + CO_2$$

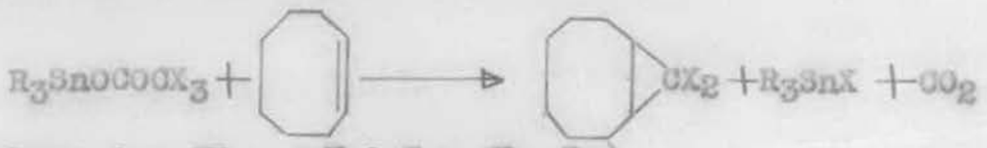
$$\left[\text{Where } R' = C_6H_5 \text{ or } SnR_3\right]$$

Thermal decomposition of triorganotin formate yields the corresponding hydride and this reaction is used sometimes for the preparation of hydrides (76).

$$R_3SnOCOH \xrightarrow{\Delta} R_3SnH + CO_2$$

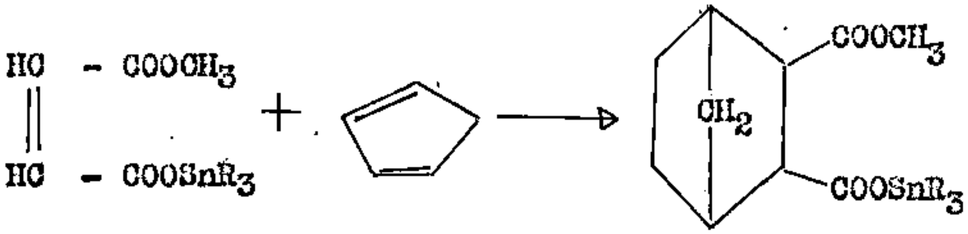
$$\left[R = n-C_3H_7,\ n-C_4H_9\right]$$

Sayferth et al (77) used successfully the reaction of triorganotin carboxylates of halogen substituted carboxylic acids with cyclooctene as a carbene transfer reaction, although the reaction mechanism is not yet established.



(Where $R = CH_3, C_6H_5$; $X = Cl, Br$)

Diels-Alder type reactions have been carried out by A.S. Mufti and R.C.Poller (32) with organotin carboxylates and dienes.



$\left[R = n\text{-}C_4H_9;\ C_6H_5 \right]$

An equilibrium is established when trialkyltin carboxylates and thiols are mixed together (78).

$$R_3SnOOCR' + R''SH \rightleftharpoons R_3SnSR'' + R'COOH$$

The reaction can be driven from left to right if the organic acid formed is volatile and can easily be removed from the equilibrium mixture.

In recent years some metallo stannoxanes have been isolated starting from organotin carboxylates. Thus silyl stannoxanes may be prepared by heating triphenyltin acetate with diphenyl diethoxy silicon at 170° for 20 hrs (79).

$$Ph_3SnOAc + Ph_2Si(OEt)_2 \longrightarrow Ph_2Si(OSnPh_3)_2 + 2EtOAc$$

On condensation of tributyltin acetate with alkoxytitanium, titanostannoxanes are formed (80).

$$\begin{tikzcd}
Bu_3SnOAc + Ti(OBu)_4 \arrow[r] & Bu_3SnOTi(OBu)_3 \arrow[d, "(HOCH_2CH_2)_3N"] \\
 & Bu_3SnOTi(OCH_2CH_2)_3N
\end{tikzcd}$$

Diorganotin dicarboxylates undergo redistribution with diorganotin dihalides, dialkoxides and dihydrides to produce mixed carboxylates of the type $R_2SnX(OCOR')$, where X =Cl, Br, I, OCH_3, H (3).

A mixed carboxylate viz., dibutyltin methoxide acetate reacts with chloral to form a new carboxylate derivative. The same compound may also be prepared by the disproportionation of $Bu_2Sn(OAc)_2$ and $Bu_2Sn\left[OCH(CCl_3)OMe\right]_2$ (3).

$$\begin{tikzcd}
Bu_2Sn(OMe)OAc + CCl_3CHO \arrow[dr] & \\
 & Bu_2Sn(OAc)OCH(CCl_3)OMe \\
Bu_2Sn(OAc)_2 + Bu_2Sn\left[OCH(CCl_3)OMe\right]_2 \arrow[ur] &
\end{tikzcd}$$

1,3 tetrabutyl 1,3 diacetoxy distannoxane reacts with $^{t}BuOOH$ to give $(^{t}BuOO)Bu_2SnOSnBu_2(OOBu^{t})$ (17,81).

$$AcOBu_2SnOSnBu_2OAc + 2Bu^tOOH \rightarrow ({}^tBuOO)Bu_2SnOSnBu_2(OOBu^t)$$

Oligomeric acetate is usually formed when a dialkyltin diacetate and a dialkyltin dialkoxide are heated at 180^0 in water for 2 hrs (82,83)

$$(x+1)Bu_2Sn(OAc)_2 + (x+1)Bu_2Sn(OBu)_2 \longrightarrow BuO(Bu_2SnO)_{2x+1}SnBu_2OAc + (2x+1)BuOAc$$

Oligomeric α-ω diacetoxy stannoxanes have also been prepared by the hydrolysis of dibutyltin diacetate in acetone. The produced acetic acid is removed by methylating with diazomethane (84).

$$Bu_2Sn(OAc)_2 + H_2O \xrightarrow{CH_2N_2} AcO(Bu_2SnO)_xSnBu_2OAc + MeOAc$$

(Where x = 1,3,7,15).

Organotin tricarboxylates may easily be hydrolysed in benzene solution to give polymeric organotin carboxylates as suggested by R.C.Poller and his co workers (15).

$$RSn(OCOR')_3 + H_2O \rightarrow \left[RSn(O)OCOR'\right]_n + 2R'COOH$$

Recent studies on polymeric organostannoic acids have arisen considerable interest about the nature of these interesting class of compounds. The organostannoic acids, RSn(O)OH are generally prepared by alkaline hydrolysis of an organotin trichloride (2).

$$RSnX_3 \xrightarrow{3NaOH} 3NaX + RSn(OH)_3 \xrightarrow{-H_2O} RSn(O)OH$$

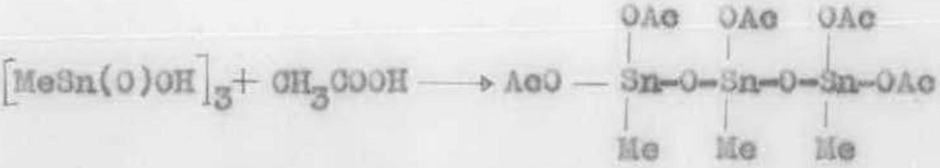
$$\left[\text{Where } X = Cl\right]$$

The hydrolysis of $RSnX_3$ proceeds through various intermediate stages. With aliphatic trihalide, $RSnCl_3$, the products are $RSn(OH)_2Cl$, $RSn(OH)Cl_2$; H_2O, $RSn(OH)Cl_2$ or $[RSn(O)Cl]_n$ depending on the reaction condition and nature of the aliphatic groups. Aryltin trichlorides, on the other hand, yields no properly defined intermediate products (37). The hydrolysis may also be induced by water alone.

The reactions of potassium or sodium stannite and alkylhalides in cold alkali (38-43) provides another source of organostannoic acid derivatives.

$$MeI + Na_2SnO_2 \longrightarrow MeSn(O)\overset{-}{O}\overset{+}{Na} + NaI$$

An interesting type of compounds is formed when stannoic acids, $[RSn(O)OH]_n$ are treated with carboxylic acids. Thus on treatment of $[MeSn(O)OH]_3$ with acetic acid, penta acyl stannoxane is produced (39).



$$[MeSn(O)OH]_3 + CH_3COOH \longrightarrow AcO-\underset{Me}{\overset{OAc}{Sn}}-O-\underset{Me}{\overset{OAc}{Sn}}-O-\underset{Me}{\overset{OAc}{Sn}}-OAc$$

Recently Sams et al (18) have identified phenyltin stearate and phenyltin undecenoate as the decomposition products of the respective triphenyltin carboxylates during long storage. They were unable to repeat the work and did not suggest any definite reason for such decomposition. However, they proposed that some sort of impurity might have cleaved the tin carbon bond resulting the polymers.

R.C.Poller and his co workers (15) have pointed out that such type of cleavage is probable if catalytic amount of water together with free carboxylic acid is present because strong carboxylic acids may cleave tin carbon bonds. In support of the above statement they reported the formation of three polymers of the same type viz. $[PhSn(O)OCOR]_n$ [where R = CCl_3, CF_3 and $C(CH_3)_3$] when triphenyltin hydroxide and the corresponding carboxylic acid were refluxed in benzene.

Scope, object and results

In view of the fact that the hexaalkyl/aryl distannoxanes have been shown to react quite readily with covalent halides (85,86), it is reasonable to expect for organotin carboxylates (which also contain tin oxygen linkage) would, therefore, undergo a variety of reactions with covalent metal halides and carboxylates. In the present investigation, action of mercuric halides, mercuric acetate, phenyl mercuric acetate and cadmium iodide on triorganotin carboxylates have been studied. Triorganotin carboxylates used in this investigation include some aryl, alkyl and carbocyclic organotin carboxylates in which the carboxylate groups have varied nature. The reactions of triphenyltin carboxylates have been studied in detail mainly because of their pronounced reactivity towards the above reagents.

Triphenyltin carboxylates react quite readily with mercuric halides at room temperature producing phenyl mercuric halides, triphenyltin halides and organotin polymers. The composition of tin polymers depends on the nature of the carboxylate groups and also on the particular mercuric halide used. For example, the reaction of triphenyltin acetate and propionate with mercuric chloride produces a polymer which contains a very few phenyl groups indicating that an extensive migration of phenyl groups from the tin atom to mercury atom has taken place. Whereas, in case of the corresponding formate, the polymer obtained contains at least one phenyl group pertin atom even after the quantitative conversion of the mercuric chloride added to phenyl mercuric chloride.

On the other hand, the conversion of mercuric chloride is only about fifty percent in case of reactions of tripropyl and tributyltin acetate with mercuric chloride whereas tricyclohexyltin acetate practically does not react with mercuric chloride under similar conditions. It has been further observed that the reactivity of triorganotin carboxylates towards mercuric chloride varies in the following sequence:

$$\mathrm{Ph} > \mathrm{Pr} \approx \mathrm{Bu} \ggg \mathrm{cyclohexyl}$$

Reactions of triphenyltin carboxylates with mercuric bromide and iodide produce polymeric compounds which contains at least one phenyl group pertin atom. The reactions involving mercuric iodide are slower and unreacted mercuric iodide has always been recovered under the similar reaction conditions. Thus a dependence of the reactions on the halogen atoms have also been observed.

The present investigation yielded a number of mono organotin polymers from the reactions of triorganotin carboxylates with mercuric salts. It has been found that when triorganotin compounds containing $\geqslant$Sn-O moiety reacts with mercuric salts, migration of organic groups takes place easily from tin atom to mercury atom resulting the formation of various types of organotin polymeric compounds. By varying the nature of carboxylate groups of triorganotin carboxylates and halogen atoms of mercury a number of polymeric compounds with the approximate composition of $\left[\mathrm{RSn(OH)_2OCOR'}\right]_n$,

$[RSn(O)OH]_n$, $[Sn(OH)_4]_n$ have been obtained. Due to the lack of facility, mossbauer spectroscopy studies of these compounds were not possible. In order to get an idea about the nature of these polymeric products, some reactions with 8-hydroxy quinoline along with chemical analysis and infrared spectroscopy have been utilised.

Some polymeric mono organotin carboxylates have recently been reported by [illegible] Sams et al (18) and R.C.Poller and his co workers (15). As mentioned earlier Sams et al, however, could not repeat their work but have suggested the presence of some impurity as a cause of such degradation of the parent triorganotin carboxylates. The present studies show conclusively that a degradation of triorganotin carboxylates to mono organotin derivatives is quite feasible by mercuric salts and may be used as a convenient route for the preparation of these compounds.

Reactions of mercuric acetate and phenyl mercuric acetate with triphenyltin acetate produce diphenyl mercury and polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$. But in the reaction of tribenzyltin acetate with mercuric acetate benzyl mercuric acetate is one of the products instead of dibenzyl mercury. This reaction, however, produces no polymeric product but a new carboxylate derivative of stannoxanes viz. 1,3 dibenzyl 1,3 dihydroxy 1,3 diacetoxy distannoxane. Mercuric acetate does not practically react with tripropyl, tributyl and tricyclohexyltin acetate in the same conditions.

It is interesting to note that cadmium iodide behaves entirely in a different way. It transforms triphenyltin formate and acetate into poly stannoxanes such as Ph_2SnO and tetraphenyltin without itself being taking part in the over all reactions. Cadmium iodide, thus, catalytically induces transformation of triphenyltin carboxylates.

PART-II

EXPERIMENTAL

EXPERIMENTAL

All the solvents used in these experiments were purified and dried as described in Vogel's practical organic chemistry (87). The petroleum ether used through out the investigation had boiling points 60°-80° unless otherwise mentioned. Mercuric chloride (B.D.H.), mercuric bromide (E.M.), mercuric iodide (S.M.), mercuric acetate (E.M.), phenylmercuric acetate (Riedel) and cadmium iodide (B.D.H.) were dried in an air oven at 105° for 12 hours and kept in a vacuum desiccator for use. All melting points were uncorrected.

Triphenyltin chloride (Fluka A.G. Switzerland) was recrystallised from petroleum ether, m.p. 105-106° [lit. (88), m.p. 106°] which was then used for the preparation of the triphenyltin carboxylates. Tricyclohexyltin bromide (carrol products, New York), m.p. 77° [lit (5), m.p. 77°] was used without further purification. Tributyltin acetate m.p. 83-84° [lit (89), m.p. 84.5-85°] (Fluka A.G. Switzerland) was used in these reactions without further purification. Diphenyltin dichloride, m.p. 42° [lit (5) m.p. 42°] obtained from Fluka A.G. was used for the preparation of polystannoxane such as Ph_2SnO.

1. Preparation of triphenyltin formate:

Triphenyltin formate was prepared by following the method of J. R. Sams et al (18). It was then recrystallised from benzene/petroleum ehter mixture and dried in vacuum for 12 hr, m.p. 201-

202° [lit (18), m.p. 201-202°] (Found: Sn = 29.99%; Calcd. for $C_{19}H_{16}SnO_2$: Sn = 30.07%).

2. Preparation of triphenyltin acetate:

Triphenyltin acetate was prepared by refluxing methanol solution of triphenyltin chloride with a slight excess of potassium acetate for 4 hr. After evaporating the solvent, triphenyltin acetate was extracted with petroleum ether and on concentration of petroleum ehter solution, pure triphenyltin acetate was obtained, m.p. 121° [lit (89), m.p. 121-122°] (Found: Sn = 29.10%; Calcd. for $C_{20}H_{18}SnO_2$: Sn = 29.04%).

3. Preparation of triphenyltin propionate:

Triphenyltin propionate was prepared by shaking etheral solution of triphenyltin chloride with an aqueous solution of a slight excess of potassium acetate (18). The product was washed successively with water and ether and was dried in vacuum for 12 hr, m.p. 122° [lit (18) m.p. 122-123°] (Found: Sn = 28.12%; Calcd. for $C_{21}H_{20}SnO_2$: Sn = 28.08%).

4. Preparation of tripropyltin acetate:

By reacting hexapropyl distannoxane (Fluka A.G.) with mercuric acetate (1:1) in ether solution at room temperature, tripropyltin acetate was obtained from the ether filtrate. After recrystallisation from ether, pure tripropyltin acetate was obtained m.p. 99° [lit (89) m.p. 100°] (Found : C = 42.98%; H = 7.71%; Sn = 38.61%; Calcd. for $C_{11}H_{24}SnO_2$: C = 43.04%, H = 7.83%, Sn = 38.71%).

5. Preparation of tribenzyltin chloride:

Tribenzyltin chloride was prepared according to the method of Schimitz-Dumont et al (90) and was recrystallised from acetone, m.p. 142° [lit (90) m.p. 142-144°] (Found: Sn = 27.57%; Calcd. for $C_{21}H_{21}SnCl$: Sn = 27.79%).

6. Preparation of tribenzyltin acetate:

By stirring tribenzyltin chloride with sodium acetate in ether (53), tribenzyltin acetate was prepared. Recrystallisation from acetone afforded pure tribenzyltin acetate, m.p. 117° [lit (89), m.p. 117-118°] (Found: Sn = 26.18%; Calcd. for $C_{23}H_{24}SnO_2$: Sn = 26.34%).

7. Preparation of tricyclohexyltin acetate:

Tricyclohexyltin acetate was prepared by refluxing tricyclohexyltin bromide with a slight excess of potassium acetate in methanol, removing the solvent and extracting the product with benzene. Crystallisation from benzene/petroleum ether mixture afforded pure Tricyclohexyltin acetate, m.p. 62° [lit (5) m.p. 62-63°] (Found: Sn = 27.68%; Calcd. for $C_{20}H_{36}SnO_2$: Sn = 27.83%).

8. Preparation of diphenyltin oxide:

Diphenyltin dichloride on hydrolysis with 10% methanolic potassium hydroxide yields diphenyltin oxide after washing thoroughly with water, methanol, benzene and drying at 100° in vacuum for 12 hr (5). IR spectrum of this compound was identical with the spectrum of diphenyltin oxide reported by Cummins et al (91) (Found: Sn = 42.51%; Calcd. for $C_{12}H_{10}SnO$: Sn = 42.60%).

9. Preparation of diphenyltin diacetate:

Diphenyltin diacetate was prepared by treating diphenyltin oxide with acetic acid in hexane (92). The hexane solution afforded pure diphenyltin diacetate after several recrystallisation, m.p. 116° [lit (92) m.p. 116-117°] (Found: Sn = 30.17%; Calcd. for $C_{16}H_{16}SnO_4$: Sn = 30.38%).

All these prepared samples were used in the subsequent reactions and also used as authentic samples for mixed melting point determinations.

Authentic samples of phenylmercuric chloride, bromide and iodide, propylmercuric chloride, triphenyltin bromide and iodide, tripropyltin fluoride, tetraphenyltin, diphenyl mercury, phenyltin chloro dioxinate and phenyltin iododioxinate were prepared previously in this laboratory and have been used for mixed melting point determinations.

10. <u>Reaction of triphenyltin formate with mercuric chloride</u>:

5.24 gm of triphenyltin formate was dissolved in 250 ml of benzene in a litre flask. To it 3.60 gm of mercuric chloride dissolved in 300 ml of ether was added slowly with stirring. A white precipitate was formed after a while but the stirring continued for 8 hr at room temperature and the whole solution was kept overnight to ensure complete reaction. The mixture was then filtered and the residue, 3.82 gm, digested in a soxhlet with benzene for about 12 hr. 1.82 gm of solid (10A), m.p. 270^0(d) was found insoluble. The benzene soluble fraction was evaporated and 2.00 gm of solid material (10B), m.p. 247-249^0 was obtained. The filtrate was slowly concentrated and the following fractions were obtained:

1) Shining leafy crystals, 1.00 gm, m.p. 248-250^0(10C)
2) Crystalline solid, 1.55 gm, m.p. 227-247^0, (10D)
3) Crystalline solid, 2.06 gm, m.p. 100-102^0 (10E)

The fractions (10B) and (10C) were found to be identical (mixed melting point determination showed no depression) and hence mixed together (10F). The fractions (10D) and (10E) were treated with petroleum ether in cold and the petroleum ether soluble fractions were mixed together, from which 2.50 gm of crystalline solid (10G), m.p. 101-105° was obtained. The petroleum ether insoluble fractions from (10D) and (10E) had identical melting point and hence they were mixed together and treated with 20 ml of hot benzene, boiled and cooled. On filtration 1.15 gm of white leafy crystal, m.p. 249-251° identical with fraction (10F) (m.m.p*) was obtained and were mixed together (10H).

Identification of solid 10G:

The solid (10G) was crystallised several times from petroleum ether to furnish a crystalline solid, m.p. 106° and identified as triphenyltin chloride by mixed melting point determination with an authentic sample of triphenyltin chloride, [lit (88) m.p. 106°].

Identification of solid 10H:

The solid (10H) on recrystallisation several times from benzene yielded leafy crystals, m.p. 251°. It was identified to be phenyl mercuric chloride by mixed melting point determination with

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* mixed melting point determination which showed no depression.

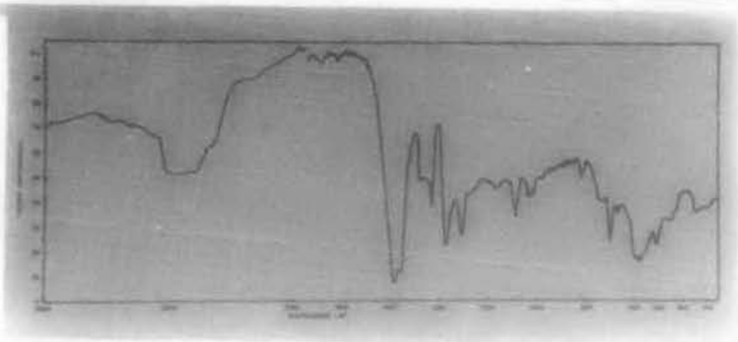


Fig. 2.1 IR spectrum of polymeric compound phenyltin dihydroxy formate, PhSn$(OH)_2$OCOH obtained from the reaction of triphenyltin formate and mercuric chloride.

an authentic sample of phenylmercuric chloride, [lit (89) m.p. 251°].

Identification of solid 10A:

The solid (10A) was identified as a polymeric organotin compound from the following observations:

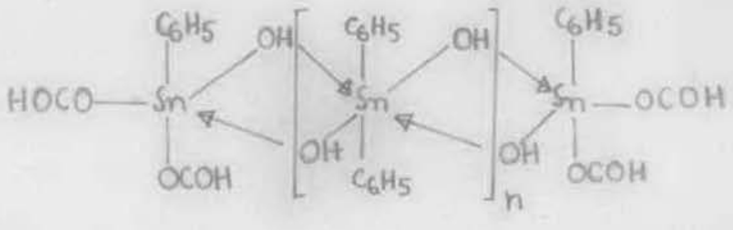
1) Insolubility in almost all common organic solvents*
2) Decomposes at 270°.
3) The IR spectrum (fig. 2.1) showed the following major bands.

$\nu(OH) = 3540\ cm^{-1};\ 3370\ cm^{-1}$

$\nu_{as}(OCO) = 1575\ cm^{-1};\ 1550\ cm^{-1}$

$\nu_{as}(Sn{-}O{-}Sn) = 560\ cm^{-1}$

On the basis of the elemental analysis and IR spectrum the polymeric compound was identified as



Where $n = 3$**

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* This polymer and other polymers described subsequently which contained hydroxyl group were found to be soluble in pyridine and dimethyl formamide.

** For this particular polymer and other polymers described subsequently, the value of 'n' was taken to be 3-4. In the absence of molecular weight data, the value of 'n' could not be obtained precisely. We have, however, taken these values of 'n' in obtaining the molecular formula which matched most closely with the experimental values of elemental analysis.

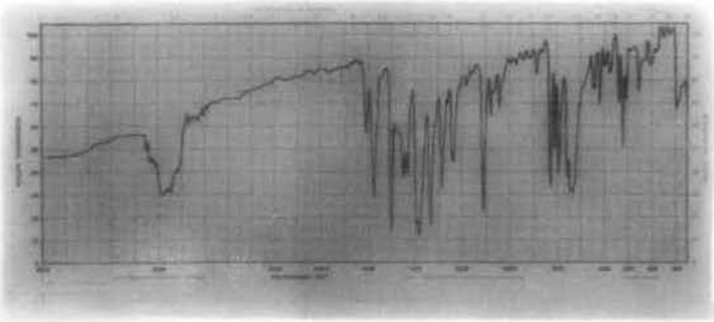

Fig. 2.2 IR spectrum of phenyltin trioxinate, $PhSn(Ox)_3$.

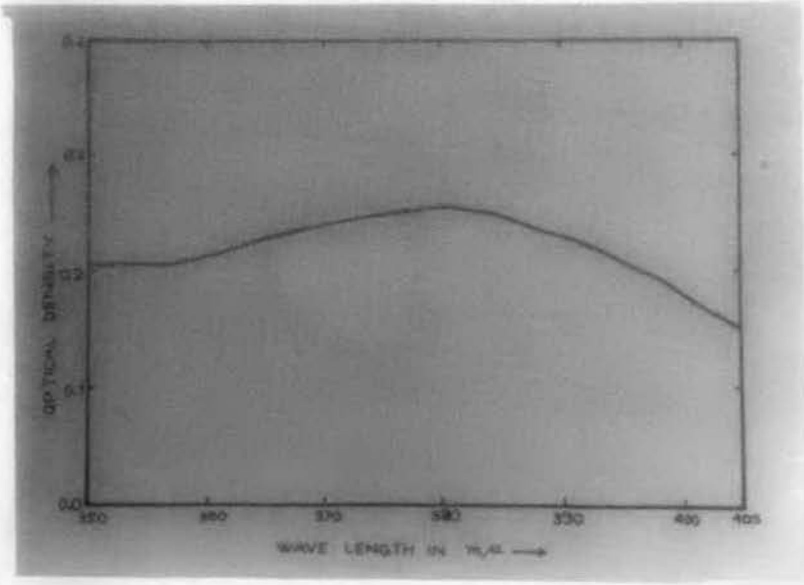

Fig. 2.2A Absorption spectrum of phenyltin trioxinate, $PhSn(Ox)_3$ in the visible region.

(Found: C = 31.99%, H = 2.65%, Sn = 42.10%; Calcd. for $C_{37}H_{40}Sn_5O_{22}$ C = 31.72%, H = 2.86%, Sn = 42.39%) with essentially the [$C_6H_5Sn(OH)_2OCOH$] units.

The solid polymeric material gave an oxine (8-hydroxyquinoline) derivative. Thus on treatment of 0.50 gm of the polymer with an excess (1.50 gm) of oxine in refluxing methanol for 4 hr, afforded a methanol insoluble yellow crystalline compound (1.10 gm). This compound was washed thoroughly with methanol, benzene and recrystallised from tetrahydrofuran/petroleum ether mixture where by the pure crystalline compound, m.p. 302-303°, identified as phenyltin trioxinate (IR spectrum fig. 2.2) was obtained [Found : C =62.60%, H = 3.61%, N = 7.07%, Sn = 18.56%; Calcd. for $C_{33}H_{23}N_3O_3Sn$: C = 63.08%, H = 3.66%, N = 6.69%, Sn = 18.95%]. The filtrate and washings afforded only unreacted oxine.

Although the solubility of $PhSnOx_3$ in methanol is very low but is sufficient enough to allow measurement of electronic transition spectrum in that solvent. The visible spectrum in methanol shows a broad band at about 380 mμ (fig. 2.2A) similar to that of $BuSnOx_3$. The observed molar extinction coefficient (6.6×10^3) is also typical of the organotin trioxinates (114).

That the yellow compound which was identified as phenyltin trioxinate contained one equivalent of phenyl group has been observed by the reaction of 0.50 gm of phenyltin trioxinate with an

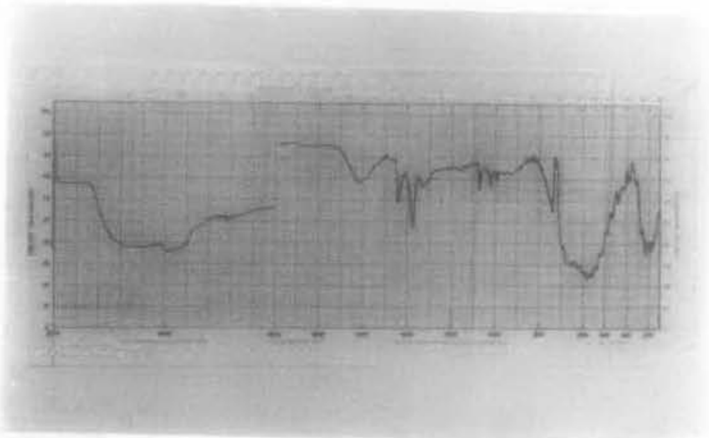

Fig. 2.3 IR spectrum of polymeric phenyl stannoic acid, $PhSn(O)OH$.

excess of mercuric chloride in refluxing benzene for 6 hr. The quantitative isolation of 0.24 gm of phenyl mercuric chloride (m.m.p) showed the presence of one equivalent of phenyl group per-tin atom in the compound.

This sample of phenyltin trioxinate was used as authentic sample.

When the reaction of triphenyltin formate and mercuric chloride was carried out in not so dried solvents (benzene/ether) the nature of polymer was found to be different. The product was identified as phenyl stannoic acid, $[C_6H_5Sn(O)OH]_n$ by elemental analysis and IR spectroscopy (fig. 2.3). (Found: C = 31.90%, H = 2.80%, Sn = 51.23%; Calcd. for $C_6H_6SnO_2$: C = 31.48%, H = 2.60%, Sn = 51.90%). The IR spectrum of this polymer was very similar to that reported by Cummins et al (91).

During long storage of the polymeric compound $[C_6H_5Sn(OH)_2OCOH]_n$ for about a year in a glass tube stoppered with bark cork, it decomposed to polymeric $[C_6H_5Sn(O)OH]_n$ as identified from IR spectrum.

The polymers from the above reactions were found not to contain any halogen as tested according to Vogel (93).

It was found that the solution after the original reaction contained chloride and formate ion. To test for these ions, the solvent after a separate run of reaction mixture was distilled cautiously in a clear, clean flask and the presence of chloride and formate ions were detected in the distilate qualitatively*(93)

11. Reaction of triphenyltin formate with mercuric bromide:

To a suspension of 4.61 gm of mercuric bromide in 400 ml ether, a solution of 5.06 gm of triphenyltin formate in 400 ml of benzene was added slowly with vigorous stirring at room temperature. The mixture was stirred for 7 hr and kept overnight. A white precipitate appeared in the solution and filtered. 3.76 gm of residue (11A) was obtained and was digested with hot benzene in a soxheet for 12 hr. The residue 1.76 gm (11B) obtained after digestion was found to be insoluble in other common organic solvents and decomposed at 270°. The benzene solution was evaporated to dryness and 2.00 gm of flaky crystals (11C), m.p. 270-276° was obtained. The original filtrate on concentration to about 30 ml of volume gave 2.57 gm of flaky crystals (11D), m.p. 270-275°. The fractions (11C) and (11D) were found to be identical (m.m.p) and were mixed together. The mixture was recrystallised several times from benzene, which furnished pure crystals, m.p. 276° and was characterised as phenylmercuric bromide by mixed melting point

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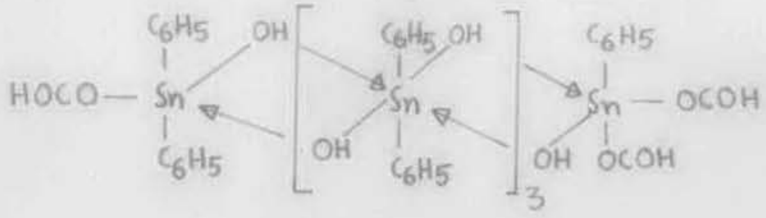
* The same procedure have been adopted to detect the formation of carboxylate/halide ions during the latter reactions.

determination with an authentic sample [lit (89) m.p. 276-280°]. The filtrate after separation of (11D) was evaporated to dryness whereby a white solid 2.70 gm, m.p. 120° (11E) was obtained which on recrystallisation from petroleum ether afforded a crystal, m.p. 122° and was identified as triphenyltin bromide by mixed melting point determination with an authentic sample [lit (94) m.p. 120.5°].

Identification of the solid 11B:

The solid (11B) was identified as a polymeric product from its physical properties as mentioned before. From elemental analysis and identical IR spectrum with fig. 2.1 it was identified as polymeric phenyltin dihydroxy formate, $[C_6H_5Sn(OH)_2OCOH]_n$ and has been formulated as



(Found: C = 31.08%, H = 2.81%, Sn = 42.20%, Calcd. for $C_{37}H_{40}Sn_5O_{22}$: C = 31.72%, H = 2.86%, Sn = 42.39%).

This polymer was found not to contain any halogen as tested qualitatively. However, the liberation of hydrogen bromide and formic acid was observed during the reaction.

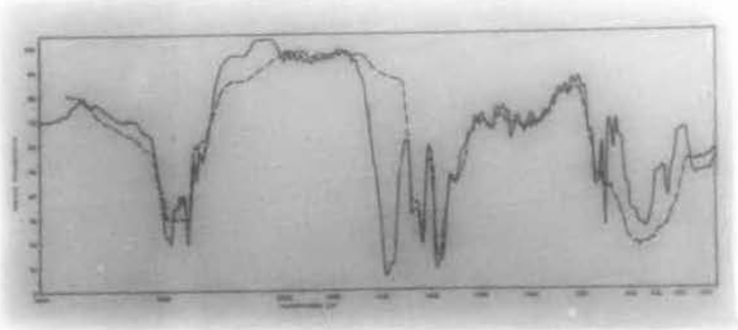


Fig. 2.3A IR spectrum of the compound obtained by heating phenyltin dihydroxy formate, $PhSn(OH)_2OCOH$ (dashed line). The spectrum of phenyltin dihydroxy formate (solid line) is shown for comparison.

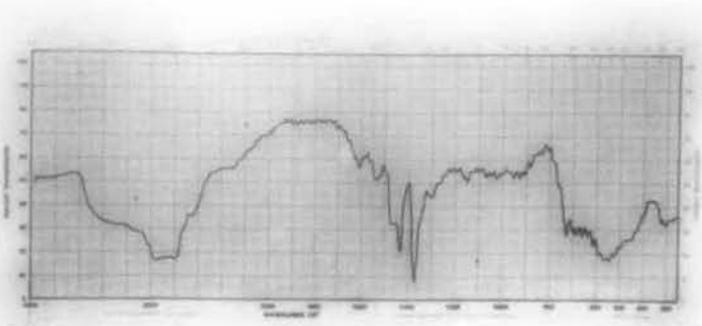


Fig. 2.4 IR spectrum of the compound $[Sn(OH)_4]_n$ containing few organic groups obtained by boiling phenyltin dihydroxy formate in dimethyl formamide.

On treatment with oxine by the method described earlier, this polymer also afforded phenyltin trioxinate, m.p. 302-303° (m.m.p).

The thermal decomposition of this polymer viz. $[C_6H_5Sn(OH)_2OCOH]_n$ was followed by IR spectroscopy and chemical tests. About 0.10 gm of the polymer was taken in a glass tube and was heated on a sulphuric acid bath at 280° for five minutes. The colour of the white material was changed to pale yellow. The gas evolved was identified as carbon monoxide and water by qualitative tests (93). The pale yellow product was identified as phenyl stannoic acid, PhSn(O)OH by IR comparison (fig. 2.3A) with standard spectrum (91). It may be mentioned here that Sn-H band is produced by heating trialkyltin formates (76). We could not detect any Sn-H bond in our case but, on the other hand, the Sn-O-Sn stretch broadened and also there was complete absence of OCO group vibrations.

The plymeric $[C_6H_5Sn(OH)_2OCOH]_n$ when dissolved in boiling dimethyl formamide, concentrated and precipitated with petroleum ether yielded a different polymeric material which by elemental analysis and IR spectrum (fig. 2.4) was identified as essentially polymeric $[Sn(OH)_4]_n$ having a very low carbon content. The low percentage of carbon may be due to the presence of a very few phenyl group acting as a terminal group (Found : C = 5.50%, H = 2.15%, Sn = 62.80%; Calcd. for H_4SnO_4 : H = 2.14%, Sn = 63.59%).

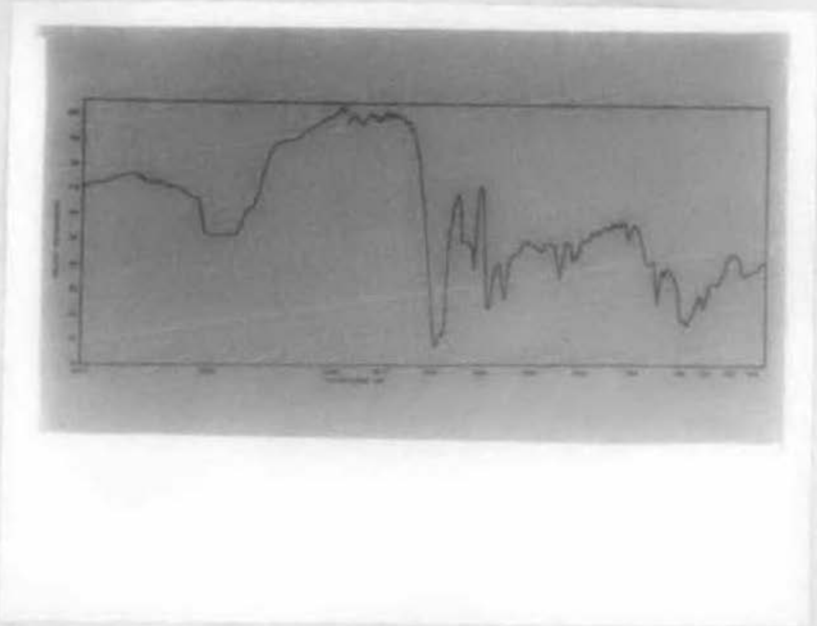
12. Reaction of triphenyltin formate with mercuric iodide:

To a solution of 2.69 gm of triphenyltin formate in 200 ml of benzene, a solution of 3.09 gm of mercuric iodide in 300 ml of ether was added slowly with stirring at room temperature for 8 hr and kept overnight . During stirring a white precipitate was formed and it was filtered off. 1.52 gm of white residue was obtained and was digested in a soxhlet with benzene for 12 hr. The residue, 1.02 gm (12A) obtained after digestion was found to be insoluble in common organic solvents and decomposed at 276°. The benzene solution on concentration yielded 0.50 gm of white solid, m.p. 266-268° (12B).

The original filtrate on slow evaporation gave the following fractions:

1) Shining crystals, 0.20 gm, m.p. 267-268° (12C)
2) Shining crystals, 0.35 gm, m.p. 262-267° (12D)
3) A crude mixture containing red and white materials, 4.15 gm (12E).

The fractions (12B), (12C) and (12D) were found to be identical (m.m.p) and mixed together. The mixture was recrystallised from benzene to give pure phenyl mercuric iodide, m.p. 269°, identified by mixed melting point determination with an authentic sample [lit (89) m.p. 266°].

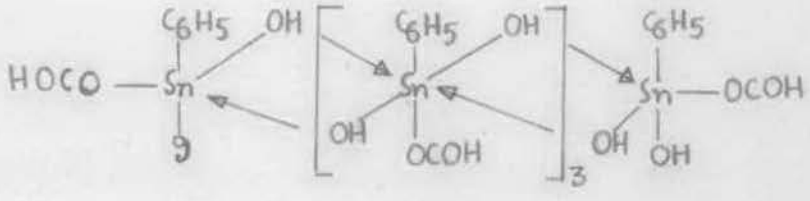


ig. 2.5 IR spectrum of polymeric compound phenyltin dihydroxy formate, $PhSn(OH)_2OCOH$ obtained from the reaction of triphenyltin formate and mercuric iodide.

The fraction (12E) was treated with 25 ml of petroleum ether and then filtered. The filtrate on evaporation afforded 0.64 gm of a white crystalline solid, m.p. 114-116° (12F) which on recrystallisation from benzene afforded crystals of melting point 120° and was identified as triphenyltin iodide by mixed melting point determination with an authentic sample [lit (89) m.p. 120-121°]. The residue after the above process was treated with 75 ml of hot benzene and filtered. The residue, 1.88 gm, which remained insoluble was identified as unreacted mercuric iodide by chemical tests according to A.I.Vogel (93). The benzene solution on evaporation yielded a white crystalline solid, 1.63 gm, m.p. 196-199°, which on recrystallisation from benzene had its melting point 200-201° and was identified as unreacted triphenyltin formate (m.m.p).

Identification of solid 12A:

The solid was identified as a polymer from its general physical properties. It showed the presence of iodide ion by qualitative chemical tests. From the elemental analysis and IR spectrum (fig. 2.5) this polymeric compound was identified essentially having the following composition.



(Found: C = 27.64%, H = 2.40%, I = 8.12%, Sn = 39.63%, Calcd. for $C_{35}H_{39}Sn_5O_{19}I$: C = 28.30%, H = 2.63%, I = 8.56%, Sn = 39.99%).

The liberation of iodide and formate ion were also detected during the course of reaction.

13. Reaction of triphenyltin acetate with mercuric chloride:

To a solution of 3.15 gm of triphenyltin acetate in 300 ml of ether, a solution of mercuric chloride, 2.09 gm, in 300 ml of ether was added with constant stirring at room temperature. A white precipitate was formed immediately, however, the stirring continued for 8 hr and the solution kept over night to ensure the complete reaction. The mixture was then filtered and a white residue, 1.70 gm, was obtained (13A). This solid (13A) was then digested in a soxhlet with benzene for 12 hr whereby a solid material 0.70 gm was left (13B). This material was insoluble in common organic solvents and infusible upto 360°. The filtrate on evaporation gave a white flaky crystal, m.p. 245-250° weighing 1.00 gm (13C).

The original filtrate on slow evaporation gave the following fractions:

1) Flaky shining crystals, 1.30 gm, m.p. 248-249° (13D)
2) White solid, 2.03 gm, m.p. 85-93° (13E)

The fraction (13E) was treated with 50 ml of petroleum ether and filtered, whereby a white flaky solid 0.10 gm, m.p. 245-248° (13F) was left. The filtrate on evaporation yielded white crystals, 1.90

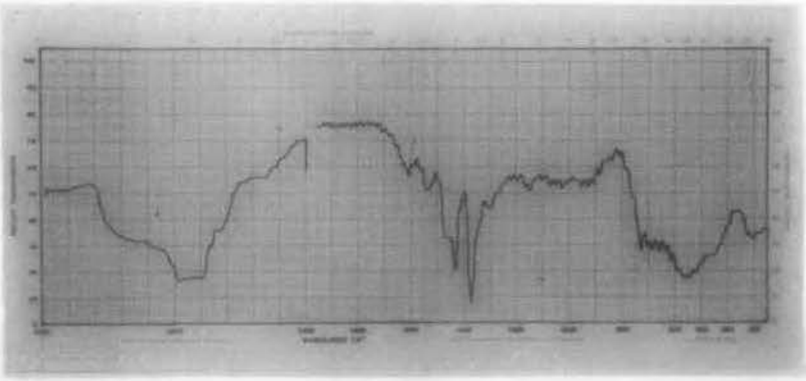


Fig. 2.6 IR spectrum of polymeric compound $[Sn(OH)_4]_n$ containing a few halogen/organic groups obtained from the reaction of triphenyltin acetate and mercuric chloride.

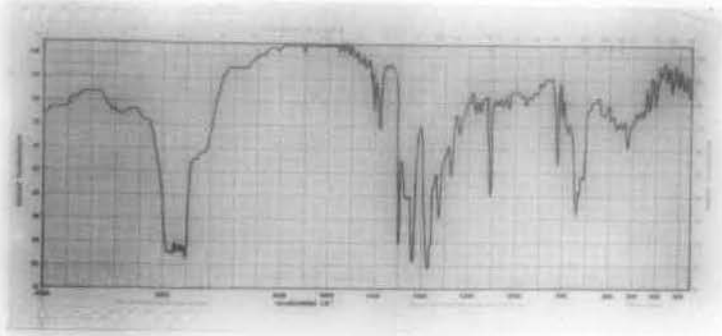
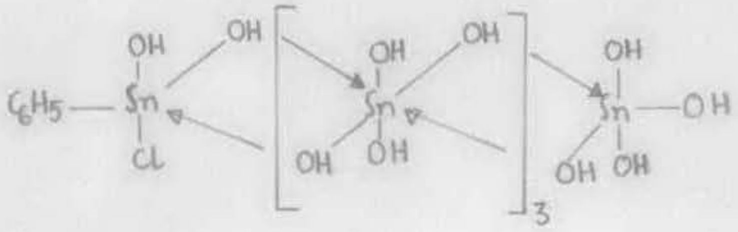


Fig. 2.7 IR spectrum of $(HO)_6Sn_2Ox_2$.

Sn, m.p. 102-104° which on further recrystallisation from petroleum ether afforded pure triphenyltin chloride, m.p. 106° (m.m.p). The fractions (13C), (13D) and (13F) were found to be identical (m.m.p) and mixed together. On further recrystallisation from benzene it afforded pure phenyl mercuric chloride, m.p. 251° (m.m.p).

Identification of the solid 13B:

The solid (13B) was found to be a polymeric compound from its general physical properties. Chlorine was detected in this polymer by qualitative chemical tests (93). From elemental analysis, IR spectrum (fig. 2.6) $\left[\nu(O-H) = 3400\ cm^{-1}, \nu_{as}(Sn-O-Sn) = 550\ cm^{-1}\right]$ and preparation of oxine derivatives this compound was identified essentially as polymeric $\left[Sn(OH)_4\right]_n$ with chlorine atom and phenyl groups probably acting as terminal groups of the polymer as suggested below:



(Found : C = 7.68%, H = 2.19%, Sn = 58.59%, Cl = 3.40%; Calcd. for

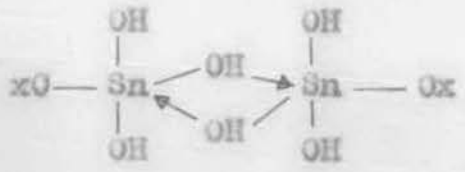
$C_6H_{23}Sn_5O_{18}Cl$: C = 7.11%, H = 1.78%, Sn = 58.65%, Cl = 3.51%).

Liberation of chloride and acetate ions have been detected qualitatively during the reaction.

The polymer gave, on treatment with oxine, two oxinates viz., phenyltin chloro dioxinate and a new organotin oxinate which has been formulated as $Sn_2(OH)_6Ox_2$. 0.50 gm of the polymer was treated with 0.80 gm of oxine in methanol solution. The mixture was refluxed for 4 hr. whereby a methanol insoluble yellow product was formed. The solution was then filtered and the residue, 0.60 gm (13G), was washed successively with hot methanol, benzene and tetrahydrofuran. It was found that the compound (13G) was insoluble in common organic solvents and infusible upto 360°. The original filtrate and the washings were mixed together and was then evaporated to dryness. The dried yellow solid was then washed thoroughly with hot petroleum ether whereby an insoluble fraction (13H) weighing 0.25 gm, m.p. 208-216° remained. The petroleum ether solution afforded only unreacted oxine (m.m.p). The yellow compound (13H) was recrystallised several times from benzene which afforded a yellow crystalline compound, m.p. 217-218° and was identified as phenyltinchlorodioxinate by mixed melting point determination with an authentic sample [lit (95), m.p. 218-219°]

The other product (13G) on the basis of elemental analysis and IR spectroscopy (fig. 2.7) was identified as dimeric $Sn_2(OH)_6Ox_2$

with bridging hydroxyl groups as follows:



(Found: $C = 32.98\%$, $H = 2.73\%$, $N = 4.43\%$, $Sn = 37.49\%$; Calcd. for $C_{18}H_{18}Sn_2N_2O_8$: $C = 34.43\%$, $H = 2.87\%$, $N = 4.46\%$, $Sn = 37.83\%$).

14. Reaction of triphenyltin acetate with mercuric bromide:

In 400 ml of ether 4.65 gm of triphenyltin acetate was dissolved. To that, 4.09 gm of mercuric bromide in 300 ml of ether was added and the suspension stirred for 6 hr at room temperature and kept over night. A white precipitate was formed and was filtered off whereby 3.84 gm of a residue (14A) was obtained. The residue was digested with benzene in a soxhlet for 12 hr and a white solid (14B), weighing 1.64 gm was left. This solid was found to be insoluble in common organic solvents and was infusible upto 360°. The benzene soluble fraction on evaporation, yielded 1.20 gm, m.p. 269-273°, of a flaky white material (14C).

The original filtrate on fractional crystallisation gave a flaky white solid, m.p. 268-274°, weighing 2.12 gm (14D) and a white solid, 1.74 gm, m.p. 115-120° (14E). The solid (14E) when treated with 50 ml of cold petroleum ether left a residue weighing 0.10 gm, m.p. 265-269° (14F). The filtrate on evaporation afforded

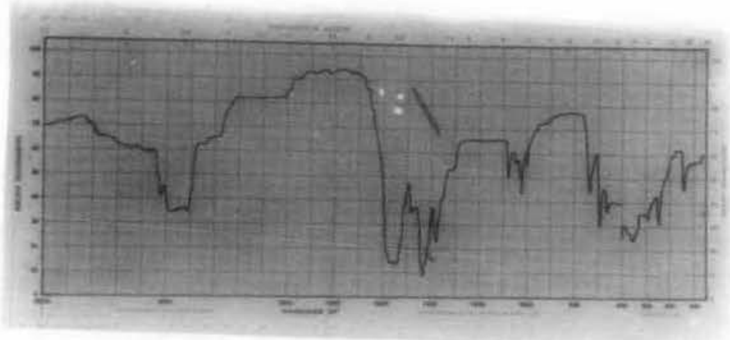


Fig. 2.8 IR spectrum of polymeric compound phenyltin dihydroxy acetate, $PhSn(OH)_2OCOCH_3$ obtained from the reaction of triphenyltin acetate and mercuric bromide.

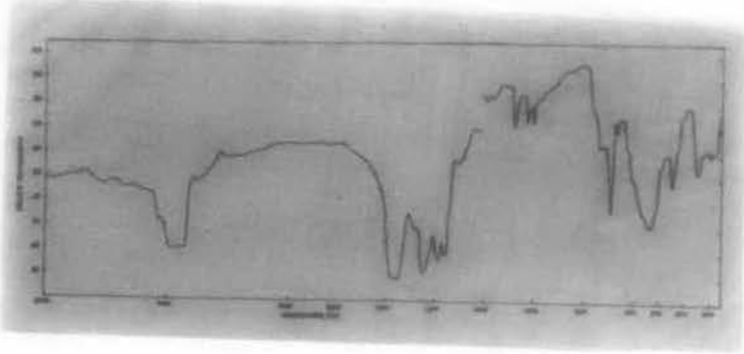


Fig. 2.9 IR spectrum of polymeric compound phenyltin dihydroxy propionate, $PhSn(OH)_2OCOCH_2CH_3$ obtained from the reaction of triphenyltin propionate and mercuric bromide.

a white crystalline compound (1.60 gm), m.p. 118-120°, which on recrystallisation from petroleum ether afforded pure triphenyltin bromide, m.p. 122° (m.m.p). The fractions (14C), (14D) and (14F) were identical (m.m.p) and were mixed together. After recrystallisation from benzene it gave pure phenyl mercuric bromide, m.p. 276° (m.m.p).

Identification of the solid 14B:

The solid was identified as a polymeric compound from its infusibility and insolubility in common organic solvents. The polymer did not contain any halogen. From elemental analysis and IR spectrum (fig. 2.3)the solid was identified as polymeric phenyltin dihydroxyacetate, $\left[C_6H_5Sn(OH)_2OCOCH_3\right]_n$.

(Found: C = 33.59%, H = 3.56%, Sn = 40.78%; Calcd. for $C_8H_{10}SnO_4$: C = 33.25%, H = 3.46%, Sn = 41.11%).

The liberation of bromide and acetate ions was detected in the solution during the reaction.

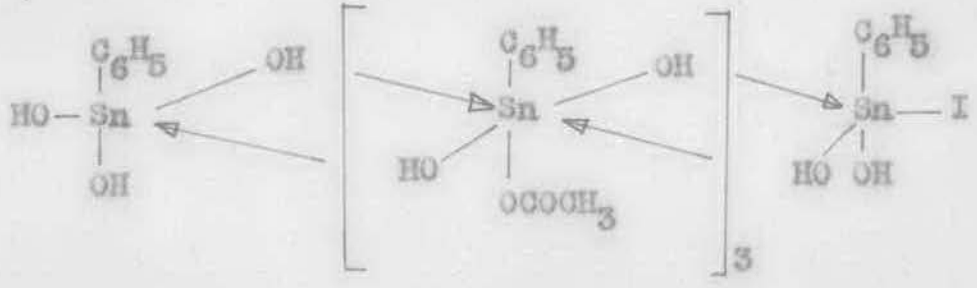
15. Reaction of triphenyltin acetate with mercuric iodide:

To a solution of 4.69 gm of triphenyltin acetate in 400 ml of ether, a solution of 5.21 gm of mercuric iodide in 1200 ml of ether was added slowly with constant stirring at room temperature. The stirring was continued for 8 hr and kept over night. After the filtration of the whole solution, 1.44 gm of a solid residue was obtained (15A). This solid after digestion with benzene in a soxhlet for 12 hr afforded a white solid, 1.30 gm (15B) which was found to be insoluble in common organic solvents and was infusible upto 360°. The filtrate after digestion was evaporated to dryness, afforded a white flaky solid, 1.10 gm, m.p. 265-269° (15C).

The original filtrate was completely evaporated and the solid obtained was first treated with 100 ml of cold petroleum ether while a portion of the solid went into solution. The petroleum ether solution on fractional crystallisation yielded two products, one of which was identified as unreacted triphenyltin acetate, m.p. 120-121° (m.m.p), 0.99 gm and the other fraction was identified as triphenyltin iodide, m.p. 120° (m.m.p), 2.15 gm. The petroleum ether insoluble portion was then treated with 150 ml of hot benzene. The benzene fraction on evaporation gave a flaky solid, m.p. 264-267°, 2.50 gm, was identical with (15C) (m.m.p) and were mixed together. After recrystallisation from benzene it was identified as phenyl mercuric bromide, m.p. 269° (m.m.p). The benzene insoluble fraction was found to be unreacted mercuric iodide (1.10 gm) by qualitative tests.

Identification of the solid 15B:

The polymeric compound (15B) showed the presence of iodine by qualitative tests. On the basis of elemental analysis, IR spectroscopy (similar spectrum with fig. 2.8) it was identified having essentially the following formula.



(Found : C = 29.07%, H = 2.65%, I = 8.38%, Sn = 39.3%; Calcd. for $C_{36}H_{45}Sn_5O_{17}I$: C = 29.39%, H = 3.06%, I = 8.64%, Sn = 40.38%).

This polymeric compound on treatment with oxine by the procedure described earlier, afforded phenyltiniodo dioxinate and phenyltin trioxinate. Thus 0.50 gm of the polymer when treated with an excess of oxine (0.70 gm) in refluxing methanol yielded 0.19 gm of phenyltiniodo dioxinate, $PhSnIOx_2$, m.p. 212^{0} (m.m.p) [lit (86) m.p. 212^{0}] and 0.30 gm of phenyltin trioxinate, $PhSnOx_3$, m.p. 302-303^{0} (m.m.p).

The formation of iodide and acetate ions during the reaction were detected.

16. Reaction of triphenyltin propionate with mercuric chloride:

3.57 gm of triphenyltin propionate was dissolved in 400 ml of benzene. To it a solution of 2.23 gm of mercuric chloride was added with stirring for 8 hr at room temperature and kept overnight. A white precipiate was formed and was filtered off. The residue, 2.30 gm (16A) was soxhleted with benzene for 12 hr whereby a white solid 0.50 gm, (16B) was left. This white compound was identified as a polymeric compound form its insolubility in common organic solvents and infusibility upto 360° as well. The benzene solution obtained after digestion was evaporated to dryness whereby a white compound 1.80 gm, m.p. $248-251^{\circ}$ was obtained (16C). The original filtrate after complete evaporation was treated with 100 ml of cold petroleum ether. The petroleum ether solution after evaporation yielded a white crystalline compound, 2.11 gm, m.p. $100-104^{\circ}$ which was identified as triphenyltin chloride after several recrystallisation from petroleum ether, m.p. 106° (m.m.p). The petroleum ether insoluble fraction, 0.40 gm, m.p. $248-250^{\circ}$ was mixed with (16C) (m.m.p) and after recrystallisation from benzene identified as phenyl mercuric chloride, m.p. 251° (m.m.p).

Identification of the solid 16B:

The polymeric compound (16B), from the elemental analysis and IR comparison with fig. 2.6 appeared to be a very similar compound as obtained from the reaction of triphenyltin acetate with mercuric chloride (experiment No. 13, polymeric compound 13B). In this compound the amount of phenyl groups present was, however, much lower as observed from the lower carbon content of the polymer.

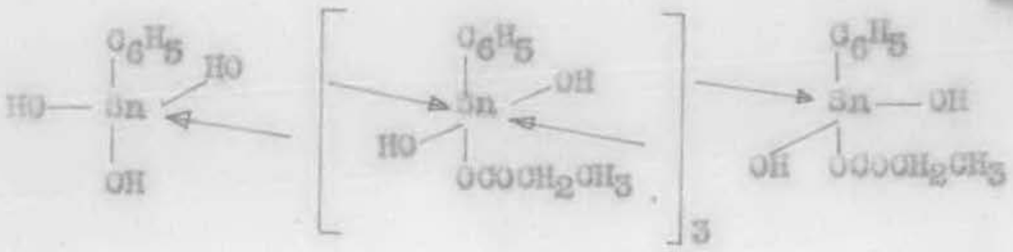
On this basis, the polymeric compound has been identified essentially as polymeric $[Sn(OH)_4]_n$ with a few phenyl/propionate as terminal groups. (Found : C = 1.79%, H = 1.67%, Sn = 62.80%; Calcd. for H_4SnO_4 : Sn = 63.59%). No chloride ion, could be detected in the polymer by qualitative tests. Liberation of chloride and propionate ions were, however, detected during the course of reaction.

17. Reaction of triphenyltin propionate with mercuric bromide:

To a solution of 2.60 gm of triphenyltin propionate in 300 ml of benzene, 2.21 gm of mercuric bromide in 400 ml of ether was added and the suspension was stirred for 8 hr at room temperature and kept overnight. A white precipitate was formed during reaction and was filtered off. The residue, 2.00 gm (17A), was digested with benzene in a soxhlet for 12 hr whereby a white compound, 0.90 gm (17B) was left. This compound, identified as polymer, was found to be infusible upto 360° and was insoluble in common organic solvents. The benzene solution after digestion, when evaporated afforded 1.10 gm of white leafy crystals, m.p. 268-271° (17C). The original filtrate was evaporated to dryness and the dried white mass was treated with 75 ml of cold petroleum ether. The petroleum ether soluble fraction after evaporation gave a white crystalline compound, 1.30 gm, m.p. 116-120° which was identified as triphenylti bromide after several recrystallisation from petroleum ether, m. 122° (m.m.p). The petroleum ether insoluble fraction, 1.02 gm, m 265-270° was identical with fraction (17C) (m.m.p) and were mixe together. The mixed compound was then recrystallised several times from benzene when a crystalline compound, m.p. 276°, was isolated and was identified as phenyl mercuric bromide (m.m.p).

Identification of the solid 17B:

This polymeric compound (17B) was on the basis of elemental analysis and IR spectrum (fig. 2.9) could be assigned the following formula.



(Found : C = 34.22%, H = 3.37%, Sn = 40.35%; Calcd. for $C_{42}H_{56}Sn_5O_{19}$: C = 34.43%, H = 3.84%, Sn = 40.75%).

Absence of bromide ion was noted in the polymer by qualitative tests.

The formation of bromide and propionate ions were detected during the course of the reaction by qualitative chemical tests.

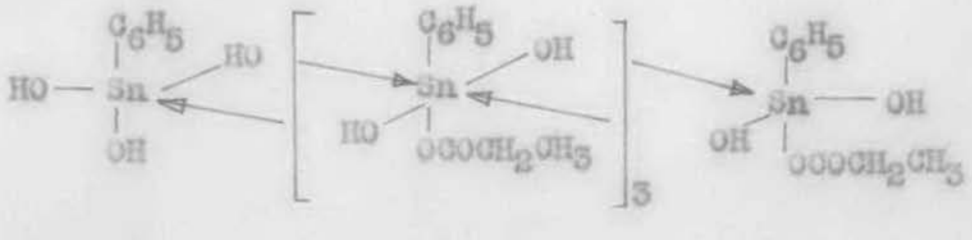
18. Reaction of triphenyltin propionate with mercuric iodide:

To a solution of 6.08 gm of triphenyltin propionate in 500 ml benzene, 6.50 gm of mercuric iodide in 900 ml of ether was added and the suspension stirred for 7 hr at room temperature and kept overnight. A white precipitate was formed and was filtered off. The residue, 1.95 gm (18A), was digested with benzene in a soxhlet for 12 hr whereby a white benzene insolube compound, 1.00 gm was obtained (18B). This was found to be a polymeric compound from its infusible nature upto 360° and insolubility in common organic solvents. The benzene solution on evaporation yielded 0.95 gm of a crystalline compound, m.p. 264-268° (18C).

The original filtrate was then evaporated to dryness and was treated with 250 ml of warm petroleum ether. The petroleum ether solution on fractional crystallisation afforded [illegible].00 gm of unreacted triphenyltin propionate, m.p. 122° (m.m.p) and 2.90 gm of triphenyltin iodide, m.p. 120° (m.m.p). The petroleum ether insoluble fraction on treatment with benzene afforded from the benzene soluble fraction, 0.75 gm of a crystalline compound, m.p. 264-268° which was identical with (18C) (m.m.p) and were mixed together. This then on recrystallisation from benzene afforded pure phenyl mercuric iodide, m.p. 269° (m.m.p). The benzene insoluble fraction, however, was identified as unreacted mercuric iodide, 3.20 gm from qualitative tests.

Identification of the solid 18B:

This polymeric compound on the basis of elemental analysis and IR comparison with fig 2.9 was found to be the same compound as obtained from the reaction of triphenyltin propionate with mercuric bromide (experiment No-17; compound-17B) and has been formulated as below:



(Found : C = 34.70%, H = 3.31%, Sn = 40.57%; Calcd. for $C_{42}H_{56}Sn_5O_{19}$: C = 34.43%, H = 3.84%, Sn = 40.75%).

Iodine was absent in this polymer, however the formation of iodide and propionate ions, were detected after the reaction.

19. <u>Reaction of tributyltin acetate with mercuric chloride</u>:

3.57 gm of tributyltin acetate was dissolved in 200 ml of ether. To that a solution of 2.77 gm of mercuric chloride in 300 ml of ether was added with stirring for 7-8 hr and kept overnight. A white precipitate which appeared in solution was filtered off. The residue thus obtained, 0.60 gm (19A), was washed thoroughly with hot benzene, other and tetrahydrofuran. It was found insoluble in all common organic solvents and infusible upto 360°. On this basis it was identified as a polymeric compound.

The filtrate was evaporated to dryness and the whole mass was treated with 20 ml of ice cold petroleum ether (bp 40-60°) and filtered rapidly. On evaporating the petroleum ether solution and repeating the same process 0.75 gm of a liquid (19B) was obtained. The insoluble fraction was then treated with 100 ml of hot petroleum ether. On fractional crystallisation, the petroleum ether solution afforded 1.40 gm of a white compound, m.p. 122-127°, which on several recrystallisation from petroleum ether was identified as butyl mercuric chloride, m.p. 127-128° [lit (89) m.p. 127-130°] (Found: C = 16.32%, H = 2.89%; Calcd. for C_4H_9HgCl : C = 16.41%, H = 3.08%), and 1.88 gm of unreacted tributyltin acetate, m.p. 84° (m.m.p). Unreacted mercuric chloride, 1.45 gm, identified by qualitative tests, was left as petroleum ether insoluble part.

Identification of the liquid 19B:

The liquid (19B) was identified as tributyltin chloride on the basis of IR comparison with standard spectrum (91) and also by converting the liquid (tributyltin chloride) to its solid fluoride derivative.

Conversion of tributyltin chloride to tributyltin fluoride:

The liquid tributyltin chloride (0.78 gm) was treated with 20 ml of 20% ethanolic solution of potassium fluoride and then heated on a water bath for 1 hr. The mixture was then poured into a large volume of cold water and subsequent filtration yielded 0.74 gm of a white solid, m.p. 208-212°. On repeated crystallisation from ethanol, pure tributyltin fluoride, m.p. 216° [lit (1) m.p. 218-219°]

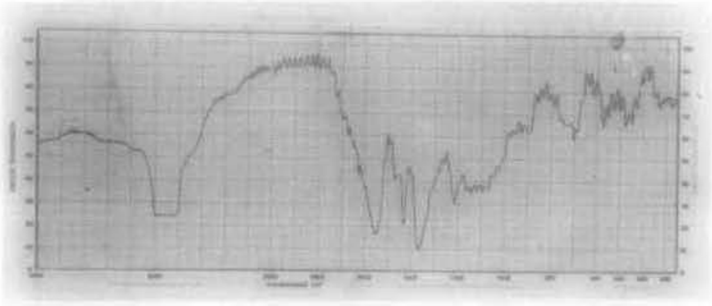


Fig. 2.10 IR spectrum of polymeric compound butyltin dihydroxy acetate, $BuSn(OH)_2OCOCH_3$ obtained from the reaction of tributyltin acetate and mercuric chloride.

was obtained. (Found: C = 46.43%, H = 8.61%, Sn = 38.13%; Calcd. for $C_{12}H_{27}SnF$: C = 46.65%, H = 8.75%, Sn = 38.45%).

Identification of the solid 19A:

The polymeric compound (19A) on the basis of elemental analysis and IR spectrum (fig. 2.10) was identified as polymeric butyltin dihydroxy acetate, $[BuSn(OH)_2OAc]_n$ (Found: C = 26.57%, H = 5.23%, Sn = 43.96%; Calcd. for $C_6H_{14}SnO_4$: C = 26.78%, H = 5.21%, Sn = 44.16%).

Chloride ion and acetate ion were detected by qualitative tests during the reaction.

20. Reaction of tripropyltin acetate with mercuric chloride:

4.60 gm of tripropyltin acetate was made into solution in 300 ml of ether. To that a solution of 4.10 gm of mercuric chloride in 600 ml of ether was added. The solution was stirred for 7-8 hr at room temperature and kept over night. A white precipitate was formed and filtered off. The residue, 0.95 gm (20A), was washed thoroughly with hot benzene, ether and tetrahydrofuran, may be considered to be a polymer because it did not melt even at 360° and insoluble in common organic solvents.

The filtrate was worked up adopting the same procedure as described in experiment No. 19. The following products were obtained:

1. Propyl mercuric chloride : 2.40 gm, m.p. 144° (m.m.p)
[lit (5) m.p. 144°]

2. tripropyltin chloride: 1.00 gm
3. unreacted mercuric chloride: 2.00 gm
4. unreacted tripropyltin acetate: 2.30 gm
   m.p. 99° (m.m.p) [lit (89) m.p. 100°]

In this case also the liquid tripropyltin chloride was converted to its solid fluoride derivative by treatment with potassium fluoride as described before. The tripropyltin fluoride had its melting point 274° (m.m.p) [lit (5) m.p. 275°].

Identification of the solid 20A:

On the basis of elemental analysis and IR spectrum (ν(OH) = 3400 cm^{-1}, ν_{as}(COO) = 1560 cm^{-1}, ν_{as}(Sn-O-Sn) = 550 cm^{-1}) the polymeric compound (20A) was identified as polymeric propyltin dihydroxy acetate, $[\mathrm{PrSn(OH)_2OAc}]_n$ (Found: Sn = 46.21%; Calcd. for $C_5H_{10}SnO_4$: Sn = 46.60%).

Qualitative chemical tests showed the formation of chloride and acetate ions after the reaction.

21. Reaction of tricyclohexyltin acetate with mercuric chloride:

4.27 gm of tricyclohexyltin acetate was dissolved in 200 ml of ether. To that, 2.71 gm of mercuric chloride in 400 ml of ether was added. The solution was stirred for 6 hr and kept overnight. No precipitate was formed during the stirring. The solution was complete evaporated and treated with 100 ml of benzene. The benzene solution afforded 4.20 gm of unreacted tricyclohexyltin acetate, m.p. 62-63^{o} (m.m.p). The benzene insoluble fraction, 2.69 gm, was identified as unreacted mercuric chloride. No other products could be isolated.

22. Reaction of diphenyltin diacetate with mercuric bromide:

To a solution of 2.35 gm of diphenyltin diacetate in 200 ml of ether, 2.16 gm of mercuric bromide in 400 ml of ether was added with stirring. After 8 hr, the stirring was discontinued and the mixture kept overnight. A white precipitate was formed which was filtered to give 2.81 gm of a white residue (22A). The residue was digested in a soxhlet for 12 hr with benzene. The benzene insoluble fraction, 1.70 gm (22B), was identified as a polymeric compound from its infusibility upto 360^{o} and insolubility in common organic solvents. The benzene solution on concentration afforded 1.11 gm of a white flaky crystalline compound, m.p. 265-267^{o} (22C).

The original filtrate on concentration yielded 1.99 gm of a compound, m.p. 266-270^{o} which was found to be identical with the compound (22C) (m.m.p) and were mixed together. Several recrystallisation of this mixture from benzene afforded a white crystalline compound, identified as phenyl mercuric bromide, m.p. 276^{o} (m.m.p).

Identification of the solid 22B:

The solid (22B), from superimpossible IR spectrum with that of the compound 14B obtained from the reaction of triphenyltin acetate with mercuric bromide (experiment No 14) was found to be the same compound having the essential composition as phenyltin dihydroxy acetate, $[C_6H_5Sn(OH)_2OCOCH_3]_n$ (Found: Sn = 40.95%; Calcd. for $C_8H_{10}SnO_4$: Sn = 41.11%).

In this case also the formation of bromide ion and acetate ion were detected after reaction by qualitative tests.

23. Reaction of polymeric phenyl stannoic dihydroxy acetate with mercuric bromide:

It was found that the reaction of polymeric phenyltin dihydroxy acetate (obtained from the experiment No. 14) with mercuric bromide did not take place at room temperature. But when 1.20 gm of the polymer was treated with 1.58 gm of mercuric bromide in 200 ml of refluxing benzene for 8 hr, the reaction took place yielding 1.50 gm of phenyl mercuric bromide (m.m.p) and a polymeric product 0.76 gm. The polymer on the basis of IR comparison with the product 13B obtained from the reaction of triphenyltin acetate with mercuric chloride (experiment No. 13) was found to be almost an identical product having the chemical composition essentially as $Sn(OH)_{4\ n}$ (Found: Sn = 62.62%; Calcd. for H_4SnO_4 : Sn = 63.39%).

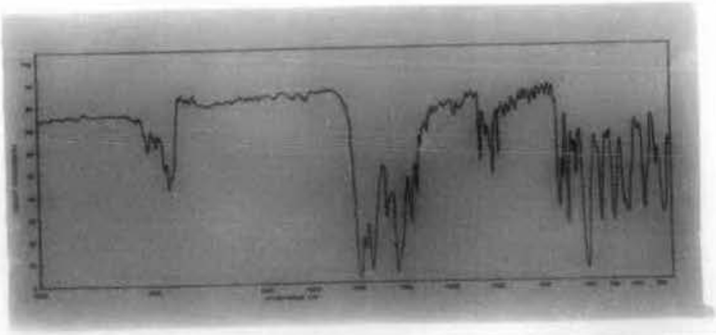


Fig. 2.11 IR spectrum of phenyl stannoic acetate, $PhSn(O)OCOCH_3$.

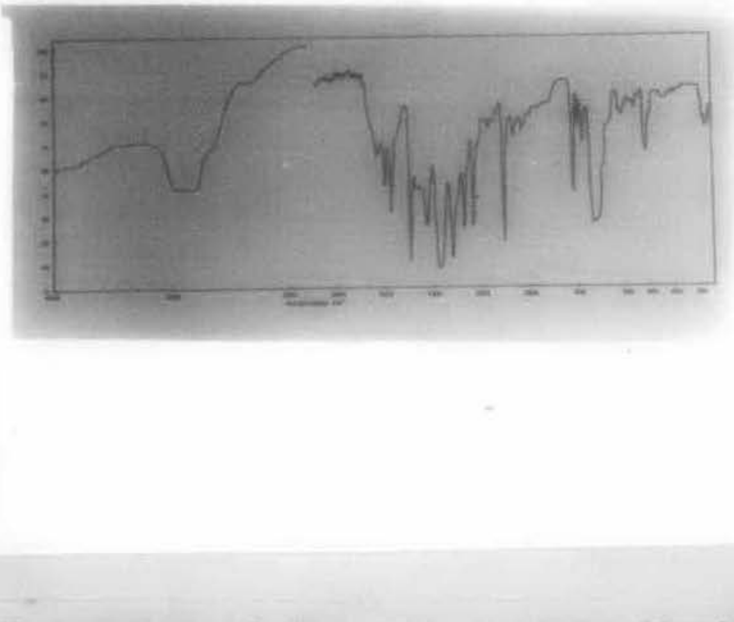


Fig. 2.12 IR spectrum of Phenyltin acetate dioxinate, $PhSn(OCOCH_3)Ox_2$.

Liberation of hydrogen halide and acetic acid during the reaction was detected.

24. Reaction of triphenyltin acetate with mercuric acetate:

To a solution of 2.57 gm of triphenyltin acetate in 400 ml of ether, 2.01 gm of mercuric acetate in 200 ml of ether was added and the suspension was stirred at room temperature for 7 hr and kept overnight. A white precipitate was formed which was filtered off. The residue, 1.76 gm (24A) infusible upto 360° was washed thoroughly with ether, benzene and tetrahydrofuran. It was found that the solid (24A) was sparingly soluble in chloroform and was recrystallised from this solvent.

The filtrate on concentration afforded 2.25 gm of a needle shaped white crystals, m.p. 122-125°. After several crystallisation from petroleum ether this crystalline compound was identified as diphenyl mercury, m.p. 124° [lit (89) m.p. 125°] by mixed melting point determination with an authentic sample of diphenyl mercury.

Identification of the solid 24A:

On the basis of general physical properties, elemental analysis and IR spectrum (fig. 2.11) the solid (24A) was identified as polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$ (Found: C = 34.98%, H = 2.73%, Sn = 43.25%; Calcd. for $C_8H_8SnO_3$: C = 35.46%, H = 2.96%, Sn = 43.85%).

Preparation of oxine derivative of the polymer 24A:

0.60 gm of the polymeric phenyl stannoic acetate was taken in 200 ml of methanol. To that, 0.85 gm of oxine (8 hydroxy quinoline), in 25 ml of methanol was added and the suspension was refluxed for 8 hr. The solution became clear yellow. The solvent was then completely evaporated on a water bath and the excess oxine was removed by washing with hot petroleum ether. The yellow solid 1.15 gm, m.p. 231-240^{o} obtained as petroleum ether insoluble fraction, after several recrystallisation from benzene/petroleum ether mixture afforded a yellow crystalline compound, m.p. 243-244^{o}. The compound was identified as a new organotin carboxylate oxinate viz. phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$ on the basis of IR spectrum (fig. 2.12) and elemental analysis. (Found : C = 58.06%, H = 4.04%, N = 4.64%, Sn = 21.85%; Calcd. for $C_{26}H_{20}SnN_2O_4$: C = 57.56%, H = 3.70%, N = 5.16%, Sn = 21.87%).

The same oxinate was also obtained by the exchange reaction between phenyltin chlorodioxinate and silver acetate in refluxing methanol. The isolated oxinate compound had a superimposible IR spectrum with that of the oxinate obtained from the polymer 24A and oxine. The mixed melting point determination showed no depression in melting point indicating both the compound to be same. The details of the preparation of phenyltin acetate dioxinate from phenyltin chlorodioxinate have been included in Chapter IV of the present thesis.

Tests for acetate ion in the solution after the reaction of triphenyltin acetate with mercuric acetate were performed qualitatively which gave positive result.

25. Reaction of triphenyltin acetate with phenylmercuric acetate:

To a solution of 0.98 gm of triphenyltin acetate in 150 ml of ether, 1.62 gm of phenyl mercuric acetate (1:2) in 200 ml of ether was added and the mixture was stirred at room temperature for 7 hr and kept overnight. The whole solution was filtered whereby a residue (25A) weighing 0.65 gm was obtained. The residue was found to be insoluble in common organic solvents and was washed throughly with benzene, ether etc. It, however, was found to have a little solubility in chloroform and was crystallised from chloroform. This was found to be infusible upto 360°.

The filtrate on evaporation afforded a white crystalline compound, 1.60 gm, m.p. 120-124° which was identified as diphenyl mercury, m.p. 124° by mixed melting point determination with an authentic sample after several recrystallisation from petroleum ehter.

Identification of the solid 25A:

This solid on the basis of IR comparison with authentic spectrum of polymeric phenyl stannoic acetate and preparation of oxine derivative viz., phenyltin acetate dioxinate was identified as phenyl stannoic acetate polymer, $\left[\mathrm{PhSn(O)OAc}\right]_n$.

The formation of acetic acid during the reaction was detected by qualitative tests.

The reaction of triphenyltin acetate with phenyl mercuric acetate in 1:1 ratio was also carried out in the similar condition as stated above. The products obtained are essentially same excepting that in this case fifty percent unreacted triphenyltin acetate was isolated. This indicated that this reaction also proceeded in 1:2 ratio of the reactants.

26. Reaction of tribenzyltin acetate with mercuric acetate:

2.80 gm of tribenzyltin acetate was dissolved in 300 ml of ether. Mercuric acetate 3.95 gm (1:2) in 400 ml of ether was added to the etheral solution of tribenzyltin acetate. The suspension was stirred for 8 hr at room temperature and kept overnight. The solution was clear and evaporated to dryness. The dried mass was then treated with petroleum ether. The petroleum ether solution was then slowly evaporated whereby 4.30 gm of a crystalline white solid m.p. 122-128° was obtained. This was then recrystallised several times from petroleum ether and was identified as benzyl mercumic acetate, m.p. 128-129° (fig. 2.15). (Found : C = 30.99%, H = 2.98%; Calcd. for $C_9H_{10}HgO_2$: C = 30.85%, H = 2.86%).

The petroleum ether insoluble fraction, 1.80 gm, m.p. 135-140° was crystallised several times from benzene which afforded a white crystalline compound m.p. 142-143° (26A).

Identification of the compound 26A:

On the basis of elemental analysis and IR spectrum the solid

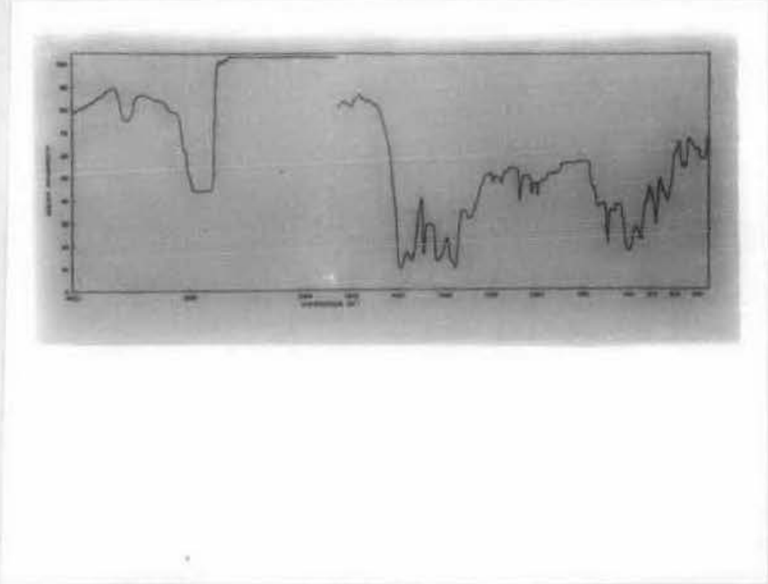
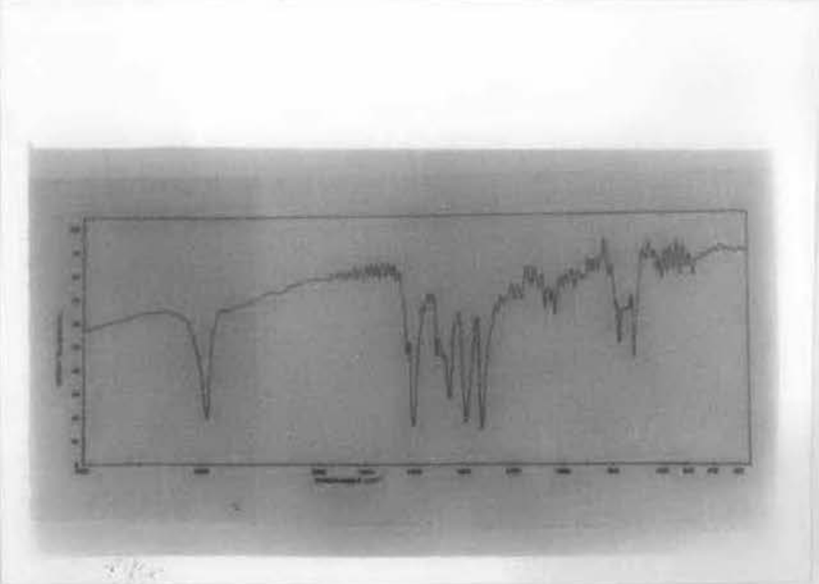


Fig. 2.13 IR spectrum of 1,3 dibenzyl 1,3 dihydroxy 1,3 diacetoxy distannoxane, BzAcO(OH)Sn(OH)OAcBz.



ig. 2.15 IR spectrum of benzylmercuric acetate, $BzHgOCOCH_3$.

had been characterised as 1,3 dibenzyl 1,3 dihydroxy 1,3 diacetoxy distannoxane, Bz(OH)OAcSnOSnOAc(OH)Bz. (Found: C = 36.33%, H = 3.47%, Sn = 40.23%; Calcd. for $C_{18}H_{22}Sn_2O_3$: C = 36.78%, H = 3.74%, Sn = 40.41%).

On the basis of the comparison of IR spectra of tribenzyltin acetate, hexabenzyl distannoxane and this new compound 26A (fig. 2.13), the following assignments of the major bands were made:

3520 cm^{-1} = OH stretching
1590 cm^{-1}, 1540 cm^{-1} = OCO stretching (asymmetric)
605 cm^{-1} = Sn-O-Sn stretching. (asymmetric)

Since this compound did not afford dibenzyltin dioxinate on treatment with oxine, it may be reasonable to believe that $\genfrac{}{}{0pt}{}{Bz}{Bz}\!>\!Sn<$ grouping possibly was not present in this compoud.

Formation of acetic acid during the reaction was observed by qualitative tests as described earlier.

27. Reaction of tripropyltin acetate with mercuric acetate:

To a 300 ml etheral solution of 3.08 gm of tripropyltin acetate, 3.20 gm of mercuric acetate in 400 ml of ether was added and stirred for 6 hr at room temperature and kept overnight. After that the whole solution was evaporated on a water bath and the solid thus obtained was treated with 200 ml of hot petroleum ether. The petroleum ether solution yielded 3.05 gm of unreacted tripropyltin acetate (m.m.p). The petroleum ether insoluble fraction was found to be unreacted mercuric acetate, 3.18 gm, by qualitative tests and melting point determination. Hence it was observed that practically no reaction took place.

28. Reaction of tributyltinacetate with mercuric acetate:

Tributyltin acetate and mercuric acetate in ethereal suspension was stirred for 8 hr in 1:1 proportion at room temperature. By working up the reaction mixture by the same procedure as described in experiment No. 27, tributyltin acetate and mercuric acetate could be recovered in original quantities.

29. Reaction of tricyclohexyltin acetate with mercuric acetate:

Quantitative amount of unreacted tricyclohexyltin acetate and mercuric acetate were recovered after a 1:1 proportion of ethereal solution of tricyclohexyltin acetate and mercuric acetate was stirred for 8 hr at room temperature.

30. Reaction of triphenyltin acetate with cadmium iodide:

2.63 gm of triphenyltin acetate was dissolved in 400 ml of ether. To that, 2.35 gm of solid cadmium iodide was added and the suspension was stirred for 8 hr at room temperature and kept over-

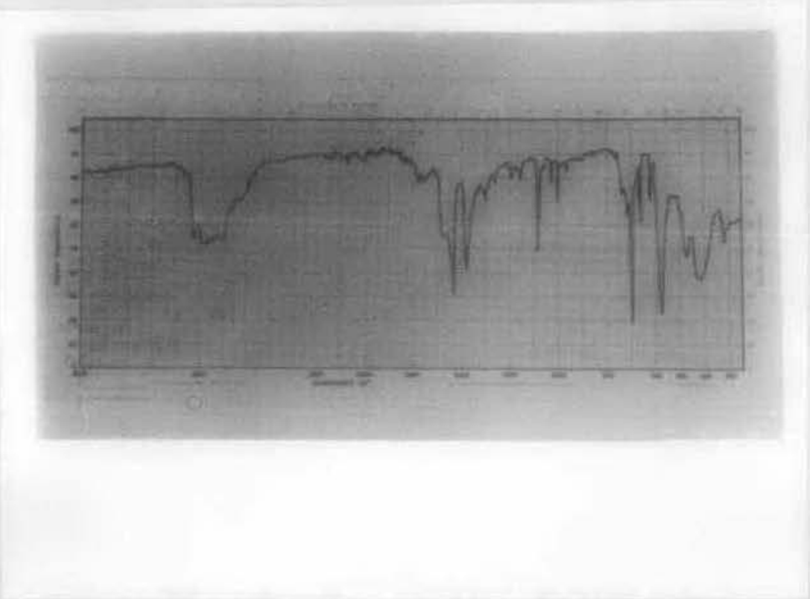


Fig. 2.14 IR spectrum of diphenyltin oxide, Ph_2SnO.

night. The whole solution was evaporated to dryness and the solid mass was treated with 150 ml of methanol and filtered. The methanol solution on concentration afforded 2.30 gm of unreacted cadmium iodide identified by qualitative chemical tests. The methanol insoluble fraction was then treated with 100 ml of hot benzene and the benzene solution on concentration afforded a white crystalline solid, 1.23 gm, m.p. 218-222°, which on repeated crystallisation from benzene afforded a white crystalline compound, m.p. 224°, identified as tetraphenyltin by mixed melting point determination with authentic sample of tetraphenyltin [lit (88), m.p. 225°]. The benzene insoluble fraction, 0.85 gm, was found to be insoluble in all common organic solvents and was infusible upto 360°. This solid was identified as polymeric stannoxane of the type Ph_2SnO on the basis of IR comparison (fig. 2.14) with standard spectrum (91) and preparation of oxine derivative, diphenyltindioxinate.

Preparation of oxine derivative of the polymeric product:

The oxine derivative was prepared according to Kupchik et al (115). The solid was treated with hot alcoholic solution of oxine. A yellow crystalline product was isolated which on further crystallisation from benzene afforded diphenyltin dioxinate, m.p. 248-249° [lit (115) m.p. 254-256° and lit (116) m.p. 248°], identical (m.m.p) with an authentic sample of diphenyltin dioxinate.

The same products viz., tetraphenyltin and polymeric diphenyltin oxide could be isolated even if a very small amount of cadmium iodide was used. This indicated that cadmium iodide did not take part in the overall reaction but acted as a catalyst.

Test for acetic acid gave a positive result in the solution after the completion of the reaction.

31. Reaction of triphenyltin formate with cadmium iodide:

3.40 gm of triphenyltin formate was stirred with 3.21 gm of cadmium iodide in 300 ml of tetrahydrofuran for 8 hr and kept overnight. The solvent was evaporated and the solid was worked up following the method as described in experiment No. 30. 1.46 gm of tetraphenyltin (m.m.p) and 1.24 gm of polystannoxane of the type Ph_2SnO (identified by IR comparison and preparation of oxine derivative) were isolated.

Formation of formic acid was detected qualitiatively in the solution after reaction adopting the procedure mentioned earlier.

Infrared spectral data for different polymeric compounds are presented here in tabular form. Nujol mull have been used in all the cases. The following abbreviations have been used:

s = strong
m = medium
w = weak
v = very
b = broad
sh = shoulder

Table - IV

Spectral data (in cm^{-1}) of the Polymeric Compounds of the type $PhSn(OH)_2OCOH$:

Products obtained from the reactions of			
$Ph_3SnOCOH$ $+HgCl_2$	$Ph_3SnOCOH$ $+HgBr_2$	$Ph_3SnOCOH$ $+HgI_2$	Suggested assignments
3540 w,b	3540 w,b	3540 w,b	-OH stretch
3370 w,b	3370 w,b	3370 w,b	
1575 v,s	1580 v,s	1580 v,s	ν_{as}(OCO)
1550 s	1550 s	1545 s	
1300 w	1300 w	1300 w	
1160 w	1160 w	1160	C-H in plane deformation
1075 m	1075 m	1070m	C-H in plane deformation
1025 w	1020 w	1020 w	
1000 w	1000 w	1000 w	Ring vibration
725s	725 s	725 s	C-H out of plane deformation
690 s	690 s	690 s	
660 w	660 w	660 m	
560 s,vb	560 s,v,b	560 s,vb	ν_{as}(SnOSn)
500 vw	500 sh	500 vw	
480 vw	480 sh	480 vw	
440 m	440 m	440 m	ν_{B_1}

Contd...

Table-IV (Contd.)

Products obtained from the reactions of $Ph_3SnOCOH$ + $HgCl_2$	$Ph_3SnOCOH$ + $HgBr_2$	$Ph_3SnOCOH$ + HgI_2	Suggested assignments
340 w	340 m	330 m	
280 w	285 w	280 w	ν_s(SnPH)

Table-V

Spectral data (in cm^{-1}) of the polymeric compounds of the type $PhSn(OH)_2OCOCH_3$.

Products obtained from the reactions of $Ph_3SnOCOCH_3$ + $HgBr_2$	$Ph_3SnOCOCH_3$ + HgI_2	Suggested assignments
3540 w,b	3540 w,b	-OH stretch
3370 w,b	3380 w,b	
1560 vs,b	1560 vs,b	ν_{as}(OCO)
1160 ww	1160 w	C-H in plane deformation
1075 m	1080 m	C-H in plane deformation
1025 m	1030 m	

Contd..

Table-V

Products obtained from the reactions of		
$Ph_3SnOCOCH_3$ $+ HgBr_2$	$Ph_3SnOCOCH_3$ $+ HgI_2$	Suggested assignments
1005 w	1010 m	Ring vibration
730 s	730 s,sh	C-H out of plane deformation
690 s	695 s	
665 m	670 vw	
560 s,b	570 s,b	ν_{as}(SnOSn)
500 w	505 vw	
475 w	480 w	
445 m	440 w	ν_{B_1}
340 m	335 s	
270 vw	275 vw	ν_s(SnPh)

Table- VI

Spectral data (in cm^{-1}) of the polymeric compounds of the type $PhSn(OH)_2OCOCH_2CH_3$:

Products obtained from the reactions of		
$Ph_3SnOCOCH_2CH_3$ + $HgBr_2$	$Ph_3SnOCOCH_2CH_3$ + HgI_2	Suggested assignments
3550 w,b	3540 w,b	-OH stretch
3370 w,b	3370 w,b	
1880 vw	1880 vw	
1820 vw	1820 vw	
1580 s	1580 s	$\nu_{as}(OCO)$
1540 s	1550 s	
1160 vw	1160 w	C-H in plane deformation
1080 m	1080 m	C-H in plane deformation
1020 w	1025 w	
1005 w	1010 w	Ring vibration
800 w	810 w	C-C sym stretch
725 m	730 m	C-H out of plane deformation
690 s	690 s	
660 vw	660 vw	
560 s,b	570 s,b	$\nu_{as}(SnOSn)$
500 m	500 m	
450 m	450 w	νB_1
340 m	340 w	
270 vw	275 vw	$\nu_s(SnPh)$

Table- VII

Spectral data (in cm^{-1}) of the polymeric compound, PhSn(O)OH:

Products obtained from the reactions of		
$Ph_3SnOCOH$* + $HgCl_2$ in solvents (not properly dried)	$Ph_3SnOCOH$** + $HgBr_2$ which was heated to 280°	Suggested assignments
3400 s,vb	3400 s,vb	-OH stretch
1625 w	1620 w	
1300 vw	1300 vw	
1170 vw	1170 vw	C-H in plane deformation
1150 vw	1150 vw	
1000 w	1000 w	Ring vibration
950 vw,b	950 vw,b	
725 s	725 m	C-H out of plane deformation
690 s	695 m	
560 s,vb	560 s,vb	ν_{as}(SnOSn)
315 w,b	300 m,b	

* Described in experiment No. 10

** Described in experiment No. 11

Table-VIII

Spectral data (in cm^{-1}) of the polymeric compound $[Sn(OH)_4]_n$ containing few Ph/halogen/carboxylate groups:

Products obtained from the reactions of			
$Ph_3SnOCOCH_3$ + $HgCl_2$	$Ph_3SnOCOCH$* + $HgBr_2$ after D.M.F. treatment	$Ph_3SnOCOCH_2CH_3$ + $HgCl_2$	Suggested assignments
3400 s,vb	3400 s,vb	3400 s,vb	-OH stretch
1620 vw	1620 vw	1620 vw	ν_{as}(OCO)
1540 vw	1550 vw	1540 vw	
1300 vw			
1150 vw		1170 vw	C-H in plane deformation
		1155 vw	
950 vw,b	950 vw,b	950 vw,b	-OH deformation
725 s	725 m	725 m	C-H out of plane deformation
550 s,vb	570 s,vb	560 s,vb	ν_{as}(SnOSn)
300 wb	300 wb	300 wb	

---

* Described in experiment No. 11.

Table- IX

Spectral data (in cm^{-1}) of the polymeric compound of the type $RSn(OH)_2OCOCH_3$:

Products obtained from the reactions of		
$Bu_3SnOCOCH_3$ + $HgCl_2$	$Pr_3SnOCOCH_3$ + $HgCl_2$	Suggested assignments
3450 w,b	3470 w,b	-OH stretch
1560 s,b	1560 s,b	$\nu_{as}(OCO)$
1215 m		CH_3 sym deformation + CH_3 asym rock + C-C asym stretch + C-C-C asym deform.
1150 w	1150 w	CH_3 sym rock
1020 w	1010 w	CH_3 asym rock
890 w	800 m	C-C sym stretch
760 w		
730 w		
700 m	690 w	
630 w	680 w	
570 m	560 w,b	$\nu as(SnOSn)$
470 w		
440 w	380 m	C-C-C asym. deform.
330 w	335 w	

PART - II

DISCUSSION

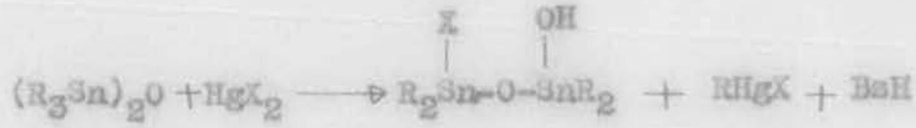
DISCUSSION

The reactions of mercuric halides with triorganotin carboxylates are some what different, compared to their reactions with hexa alkyl/aryl distannoxanes (85,86). Hexa alkyl/aryl distannoxanes react with mercuric halides in the following manner:

1. $(R_3Sn)_2O + HgX_2 \longrightarrow R_3SnX + R_4Sn + [R_2SnO]_n + RHgX$

$[$Where R = Ph, Pr; X = Cl, Br, I$]$

2.



$$(R_3Sn)_2O + HgX_2 \longrightarrow R_2\overset{\overset{X}{|}}{Sn}-O-\overset{\overset{OH}{|}}{Sn}R_2 + RHgX + BsH$$

$[$Where R = Bs; X = Cl $]$

on the other hand, the reactions of triorganotin carboxylates with mercuric halides may be described as follows:

3. $R_3SnOCOR' + HgX_2 \longrightarrow R_3SnX + [RSn(OH)_2OCOR']_n + RHgX$

$[$Where R = Ph, Pr, Bu; X = Cl, Br, I; R' = H, CH_3, $C_2H_5$$]$

4. $R_3SnOCOR' + HgX_2 \rightarrow R_3SnX + [Sn(OH)_4]_n + RHgX$

$[$Where R = Ph; X = Cl; R' = CH_3, $C_2H_5$$]$

It is interesting to note that in case of triorganotin carboxylates dealkyl/arylation leads to the formation of polymeric products containing one phenyl group pertin atom except for a very few cases e.g., the reactions of triphenyltin acetate and propionate with mercuric chloride, where the dearylation is almost complete.

The products and stoichiometry of the reactions of triorganotin carboxylates with mercuric halides may be explained by the following steps:

A.

1. $R_3SnOCOR' + HgX_2 \longrightarrow R_2SnX(OCOR') + RHgX$
2. $R_2SnX(OCOR') \quad + \quad R_3SnOCOR' \rightarrow R_2Sn(OCOR')_2 + R_3SnX$
3. $R_2Sn(OCOR')_2 + HgX_2 \longrightarrow RSnX(OCOR')_2 + RHgX$
4. $RSnX(OCOR')_2 + 2HOH \longrightarrow RSn(OH)_2OCOR' + HX + R'COOH$

The overall reaction is $R_3SnOCOR' + 2HgX_2 + 2H_2O \rightarrow R_3SnX + RSn(OH)_2OCOR' + 2RHgX + HX + R'COOH$

[When $R = Ph;\ R' = H;\ X = Cl,\ Br,\ I$
$R = Ph;\ R' = CH_3;\ X = Br,\ I$
$R = Pr,\ Bu;\ R' = CH_3;\ X = Cl$
$R = Ph;\ R' = C_2H_5;\ X = Br,\ I$]

B.

1. $\mathrm{R_3SnOCOR' + HgX_2 \longrightarrow R_2SnX(OCOR') + RHgX}$

2. $\mathrm{R_2SnX(OCOR') + R_3SnOCOR' \longrightarrow R_2Sn(OCOR')_2 + R_3SnX}$

3. $\mathrm{R_2Sn(OCOR')_2 + HgX_2 \longrightarrow RSnX(OCOR')_2 + RHgX}$

4. $\mathrm{RSnX(OCOR')_2 + R_3SnOCOR' \longrightarrow RSn(OCOR')_3 + R_3SnX}$

5. $\mathrm{RSn(OCOR')_3 + HgX_2 \longrightarrow SnX(OCOR')_3 + RHgX}$

6. $\mathrm{SnX(OCOR')_3 + 4HOH \longrightarrow Sn(OH)_4 + HX + 3R'COOH}$

The overall reaction is therefore,

$$\mathrm{3R_3SnOCOR' + 3HgX_2 + 4H_2O \longrightarrow 2R_3SnX + Sn(OH)_4 + 3RHgX + HX + 3R'COOH}$$

[Where $\mathrm{R = Ph;\ R' = CH_3,\ C_2H_5;\ X = Cl}$]

carboxylate-halogen exchange, shown in second (mechanism A and B) and fourth (mechanism B) steps, have been postulated to account for the formation of triorganotin halides. Similar exchange reactions are known to occur in the reactions of mercuric halides with triorganotin oxinates (86) where the following mechanism has been proposed to account for the products obtained:

C.

1. $\mathrm{Ph_3SnOx + HgX_2 \longrightarrow Ph_2Sn(X)Ox + PhHgX}$

2. $Ph_2Sn(X)Ox + HgX_2 \longrightarrow PhSn(X)_2Ox + PhHgX$

3. $PhSn(X)_2Ox + Ph_3SnOx \longrightarrow PhSn(X)Ox_2 + Ph_3SnX$

$$2Ph_3SnOx + 2HgX_2 \longrightarrow Ph_3SnX + PhSn(X)Ox_2 + 2PhHgX$$

[Where Ox = 8-hydroxy quinolinato, X = Cl, Br, I]

Since, the triorganotin carboxylates are penta coordinated like triorganotin oxinates, a similar course of reaction is, therefore, expected for both types of compounds. Thus the similarity between the mechanism A and C is obvious. However, the final products in the reactions of oxinates i.e., $RSn(X)Ox_2$ are quite stable and can be isolated. But the corresponding carboxylates are expected to be easily hydrolysed like $RSn(OCOR')_3$ (15) so that the final products in these reactions are $RSn(OH)_2OCOR'$ type polymers, instead of $RSnX(OCOR')_2$. The extent of hydrolysis appears to be dependent on the water content of the solvents. Since the complete hydrolysis leading to the formation of $RSn(O)OH$ has been found to take place in ordinary ether/benzene mixtures which were not dried before use. It may, however, be noted even in freshly dried solvents partial hydrolysis to $RSn(OH)_2OCOR'$ takes place probably due to moisture present which can not be excluded in our reaction conditions. For, reactions of triphenyltin acetate and propionate with mercuric chloride, it proceeds probably upto $SnX(OCOR')_3$ before the hydrolysis to take place to produce polymeric $Sn(OH)_4$ as shown in mechanism (B). Such type of preferential hydrolysis may be attributed to the difference in acid strength of the carboxylic acids of the respective carboxylates. With the increase in the polarity of the Sn-O bond of the carboxylate the contraction of 'd' orbitals of tin atom would be more pronounced. This may result into a nucleophilic attack at tin atom by a nucleophile e.g., water, hydrolysing the carboxylate groups. Thus formic acid being the strongest among the series studied, is easily hydrolysed at third step of mechanism A to produce the polymeric product. It has been observed that this polymer once formed, does not react further with mercuric halides at room temperature. Hence the competition between mercuric halides and moisture to react with $RSnX(OCOR')_2$ would determine the final step of the reaction. From the polymeric product obtained from the reactions of triphenyltin acetate and propionate with mercuric chloride, it is more likely that the reaction of mercuric chloride is faster than the hydrolysis reaction, at least in these two cases.

Reaction of diphenyltin diacetate with mercuric bromide provides a significant clue to the course of the reactions. From the above reaction, phenyl mercuric bromide and polymeric phenyltin dihydroxy acetate have been isolated. The isolation of same polymer from the reaction of triphenyltin acetate with mercuric bromide suggests that diphenyltin diacetate is an intermediate in this reaction; in agreement with the postulated mechanism. Isolation of phenylmercuric bromide and polymeric phenyltin dihydroxy acetate only, signifies a straight out reaction involving migration of phenyl group from tin atom to mercury atom has taken place in the third step (mechanism A and B). Similar path of reactions could have been followed in case of other carboxylates.

It has been observed that for a given triorganotin carboxylate the reaction is much more slower with mercuric iodide in comparison with corresponding chloride and bromide.

Though mercuric chloride quantitatively reacts with triphenyltin carboxylates, the reactions of tripropyl and tributyltin acetate with mercuric chloride are incomplete and proceed only upto fifty percent conversion of mercury to the respective alkyl mercuric chloride. The reaction of tricyclohexyltin acetate is still slower and practically does not react with mercuric chloride in our reaction conditions. Although these experiments have not been designed to study the kinetics of the reactions, the results suggest the following probable sequence showing the relative ease with which the above organic groups migrate from tin atom to mercury:

$$\mathrm{Ph} > \mathrm{Pr} \approx \mathrm{Bu} >>> \text{cyclohexyl}$$

This sequence is common to all metal carbon bond cleavage reactions in polar solvents (96-100) which are believed to proceed through electrophilic substitution at the carbon atom. The same sequence is predicted for electrophilic substitution reactions by the reactivity indices recently proposed (101-103). The present reactions are, therefore, essentially electrophilic substitutions at the carbon atom of Sn-C bond, though nucleophilic assistance by the halogen atom can not be completely ruled out.

It is interesting to note that reaction of triphenyltin acetate with mercuric acetate produces polymeric phenyl stannoic acetate and diphenylmercury. On the basis of the nature of the products and stoiciometry obtained in the reaction, the following mechanism may be proposed:

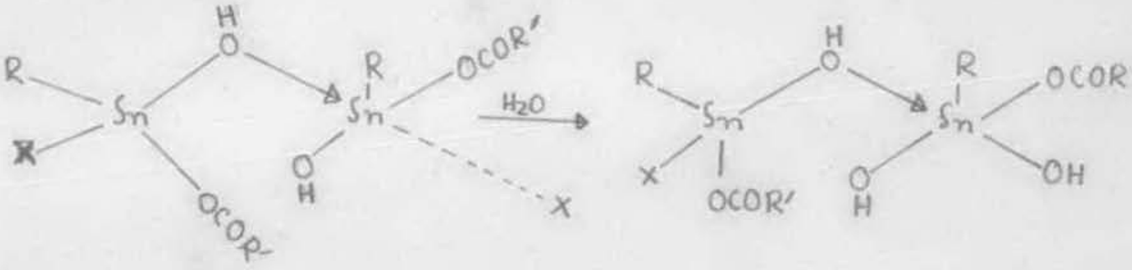
D.

1. $Ph_3SnOAc + Hg(OAc)_2 \longrightarrow Ph_2Sn(OAc)_2 + PhHgOAc$
2. $Ph_2Sn(OAc)_2 + PhHgOAc \longrightarrow PhSn(OAc)_3 + Ph_2Hg$
3. $PhSn(OAc)_3 + HOH \longrightarrow PHSn(O)OAc + 2AcOH$

$$Ph_3SnOAc + Hg(OAc)_2 + HOH \longrightarrow PhSn(O)OAc + Ph_2Hg + 2AcOH$$

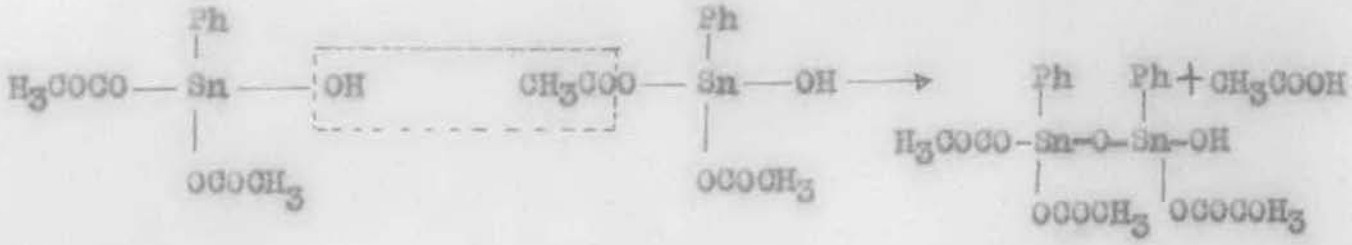
Comparison of reactions of most of the triorganotin carboxylates with mercuric halides and that of triphenyltin acetate with mercuric acetate reveal two important features. Firstly, in the former reactions mercuric halides are converted to the corresponding organo mercuric halides whereas in the later case diphenyl mercury is produced instead of phenyl mercuric acetate. This is probably due to the greater reactivity of phenyl mercuric acetate with organotin carboxylates than the corresponding organo mercuric halides. It has been observed that phenyl mercuric acetate reacts readily with triphenyltin acetate at room temperature to produce diphenyl mercury and phenyl stannoic acetate polymer. Secondly, the polymeric products (except for triphenyltin acetate and propionate with mercuric chloride) obtained in the former reactions are mostly of the type $RSn(OH)_2OCOR'$ while that obtained from the later reaction is of the type $PhSn(O)OCOCH_3$. These two polymers probably owe their formation to the hydrolysis of $RSnX(OCOR')_2$ and $PhSn(OCOCH_3)_3$ respectively as suggested in the mechanisms. One possible reason~~s~~ for this difference ~~is~~ in hydrolysis behaviour may be the difference in coordination numbers of tin atom in two intermediates. Thus in case of $RSnX(OCOR')_2$ (very likely to contain a hexa coordinated tin atom due to the presence of two chelated/bridging carboxylate groups) hydrolysis of one of the carboxylate groups will lead to the formation of penta coordinated $RSnX(OCOR')OH$. In this situation, the hydroxyl group may further coordinate strongly with the tin atom of another such molecule. This process would strongly polarise the Sn-X bond rendering the displacement of the halogen atom by -OH group more facile according to the following scheme:

$$RSnX(OCOR')_2 + HOH \longrightarrow RSnX(OCOR')OH + CH_3COOH$$



On the other hand, hydrolysis of $PhSn(OAc)_3$ would initially lead to $PhSn(OAc)_2OH$ which, unlike $RSnX(OCOR')OH$ is a hexa-coordinated species and hence further intermolecular coordination is very unlikely. In such a situation intermolecular condensation would be preferable due to the formation of more stable polystannoxanes as indicated below:

$$PhSn(OCOCH_3)_3 + HOH \longrightarrow PhSn(OCOCH_3)_2OH + CH_3COOH$$



$$H_3COCO-\overset{Ph}{\underset{OCOCH_3}{Sn}}-\boxed{OH \qquad CH_3COO}-\overset{Ph}{\underset{OCOCH_3}{Sn}}-OH \longrightarrow H_3COCO-\overset{Ph}{\underset{OCOCH_3}{Sn}}-O-\overset{Ph}{\underset{OCOCOH_3}{Sn}}-OH + CH_3COOH$$

Reaction of tribenzenyltin acetate with mercuric acetate is different from the corresponding reaction of triphenyltin acetate, for it produces benzylmercuric acetate and 1,3 dibenzyl 1,3 dihydroxy 1,3 diacetoxy distannoxane. Considering stoichiometry of the reaction, the following mechanism has been postulated:

E

1. $Bz_3SnOAc + Hg(OAc)_2 \longrightarrow Bz_2Sn(OAc)_2 + BzHgOAc$

2. $Bz_2Sn(OAc)_2 + Hg(OAc)_2 \longrightarrow BzSn(OAc)_3 + BzHgOAc$

3. $BzSn(OAc)_3 + HOH \longrightarrow \frac{1}{2}Bs(OAc)OHSnBz(OAc)OH + AcOH$

$$Bz_3SnOAc + 2Hg(OAc)_2 + HOH \longrightarrow \frac{1}{2}Bz(OAc)OHSnBz(OAc)OH + 2BzHgOAc + AcOH$$

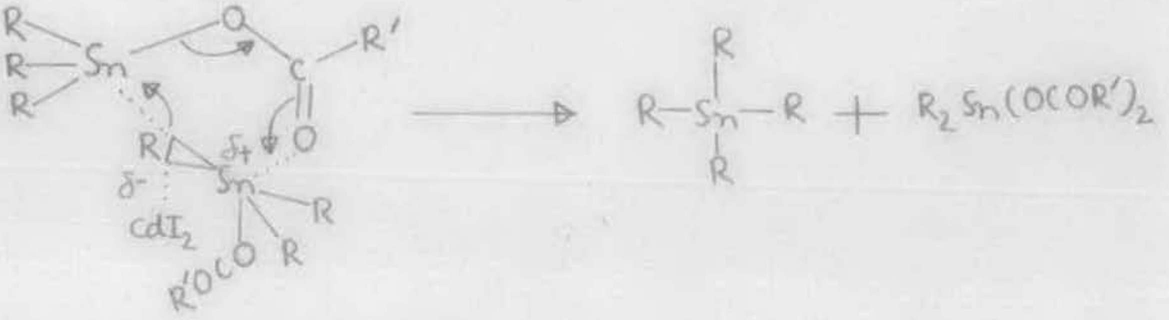
Isolation of benzylmercuric acetate, BzHgOAc, signifies that this compound is stabler than its phenyl analogue. For the same reason as with the hydrolysis of $PhSn(OAc)_3$, $BzSn(OAc)_3$ as postulated in the mechanism E, will then probably be converted to the distannoxane isolated. Few dimeric benzyl stannoxanes with halogen and α-nitroso β-naphthol groups have been isolated (86,104). These compounds probably have a ladder structure where further condensation is not possible.

Reactions of tripropyltin acetate, tributyltin acetate and tricyclohexyltin acetate with mercuric acetate are extremely slow and practically no reactions take place at ordinary temperature.

Since the following sequence of reactivity of the triorganotin carboxylates with mercuric acetate is observed, electrophilic attack at carbon bonded to tin atom probably has taken place, though a neucleophilic assistance by the acetate group may not be ruled out:

$Ph > Bz \ggg Pr \gtrsim Bu \gtrsim$ cyclohexyl.

Cadmium iodide induces a disproportionation reaction on triphenyltin acetate and formate producing tetraphenyltin and diphenyltin oxide (polymeric). Similar disproportionation is known in case of tetramethyl silicon and aluminium tribromide (105). Same type of mechanism may be proposed in these cases:



Diphenyltin diacetate may then undergo hydrolysis due to the presence of moisture to produce the polymeric stannoxanes of the type $[Ph_2SnO]n$.

A few suggestions about the structural aspects of the polymeric compounds:

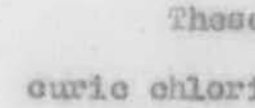
Three distinct types of organotin polymeric products have been isolated during the investigation of the reactions of triorganotin carboxylates with mercuric halides. These polymeric products on the basis of chemical composition and physical properties have been formulated as $[PhSn(O)OH]n$, $[RSn(OH)_2OCOR']_n$ (where $R = Ph, Pr, Bu$ and $R' = H, CH_3, C_2H_5$) and $[Sn(OH)_4]_n$ containing a few phenyl/halogen/carboxylate groups. It is to be noted that whenever mercuric halides react with triorganotin carboxylates, it produces one of these types of polymer and may be used as a very convenient route for the preparation of these polymeric compounds in good yield.

Mercuric acetate and phenylmercuric acetate, on the other hand, react with triphenyltin acetate to produce polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$.

A discussion of some of the structural aspects on the basis of infrared spectral data and preparation of oxine derivatives may be worthwhile. The molecular weight determination of these polymers could not be possible because of their general insolubility in common organic solvents and infusibility upto 360°. It may be mentioned that it is not possible to characterise each of the IR bands, the characterisation is usually based on the known spectral data and sometimes tentative assignments have been made.

A. $Sn(OH)_4$ type polymers containing a few phenyl/halogen/carboxylate groups:

These polymers have been isolated in the reactions of mercuric chloride with triphenyltin acetate and triphenyltin propionate. The infra red spectral study reveals that this type of compound has a strong and broad band at 3600-3300 cm^{-1} (fig. 2.6) which may be attributed to -OH stretching frequency. This type of absorption in the above mentioned region is indicative of the presence of

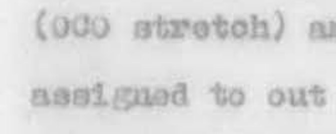


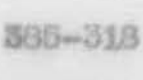
$>Sn\begin{smallmatrix}OH\\OH\end{smallmatrix}Sn<$ group (104).

Comparison of IR spectrum of this compound with that of triphenyltin acetate leads us to conclude that the medium and broad band at 600-500 cm^{-1} owe its origin to the Sn-O-Sn stretch and is in good agreement with the range 643-580 cm^{-1} reported for polymeric mono and diorgano stannoxanes by Brown, Okawara and Rochow (106).

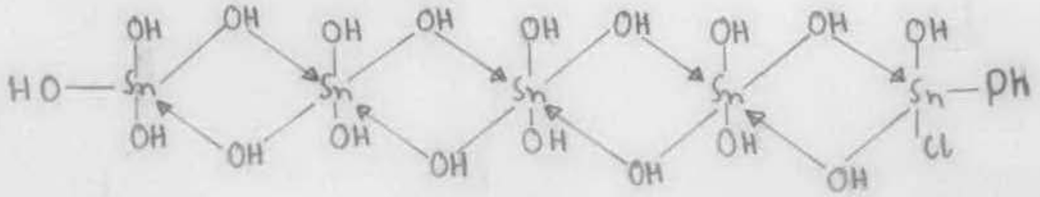
Because of the mode of preparation of this type of polymer, there remains a probability that a few phenyl/acetate/chlorine group to be used as terminal groups of the large polymer. This is supported by the presence of a very weak band at 1570-1540 cm^{-1} (OCO stretch) and very weak absorption at 725 cm^{-1} which may be assigned to out of plane C-H vibration of phenyl ring. The Sn-Cl stretching band generally appears at 335-318 cm^{-1} (107, 109), though there is some weak absorption at this region, the exact Sn-Cl stretching frequency, however, could not be assigned with certainity in this polymer. The elemental analysis of this polymer also suggests the presence of a few phenyl/acetate/chlorine groups.

It is interesting to note that treatment of this polymer with oxine (8-hydroxy quinoline) produces two distinct type of compound viz., phenyltin chloro dioxinate, $PhSnClOx_2$ and



in 1:2 proportion. The isolation of $PhSnClOx_2$ reasonably indicates the presence of  $\overset{|}{\underset{|}{Sn}}<^{Ph}_{Cl}$ group in the polymer. The stoichiometry of the products obtained signifies that every fifth tin atom contains a phenyl and chlorine group which might act a

terminal groups of the polymer. Thus the polymer probably involve five tin atoms per molecule and the probable structure may be written as below:



B. $RSn(OH)_2OCOR'$ type of polymer:

This type of polymer has been isolated in the reactions of triorganotin carboxylates (organic group = Ph, Bu, Pr and carboxylate group = $-OCOH$, $-OCOCH_3$ and $-OCOCH_2CH_3$) with mercuric halides except for the reaction of triphenyltin acetate and propionate with mercuric chloride. Infrared spectrum of this type of polymeric compounds gives an idea about the general nature of the polymeric compounds. Comparison of IR spectrum of these polymers with the corresponding triorganotin carboxylate reveals some important features. Two weak but broad bands appear in these polymers at 3540 cm^{-1} and 3370 cm^{-1} and are characterestics of the O-H stretching mode of $-\overset{|}{\underset{|}{Sn}}\underset{OH}{\overset{OH}{\rightleftarrows}}\overset{|}{\underset{|}{Sn}}$-group (104) and hence $-\overset{|}{\underset{|}{Sn}}\underset{OH}{\overset{OH}{\rightleftarrows}}\overset{|}{\underset{|}{Sn}}$-group is present in these polymers (fig. 2.1).

The two strong bands at ~1575 cm^{-1} and ~1550 cm^{-1} may be assigned to the OCO stretching mode which clearly indicates that these vibrations are not due to free carboxylate groups rather than chelating or ionic carboxylates. The presence of two such stretching frequency of OCO group indicates that probably two types of OCO group are present in these polymers, though the exact nature of these groups is not known.

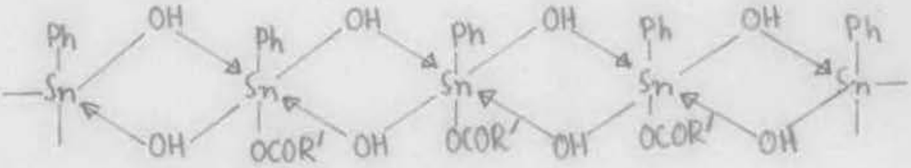
H.C.Henry and J.G.Noltes have assigned the 1080 cm^{-1} band to the C-H in plane deformation mode and to be the characteristic of phenyl group bonded to tin atom. The presence of a ~1080 cm^{-1} band indicates the presence of such group in these polymers.

R.C.Poller (109) assigned the ~450 cm^{-1} band in triphenyltin compounds to the substituent sensetive 16b (B_1) mode of a mono substituent benzene. In this polymeric compound the appearance of a slightly shifted ~450 cm^{-1} band may be taken as a further evidence of a phenyltin group in these compounds.

Several workers (110-112) have identified the ν_{as} (Sn-O-Sn) vibration at about 775 cm^{-1} in hexaphenyldistannoxanes. As mentioned before the corresponding vibration in mono and dialkyl stannoxanes is found in the range of 643 -545 cm^{-1}. So the strong broad bands at 580-520 cm^{-1} present in this type of polymer may be assigned to ν_{as}(Sn-O-Sn) vibration as because no other strong absorption is expected to occur in this region. The lowering of (Sn-O-Sn) frequency is probably due to the presence of $\underbrace{OSnOSn}$ ring system as suggested by Okawara (113).

It may be mentioned that there is a medium to strong band at 340 cm^{-1} in these polymeric compounds obtained from different sources. The Sn-Cl stretching vibration usually occurs in this region. But it is highly unlikely this band to be assigned to Sn-Cl stretching vibration, for this band is always present whatever may be the parent compounds used for the preparation of this type of polymeric compound. Comparison of IR spectrum of this type of polymer with that of $Sn(OH)_4$ type and RSn(O)OCOR' type of polymeric compounds leads us to tentatively assign this 340 cm^{-1} band to be associated with Sn-Ph vibration.

On the basis of the above mentioned information together with chemical composition and isolation of phenyltin trioxinate (which provides an evidence for the presence of one phenyl group pertin atom) the basic structure of the phenyl derivatives may be suggested as follows:



The terminal groups may be OH, halogen or carboxylate groups.

On the basis of the similar arguments the butyl and propyl derivatives of this type of polymers may be suggested to have the above type of structure.

C. PhSn(O)OAc type polymer:

This type of polymers have been isolated in the reactions of triphenyltin acetate with mercuric acetate and phenyl mercuric acetate.

The IR spectrum of this polymeric compound have been interpreted on the basis of comparison with the spectrum of triphenyltin acetate. The bands at 1570 cm^{-1} and 1540 cm^{-1} may be assigned to the asymmetric OCO stretching which arises either from chelating or ionic carboxylate groups. The same type of carboxylate stretching vibrations have also been reported by J.R.Sams and his co-workers (18). These two bands signify probably the presence of two different type of carboxylate groups.

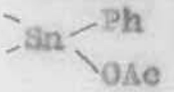
The 1070 cm^{-1} band may be assigned to the C-H in plane deformation mode of phenyl group (108) and establishes the presence of phenyl group in this polymer.

The strong band at 610 cm^{-1} may be assigned to the νas(Sn-O-Sn) stretching frequency as because no such strong band should appear in this region (110-112). The presence of (Sn-O-Sn) stretching vibration minimises the probability of carboxylate group to act as bridge between tin atoms (18).

As mentioned earlier, the presence of 440 cm^{-1} band furnishes further proof of phenyltin group in this compound.

A medium absorption at 280 cm^{-1} may be assigned to νas(Sn-Ph) vibration as has been suggested by R.C.Poller (109).

Oxine derivative, that obtained from the reaction of this polymer with oxine has been characterised as phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$. This obviously suggests the presence of



$>Sn\begin{smallmatrix}\diagup Ph\\ \diagdown OAc\end{smallmatrix}$ group in the polymer.

On the basis of the above informations we, like Poller (15), feel that this polymeric compound is probably linear with bridging oxygen atoms with ionic or chelating carboxylate groups.

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PART - III

ACTION OF MERCURIC ACETATE ON HEXAORGANO DISTANNOXANES AND SOME RELATED REACTIONS.

Introduction:

The present state of knowledge about the organostannoxanes and organotin hydroxides is reviewed by a number of authors (1-4). Some of the important features of their chemistry may be recapitulated here.

Preparation of Organotin hydroxides and stannoxanes:

Organotin hydroxides are prepared most conveniently by shaking an etheral solution of the organotin halide with an aqueous solutions of potassium, sodium or ammonium hydroxides (1)

$$R_3SnX + MOH \longrightarrow R_3SnOH + MX$$

$$R_2SnX_2 + 2MOH \longrightarrow \underset{2Mx}{\underset{+}{R_2Sn(OH)_2}} \longrightarrow R_2SnO + H_2O$$

$$RSnX_3 + 3MOH \longrightarrow \underset{3MX}{\underset{+}{RSn(OH)_3}} \longrightarrow RSn(O)OH + H_2O$$

The trihydroxides, $RSn(OH)_3$ and the dihydroxides, $R_2Sn(OH)_2$ generally undergo immediate dehydration resulting polymeric organostannoic acids; $RSn(O)OH$ and polystannoxanes of the type R_2SnO. The R_3SnOH compounds are, however, more stable and less readily dehydrated to $(R_3Sn)_2O$ compounds.

Aryldiazonium salts with stannous chloride (5) produce Ar_2SnO and Ar_3SnOH. Triaryl tin hydroxides may also be prepared by the cleavage of tin carbon bond (6).

The hexa organo distannoxanes, $(R_3Sn)_2O$ compounds are generally prepared by removing a molecule of water from the corresponding hydroxide. This dehydration can be brought about by two methods viz., (1) distilling the organotin hydroxide under reduced pressure and (2) by heating the organotin hydroxide in a vacuum desiccator using dehydrating agents (6, 7-14). The hexaorgano distannoxanes which are not easily hydrolysed may be prepared by refluxing the corresponding halide with aqueous alkali (15).

Hexaorgano distannoxanes may also be obtained by a number of other methods (16-21).

Physical properties of organotin hydroxides and organo stannoxanes:

Some representatives of organotin hydroxides and organo stannoxanes along with their physical characteristics are given in table I (1-4).

Table-I

Compound	Type	m.p. (^oC)	bp (^oC/mm)
1. Triphenyltin hydroxide	R_3SnOH	119-120	-
2. Tributyltin hydroxide	"	-	186-189/5

Contd..

Table-I (Contd.)

Compound	Type	m.p. (°C)	bp(°C/mm)
3. Dicyclohexyltin dihydroxide	$R_2Sn(OH)_2$	291(d)	-
4. Dibutyl chlorotin hydroxide	$R_2Sn(X)OH$	105-107	-
5. Diphenyltin oxide	R_2SnO	-	-
6. Dipropyltin oxide	"	-	-
7. Hexaphenyl distannoxane	$(R_3Sn)_2O$	120	-
8. Hexapropyl distannoxane	"	-	142-144/1

Organotin hydroxides are generally solid with well defined melting points and are soluble in common organic solvents. Molecular weight determinations of trimethyltin hydroxide and tribenzyltin hydroxide have shown that, these compounds are somewhat associated in refluxing benzene (17, 22) and the molecular weight depends on the concentration of the solution.

The poly stannoxanes, R_2SnO, are polymeric solid and in most cases do not melt even at higher temperatures. Usually they are insoluble in common organic solvents and also in water.

Cummins and Dunn (23) have made an excellent survey on the infrared spectra of a large number of organotin compounds. They have reported that R_2SnO and $(R_3Sn)_2O$ type compounds give a strong band near 770 cm^{-1} which has been ascribed to a stretching vibration of Sn-O-Sn group as it disappears during any reaction involving oxygen atom. All the mono and disubstituted stannoxanes exhibit a strong band near 530 cm^{-1} which disappears on reaction and hence must also be associated with a tin oxygen stretching mode. Triphenyltin hydroxide exhibits a strong band at 3620 cm^{-1} and a strong doublet near 910 cm^{-1} and 894 cm^{-1}. Deuteration shifts these bands to 2669 cm^{-1} and 673 cm^{-1}. It seems likely that these bands are associated with an -O-H stretching mode and -O-H deformation frequency. This observations are in excellent agreement with those of Friebe and Kelker (24).

Other workers like R.C.Poller (25), Friebe and Kelker (24) and Ross et al (26) have studied the structure of triphenyltin hydroxide and hexaphenyl distannoxane by infrared techniques. The strong band at about 570 cm^{-1} have been assigned to the Sn-O-Sn stretching mode which is in good agreement with the range 643-580 cm^{-1} reported by Brown, Okawara and Rochow (27) for methyltin compounds containing Sn-O-Sn linkages. Sn-O vibration in certain trisubstituted organotin hydroxides and hexa substituted distannoxanes occurs at 900-750 cm^{-1}. Poller (25) suggested an overlap between the oxygen 'p'-orbitals and tin 'd' orbitals which increase the force constant of Sn-O bond leading to a higher vibrational frequency for these compounds. The characteristic 777 cm^{-1} band for hexaphenyldistannoxane and 912 cm^{-1}, 898 cm^{-1} bands of triphenyltin hydroxide can be used to distinguish these compounds. Poller (28) has shown that a band at 828 cm^{-1} in hexa O-phenoxy phenyl distannoxane can be assigned to Sn-O-Sn stretching frequency.

Cummins (29) has suggested that the difference in $d\pi - p\pi$ overlap given as a reason by Poller for the differences in the Sn-O-Sn stretching frequency of mono, di and hexaphenyl stannoxane are probably insufficient. From a study of appropriate models, he concluded that usual p-bonding angle cannot be accommodated in hexaphenyl distannoxane and that an s-p hybridisation of the oxygen atom is likely. This will increase the bond angle considerably and hence the asymmetric Sn-O-Sn stretching mode will appear at higher frequency. This appears to be more reasonable since the Sn-O-Sn vibration in hexa O-phenoxy phenyl distannoxane, where the angle is expected to open up still further due to steric reasons, appears at higher frequency (828 cm^{-1}) compared to that in hexaphenyl distannoxane (777 cm^{-1}).

The mossbauer studies on polystannoxanes (R_2SnO) have suggested a five coordinated rather than a four coordinated structure (30) and the degree of polymerisation decreases as the size of the alkyl groups increases (31).

Chemical properties of organo stannoxane and organotin hydroxide:

Thermal decomposition of triphenyltin hydroxide (32) leads to the formation of tetraphenyltin; Ph_4Sn, polystannoxane; Ph_2SnO and water. Schmitz-Dumont (33) also obtained the same products and proposed hexaphenyl distannoxane as an intermediate:

$$2Ph_3SnOH \longrightarrow (Ph_3Sn)_2O + H_2O \longrightarrow Ph_2SnO + Ph_4Sn$$

Thermal decomposition of trimethyltin hydroxide (17), triethyltin hydroxide (9,21,34), dimethyltin oxide and diethyltin oxide (9, 17) have been studied by various workers. It has been found that the decomposition of triethyltin hydroxide follows a different path:

$$Et_3SnOH \longrightarrow Et_2SnO + C_2H_6$$

$$3Et_2SnO \longrightarrow (Et_3Sn)_2O + SnO_2$$

Kupchik et al (35) studied the reaction of triphenyltin hydroxide with N-bromo succinimide and isolated Ph_2SnO, Ph_4Sn along with other products. The formation of tetraphenyltin has been explained through the formation of hexaphenyl distannoxane by the hydrolysis of Sn-N bond.

Most of the hexaorgano distannoxanes are sensetive toward basic hydrolysis, forming organotin hydroxides. Trimethyltin hydroxide reacts with sodium to give hexamethyl ditin in liquid ammonia (36)

$$2Me_3SnOH + 2Na \xrightarrow{(l)NH_3} Me_3Sn\text{-}SnMe_3 + 2NaOH$$

Organotin hydroxides and organostannoxanes react with halogen acids to form the appropriate organotin halides (1)

$$R_3SnOH + HX \longrightarrow R_3SnX + H_2O$$

$$R_2SnO + 2HX \longrightarrow R_2SnX_2 + H_2O$$

With organic acids or their anhydrides organostannoxanes and hydroxides produce esters of the following types (1-4, 37,38):

$$R_3SnOH + R'COOH \longrightarrow R_3SnOCOR' + H_2O$$

$$R_2SnO + (R'CO)_2O \longrightarrow R_2Sn(OCOR')_2$$

$$(R_3Sn)_2O + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O$$

$(n\text{-}Bu_2\ allyl\ Sn)_2O$ reacts with acetic acid (39) to produce $\left[n\text{-}Bu_2(OAc)\ Sn\right]_2O$ according to the equation:

$$(n\text{-}Bu_2allyl\ Sn)_2O + CH_3COOH \longrightarrow \left[n\text{-}Bu_2(OAc)Sn\right]_2O + CH_2 = CHCH_3$$

(where allyl = $CH_2{:}CHCH_3$ and OAc = CH_3COO)

This reaction is quite feasible because of the much lower stability of (n-Bu_2 allyl Sn)$_2$O compound.

More recently halo carboxylates have been prepared by Okawara et al (39) by the reaction of $(R_2SnCl)_2O$ and acetic acid, RCOOH e.g,

$$(R_2SnCl)_2O + 2RCOOH \longrightarrow 2R_2SnCl(OCOR) + H_2O$$

A few mixed compounds such as $Bu_2Sn(OAc)OSn(OMe)Bu_2$ are known (40). In recent years reactions of hexa organo distannoxane with thio acids, phosphorous acids (41,42), boric acid and fluoboric acid (43, 44) have been used to prepare the corresponding esters.

Organotin hydroxides and oxides also react with alcohol, phenol or mercaptan directly forming the organotin alkoxides, phenoxides and mercaptides (1-4)

$$(R_3Sn)_2O + 2R'OH \longrightarrow 2R_3SnOR' + H_2O$$

$$(R_3Sn)_2O + 2R'SH \longrightarrow 2R_3SnSR' + H_2O$$

Very recently, Paul et al (45) have prepared triorgano and diorgano tin chlorides by the reaction of hexa organo distannoxanes and diorganotin oxides with thionyl chloride. The yields are almost quantitative.

$$R_3SnOSnR_3 + SOCl_2 \longrightarrow 2R_3SnCl + SO_2$$

$$R_2SnO + SOCl_2 \longrightarrow R_2SnCl_2 + SO_2$$

Datta, Majee and Ghosh (46,47) have studied the reactions of hexaorganodistannoxanes with mercuric halides, zinc chloride, aluminium chloride and cadmium iodide. Reactions of mercuric halides in most cases produce organomercuric halides, triorganotin halides and polymeric organostannoxanes, R_2SnO.

The Sn-O bond of stannoxanes could be added to a variety of reagents such as, isocyanate, isothiocyanate, aldehyde, nitrile, carbonmonoxide etc. (48-53). A few such reactions are given below:

$$EtN = C = O + (Bu_3Sn)_2O \longrightarrow Bu_3SnNEtCOOSnBu_3$$

$$CCl_3CHO + (Bu_3Sn)_2O \longrightarrow Bu_3SnOCH(CCl_3)OSnBu_3$$

$$O = C = O + (Bu_3Sn)_2O \longrightarrow Bu_3SnOCOOSnBu_3$$

The reactions of hexalkyl distannoxane with dialkyl carbonate provide a new route for the preparation of trialkyltin alkoxides (54).

$$(R_3Sn)_2O + R'_2CO_3 \longrightarrow 2R_3SnOR' + CO_2$$

Number of organotin oxinates (oxine = 8-hydroxy quinolinol) have been prepared by the reaction of hexa organodistannoxanes with oxine (HOx) (55-58).

$$(R_3Sn)_2O + 2HOx \longrightarrow 2R_3SnOx + H_2O$$
$$R_2SnO + 2HOx \longrightarrow R_2SnOx_2 + H_2O$$

Some of these oxinates are effective fungicides and are used as wood preservatives.

Scope, object and result:

In view of the fact that hexa alkyl/aryl distannoxanes (46, 47) and triorganotin carboxylates (both containing Sn-O linkages) undergo facile reactions with mercuric halides, it would be expected for hexa alkyl/aryl distannoxanes to undergo similar reactions with other covalent mercury salts such as mercuric acetate. It may be pointed out here that mercuric acetate produces diphenyl mercury instead of phenyl mercuric acetate in the reactions with triorganotin acetate unlike the corresponding halides which lead to the formation of phenylmercuric halides. In the present investigation action of mercuric acetate on a few hexa alkyl/aryl distannoxanes have been studied. The distannoxanes used in these reactions include hexa phenyl/benzyl/propyl/butyl derivatives.

All the distannoxanes have been found to react quite readily with the mercuric acetate at ordinary temperature. The course of reaction is dependent on the nature of the organic groups. For example, the action of mercuric acetate on $(Ph_3Sn)_2O$ gave diphenyl mercury; Ph_2Hg, triphenyltin acetate; Ph_3SnOAc and polymeric phenyl stannoic acetate; $[PhSn(O)OAc]_n$, where as hexa benzyl distannoxane leads to the formation of a new functionally substituted distannoxane viz., 1,3 dibenzyl 1, 1,3,3 tetraacetoxy distannoxane; $Bz(OAc)_2SnOSn(OAc)_2Bz$ together with benzyl mercuric acetate;

BzHgOAc. The formation of functionally substituted distannoxane from this reaction can be used as a new route for the preparation of such compounds.

It is also interesting to note that dealkylation does not take place in the reactions of mercuric acetate with $(R_3Sn)_2O$ (where R = Pr, Bu) but the products are R_3SnOAc and HgO, where as mercuric halides react with $(R_3Sn)_2O$ (R = Pr, Bu) with the formation of R_3SnCl, RHgCl and R_2SnO. Since the reactions of mercuric acetate with $(R_3Sn)_2O$ (R = Pr, Bu) are clear cut and quantitative yield of R_3SnOAc is obtained, these reactions may be used as very convenient route for the preparation of trialkyltin acetates.

The reaction of bis(triphenyltin) sulphide with mercuric acetate have also been investigated to see whether or not bis (triphenyltin) sulphide behaves similar to the corresponding stannoxane. In this case, instead of arylation of mercury only mercuric sulphide and triphenyltin acetate are produced according to the following equation:

$$(Ph_3Sn)_2S + Hg(OAc)_2 \longrightarrow 2Ph_3SnOAc + HgS$$

The difference in the behaviour of mercuric acetate towards bis (triphenyltin) sulphide as compared to hexaphenyldistannoxane may be attributed to the stronger affinity of mercury towards sulfur.

The formation of diphenyl mercury in the reactions of $(Ph_3Sn)_2O$ and $Hg(OAc)_2$ has been explained by assuming the great instability of SnOHg bonded system, vis-a-vis, the ease of migration of phenyl groups from tin atom to mercury atom.

EXPERIMENTAL

All the solvents were purified and dried as described in Vogel's practical chemistry (61). The petroleum ether used had its boiling range 60-80° unless otherwise mentioned. Mercuric acetate (G.R./E.M) and phenylmercuric acetate (Riedel) used in these reactions were dried in vacuum for 12 hr before use. Triphenyltin chloride, diphenyltin dichloride, hexa propyl and butyl distannoxanes all obtained from Fluka A.G., Switzerland were used without further purification. All melting points were uncorrected.

1. Preparation of hexaphenyl distannoxane:

Hexaphenyl distannoxane was prepared by the reaction of triphenyltin chloride with sodium hydroxide as described by Van Rij (62). Crude product on repeated crystallisation from a mixture of petroleum ether and benzene gave crystals of melting point 122° [lit (63) m.p. 123-124°]. It was dried in air and finally in vacuum at room temperature for 12 hr. (Found: C = 60.80%, H = 4.49%; Calcd. for $C_{36}H_{30}Sn_2O$: C = 60.41%, H = 4.42%).

2. Preparation of tribenzyltin chloride:

Tribenzyltin chloride was prepared according to the method of Schmitz-Dumont et al (64) and was recrystallised from acetone, m.p. 142° [lit (64) m.p. 142-144°].

3. Preparation of hexabenzyl distannoxane:

Hexabenzyl distannoxane was prepared (65) by shaking an etheral solution of tribenzyltin chloride with 30% aqueous solution of potassium hydroxide. The product was recovered from ether layer and finally crystallised from acetone, m.p. 118-122° [lit (65) m.p. 120°]. (Found: C = 62.91%, H = 5.12%, Calcd. for $C_{42}H_{42}Sn_2O$: C = 63.05%, H = 5.28%).

This sample of hexabenzyl distannoxane was used as authentic sample for mixed melting point determination.

4. Preparation of bis(triphenyltin) sulphide:

To a solution of 25 gm of triphenyltin chloride in 300 ml of ethanol, 15 ml of pyridine was added and then H_2S gas was passed for half an hour. The white precipitate obtained was filtered and crystallised from acetone. Pure crystals of bis(triphenyltin) sulphide m.p. 142° [lit (1) m.p. 141.5-143°] was obtained. (Found: C = 58.70%, H = 4.56%; Calcd. for $C_{36}H_{30}Sn_2S$: C = 59.03%, H = 4.38%).

5. Preparation of polymeric diphenyltin oxide:

Diphenyltin oxide was prepared by treating etheral solution of diphenyltin dichloride with aqueous solution of sodium hydroxide in excess (2). The white compound was washed thoroughly with water, ether etc. and dried at 90° in vacuuo for several days. (Found:

Sn = 40.82%; Calcd. for $C_{12}H_{10}SnO$: Sn = 41.11%).

6. Reaction of hexaphenyl distannoxane with mercuric acetate (1:1):

To a solution of 7.1. gm of hexa phenyl distannoxane in 600 ml of ether was added 3.18 gm of mercuric acetate in 300 ml and was stirred at room temperature for 8 hr and kept overnight. A white precipitate was formed and was filtered off. The residue 2.89 gm (6A) was washed thoroughly with benzene, ether and was found to be infusible upto 360°. The residue was found to be slightly soluble in chloroform and was recrystallised from this solvent. The filtrate was completely evaporated whereby a white solid (7.48 gm), m.p. 100-115° was obtained (6B). The solid, 6B, was fractionally crystallised from petroleum ether (40-60°) which afforded a solid, 2.90 gm, m.p. 116-118° (6C) as first fraction and was isolated. The filtrate on further concentration yielded 1.68 gm, m.p. 105-118°, of a white solid (6D). The mother liquor on complete evaporation gave 2.83 gm of white crystalline solid, m.p. 118-122° (6E). The solid, 6D, on repeated crystallisation from petroleum ether (40-60°) gave two fractions of solid (i) 6E; 1.00 gm, m.p. 115-118° and (ii) 6F; 0.51 gm, m.p. 118-120°. The fractions 6C and 6F were found to be identical (m.m.p) and mixed together which on further crystallisation from carbon tetrachloride/ether mixture afforded a white crystalline solid, m.p. 122-123°, identified as triphenyltin acetate by mixed melting point determination with an authentic sample of triphenyltin acetate. The fractions 6E and 6G were found to be identical (m.m.p) and mixed together. On repeated crystallisation from petroleum ether afforded a needle shaped crystalline compound, m.p. 124° and was identified as diphenyl mercury by mixed melting point determination with an authentic sample of diphenyl mercury.

Identification of solid 6A:

The solid, 6A, was identified as a polymer from its physical properties and was identified as polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$ from its superimposible IR spectrum with an authentic sample of $[PhSn(O)OAc]_n$, preparation of oxine derivative viz., phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$ and elemental analysis. (Found: Sn = 43.41%; Calcd. for $C_8H_8SnO_3$: Sn = 43.85%).

7. Reaction of hexaphenyl distannoxane with mercuric acetate (1:2):

To a solution of 4.51 gm of hexa phenyl distannoxane in 400 ml ether, was added 4.01 gm of mercuric acetate in 600 ml of ether ~~was added~~ and the mixture was stirred at room temperature for 8 hr and kept overnight. After that the whole solution was filtered whereby 3.36 gm of a white solid was left as residue (7A). The compound, 7A, was found to be insoluble in almost all common organic solvents but was slightly soluble in chloroform and was crystallised from this solvent. This was identified as a polymer which did not melt even upto 360°. The filtrate was completely evaporated to dryness whereby a white solid, 4.39 gm, m.p. 120-124° was obtained. This compound on repeated crystallisation from petroleum ether afforded diphenyl mercury, m.p. 124° which was identified by mixed melting point determination with authentic sample of diphenyl mercury.

The organotin polymer 7A was identified as polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$ from IR comparison with authentic spectrum of phenyl stannoic acetate and preparation of oxine derivative viz., phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$.

Free acetic acid was formed during reaction as detected by qualitative chemical tests.

8. Reaction of diphenyltin oxide with phenyl mercuric acetate:

To a suspension of 2.12 gm of diphenyltin oxide in 300 ml benzene, a solution of 2.47 gm of phenyl mercuric acetate in 300 ml benzene was added and the mixture was refluxed for 7 hr and kept overnight. The whole solution was filtered where by a residue 1.90 gm was obtained. This residue was found to be infusible upto 360° and was insoluble in common organic solvents excepting chloroform. After recrystallisation from chloroform it was identified as polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$ by IR comparison with authentic sample of phenyl stannoic acetate and preparation of known oxine derivative i.e., phenyltin acetate dioxinate, PhSn(OAc)Ox

The filtrate on concentration afforded a white crystalline solid, m.p. 119-124°, weighing 2.54 gm. After several recrystallisation from petroleum ether it was identified as diphenyl mercury, m.p. 124°, by mixed melting point determination with an authentic sample of diphenyl mercury.

9. Reaction of hexapropyl distannoxane with mercuric acetate:

To a solution of 5.86 gm of hexa propyl distannoxane in 300 ml ether, 3.68 gm of mercuric acetate in 400 ml of ether was added. The mixture was stirred at room temperature for 7-8 hr and kept overnight. A yellow precipitate was formed during stirring which was filtered off. The residue, 2.43 gm, was identified as mercuric oxide (yellow variety) by qualitative chemical tests.

The filtrate on complete evaporation gave a white crystalline solid, 7.00 gm, m.p. 98-100°. This solid was recrystallised several times from petroleum ether/ether mixture which then afforded a white needle shaped crystals of m.p. 100°. This was identified as tripropyltin acetate [lit (66) m.p. 100°] by mixed melting point determination with an authentic sample of tripropyltin acetate prepared from the reaction of tripropyltin chloride (Fluka A.G) with sodium acetate (2). (Found: C = 42.98%, H = 7.75%; Sn = 38.48%; Calcd. for $C_{11}H_{24}SnO_2$: C = 43.04%, H = 7.82%, Sn = 38.71%).

10. Reaction of hexa butyl distannoxane with mercuric acetate:

A solution of 6.74 gm of hexabutyl distannoxane in 300 ml of ether was mixed with 3.60 gm of mercuric acetate in 400 ml ether. The mixture was stirred at room temperature for 8 hr and kept overnight. A yellow precipitate was formed during reaction which was filtered off. The yellow residue, 2.40 gm, was identified as mercuric oxide by qualitative chemical tests.

The filtrate on evaporation yielded a white solid, 7.65 gm, m.p. 79-81°. This solid on repeated crystallisation from petroleum ether had its m.p. 83° and was identified as tributyltin acetate [lit (66) m.p. 84.5 - 85°] by mixed melting point determination with an authentic sample of tributyltin acetate prepared by treatment of sodium acetate on tributyltin chloride (Fluka A.G.) (2) (Found : C = 47.97%, H = 8.40%, Sn = 33.71%; Calcd. for $C_{14}H_{30}SnO_2$: C = 48.17%, H = 8.60%, Sn = 34.04%).

Note: Reactions of hexapropyl/butyl distannoxane with mercuric acetate in 1:2 proportions were also carried out. The products were tri propyl/butyl tin acetate, mercuric oxide and one equivalent of unreacted mercuric acetate indicating that the reactions proceeded in 1:1 proportion.

11. Reaction of hexabenzyl distannoxane with mercuric acetate:

3.73 gm of hexabenzyl distannoxane was dissolved in 400 ml of ether. To that, 2.96 gm of mercuric acetate in 400 ml ether was added at room temperature and the mixture was stirred for 8 hr and kept overnight. The solution was then evaporated to dryness and treated with 100 ml of cold petroleum ether and filtered. The petroleum ether soluble fraction afforded 1.70 gm of a white compound which on recrystallisation from acetone was identified as unreacted

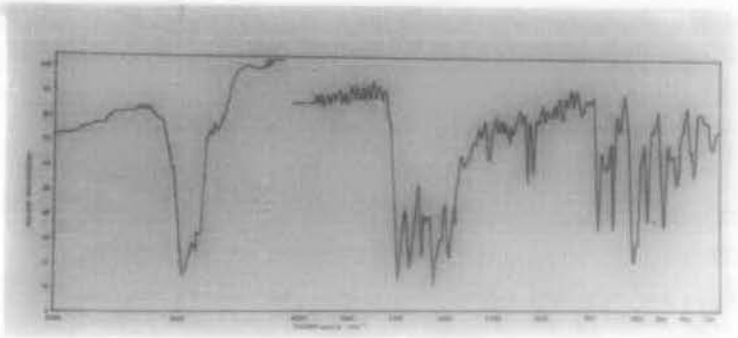


Fig. 3.1 IR spectrum of 1,3 dibenzyl 1,1,3,3 tetracetoxy distannoxane, $Bz(OAc)_2SnOSn(OAc)_2Bz$.

hexabenzyl distannoxane, m.p. 118° [lit (67) m.p. 118-120°] by mixed melting point determination with an authentic sample.

The residue was then treated with hot petroleum ether and the petroleum ether soluble fraction afforded 2.70 gm of benzyl mercuric chloride, m.p. 128-129°, identified by mixed melting point determination with authentic sample.

The petroleum ether insoluble fraction, 1.40 gm, m.p. 220-228° was recrystallised several times from benzene to afford a white crystalline compound m.p. 227-228°. This compound was identified as a new distannoxane derivative viz., 1,3 dibenzyl 1,1, 3,3 tetra acetoxy distannoxane on the basis of elemental analysis (Found: C = 39.49%, H = 3.98%, Sn = 35.21%; Calcd. for $C_{22}H_{26}Sn_2O_9$: C = 39.31%, H = 3.87%, Sn = 35.35%) and IR spectrum.

This compound on treatment with oxine in refluxing methanol did not afford dibenzyltindioxinate, Bz_2SnOx_2 which indicated that probably no  $\begin{smallmatrix}Bz\\Bz\end{smallmatrix}\!>\!Sn\!<$ grouping was present in the compound. So the two benzyl groups have been considered to occupy 1,3 positions of the new stannoxane derivative.

Comparison of infrared spectrum (Fig 3.1) of this compound with that of tribenzyltin acetate and hexabenzyl distannoxane leads to assign the following major bands to OCO group and Sn-O-Sn group frequencies.

1590 cm^{-1}, 1545 cm^{-1} = OCO stretch (asymmetric)

610 cm^{-1} = Sn-O-Sn stretch (asymmetric

12. Reaction of bis(triphenyltin) sulphide with mercuric acetate:

To a solution of 3.15 gm of bis (triphenyltin) sulphide in 400 ml of ether, 1.43 gm of mercuric acetate dissolved in 200 ml of ether was added and the suspension was stirred for 6 hr at room temperature. A black precipitate was formed during the stirring and was filtered off. The residue 1.00 gm was identified as mercuric sulphide (black **variety**) by qualitative tests. The filtrate was evaporated to dryness whereby a white solid, 3.55 gm, m.p. 115-120^{o} was obtained. This solid after several recrystallisation from petroleum ether was identified as triphenyltin acetate, m.p. 122^{o} (m.m.p). (Found: Sn = 28.89%; Calcd. for $C_{20}H_{18}SnO_2$ + Sn = 29.04%).

PART - III

DISCUSSION

DISCUSSION

Hexa alkyl/aryl distannoxanes react differently with mercuric chloride and acetate. In case of mercuric chloride, the reactions do not depend upon the nature of the organic groups (except in case of hexa benzyl distannoxane) and follow the same cyclic transition state (46, 47) in every case as have been assumed due to the isolation of similar types of reaction products. But in case of mercuric acetate, the reaction products are dependent on the nature of organic groups. For example, hexaphenyl distannoxane reacts with mercuric acetate to produce diphenyl mercury and polymeric phenyl stannoic acetate while the corresponding benzyl compound produces benzylmercuric acetate and a new carboxylate derivative of distannoxane viz., $Bz(OAc)_2SnOSn(OAc)_2Bz$. But we could only obtain tripropyl/butyl tin acetate and mercuric oxide from hexa propyl/butyl distannoxanes when treated with mercuric acetate.

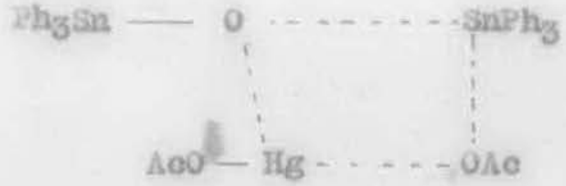
Considering the stoichiometry of the overall reaction, the reaction of mercuric acetate with hexaphenyl distannoxane in 1:1 ratio may be formulated as follows:

$$(Ph_3Sn)_2O + Hg(OAc)_2 \longrightarrow Ph_3SnOAc + Ph_2SnO + PhHgOAc$$

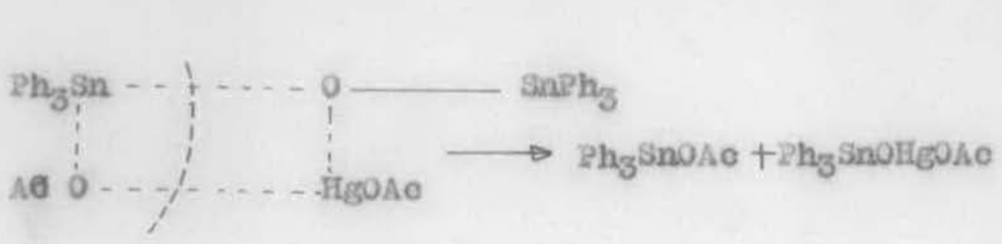
$$Ph_2SnO + PhHgOAc \longrightarrow PhSn(O)OAc + Ph_2Hg$$

$$(Ph_3Sn)_2O + Hg(OAc)_2 \longrightarrow Ph_3SnOAc + PhSn(O)OAc + Ph_2Hg$$

Since, compounds like tetraorganotin; R_4Sn (59) are attacked only verly slowly by mercuric acetate, the ease with which hexa phenyl distannoxane reacts with mercuric acetate should be associated with the presence of $\gtrdot$Sn-O-moiety in the molecule. Datta et al (46) have suggested a cyclic transition state in the reactions of hexaphenyldistannoxane and mercuric chloride involving simultaneous electrophilic attack by oxygen atom to mercury and a neucleophilic assistance at tin atom by chlorine atom. It is highly probable that the Lewis acid, mercuric acetate would involve a similar transition state in the first step of the reaction as follows:



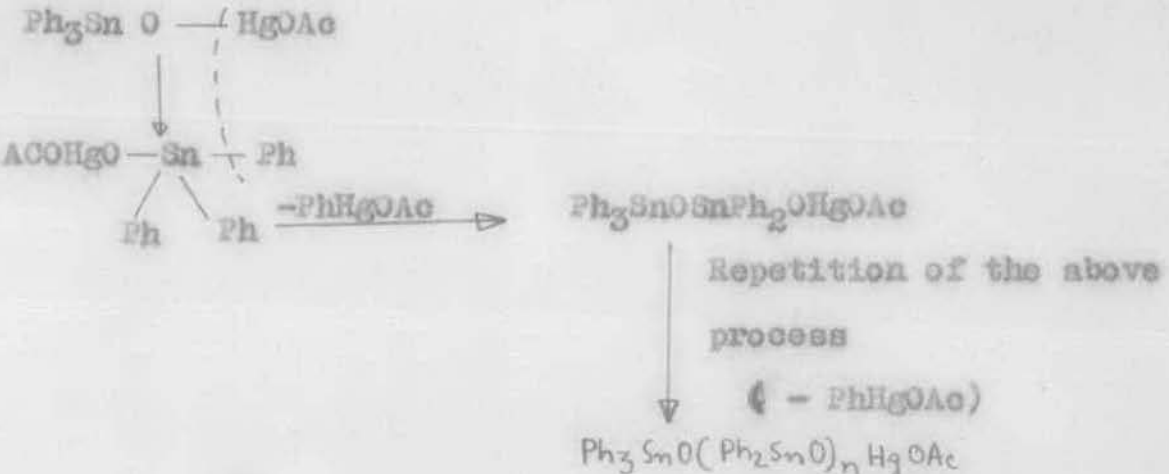
This transition state is expected to break as below:



$Ph_3SnOHgOAc$, however, could not be isolated from this reaction probably because of its highly unstable nature.

The actual mechanism by which $Ph_3SnOHgOAc$ decomposes is uncertain. Whether the intermolecular $O \rightarrow Sn\lessgtr$ interaction (I) or the intramolecular rearrangement (II) is to be preferred cannot be said definitely.

(I)

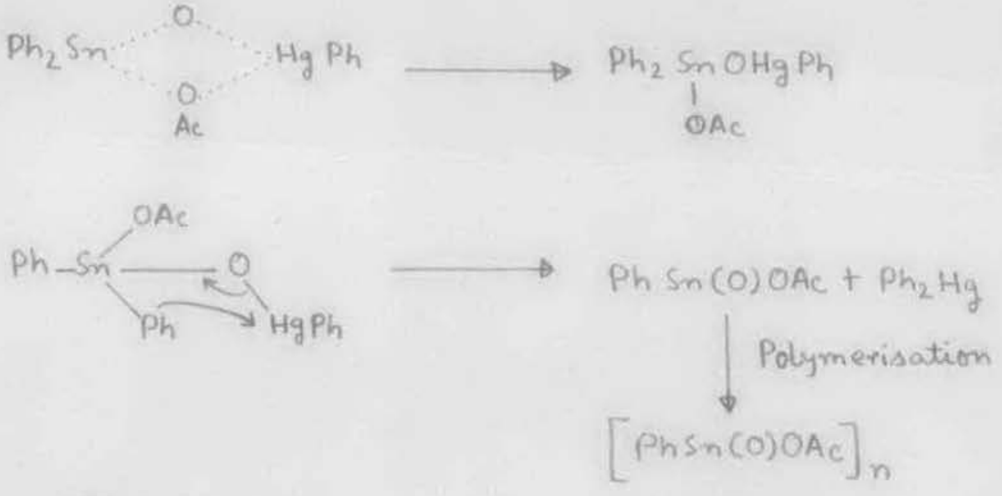


(II)

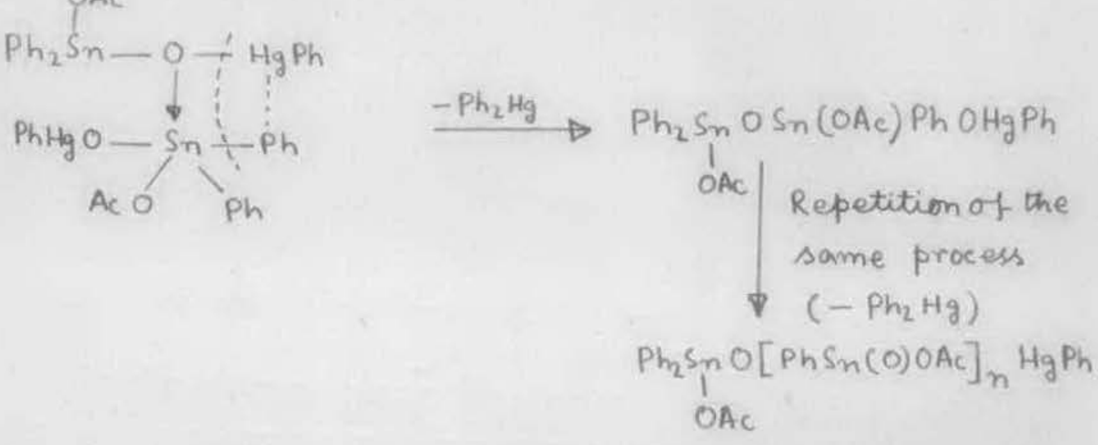
Davies et al (60) have recently reported the formation of $Bu_2\underset{\displaystyle Cl}{\underset{|}{Sn}}OHgPh$ by the reaction of Bu_2SnO with PhHgCl. From the isolation of phenyl stannoic acetate; PhSn(O)OAc and diphenyl mercury; Ph_2Hg instead of Ph_2SnO and PhHgOAc in the reaction of $(Ph_3Sn)_2O$ with

$Hg(OAc)_2$, it is likely that Ph_2SnO and PhHgOAc have reacted to produce $\mathrm{Ph_2}\underset{\substack{|\\ \mathrm{OAC}}}{\mathrm{Sn}}\mathrm{OHgPh}$ as an intermediate which may further rearrange to give Ph_2Hg and PhSn(O)OAc as shown in (III). Since from the reactions of trialkyl/aryltin carboxylates with mercuric acetate it has been observed that phenyl group has a greater tendency to migrate from tin atom to mercury, the decomposition of $\mathrm{Ph_2}\underset{\substack{|\\ \mathrm{OAc}}}{\mathrm{Sn}}\mathrm{OHgPh}$ may follow the postulated routes of either (III) intramolecular or (IV) intermolecular rearrangements. Of course, the exact course of reaction is uncertain.

(III)



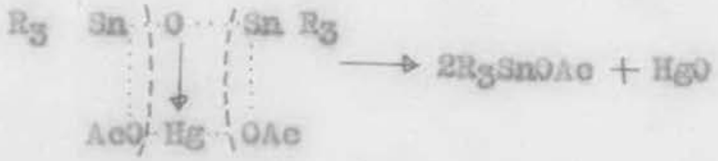
(IV)



It is interesting to note that polymeric Ph_2SnO reacts with PhHgOAc in refluxing benzene to produce diphenyl mercury and polymeric phenyl stannoic acetate (which reasonably indicates that Ph_2SnO may be an intermediate of the reaction between hexaphenyl distannoxane and mercuric acetate). The formation of these two products can be explained invoking any of the two mechanisms viz. (III) or (IV) as described earlier. It has been further observed that the reaction of Ph_2SnO with PhHgOAc does not proceed at room temperature whereas mercuric acetate definitely reacts with $(Ph_3Sn)_2O$ at room temperature. This is probably due to the fact that Ph_2SnO once polymerised needs a rather rigorous condition to undergo such reaction.

It has been mentioned thattriphenyltin acetate is one of the products of the reaction of $(Ph_3Sn)_2O$ with $Hg(OAc)_2$ in 1:1 ratio. But if the reaction is carried out with two equivalents of mercuric acetate, no triphenyl tin acetate could be isolated indicating that triphenyltin acetate can further react with excess mercuric acetate to produce more diphenyl mercury and phenyl stannoic acetate as described earlier.

That the involvement of the oxygen atom of Sn-O-Sn bond in the cyclic transition state is responsible for the difference in behaviour of mercuric acetate at least towards hexa alkyl/aryl distannoxanes studied, is supported by the reactions of mercuric acetate with hexapropyl and hexabutyl distannoxanes. In these cases only trialkyltin acetate and mercuric oxides are formed. This rather different behaviour of mercuric acetate towards hexa alkyl distannoxanes may be attributed to the inductive effect of alkyl groups that would render the oxygen atom much more negative facilitating the donation of electrons from the oxygen atom to mercury atom in the cyclic transition state producing mercuric oxide and trialkyltin acetates.



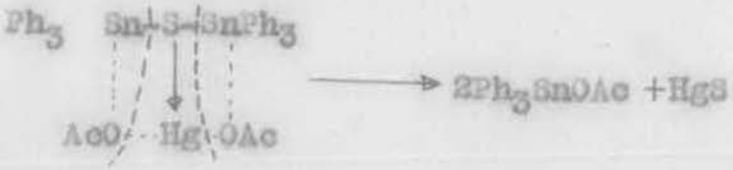
(R = Pr, Bu).

The reaction of hexabenzyl distannoxane with mercuric acetate is rather interesting. In this case quite contrary to its phenyl analogue, benzylmercuric acetate is formed together with a functionally substituted distannoxane viz., $Bz(OAc)_2SnOSn(OAc)_2Bz$ instead of a polymeric product. Considering the stoichiometry of the reaction the overall reaction may be written as follows:

$$(Bz_3Sn)_2O + 4Hg(OAc)_2 \longrightarrow Bz(OAc)_2SnOSn(OAc)_2B_z + 4BzHgOAc$$

This reaction is still under investigation and nothing can be said about the mode of formation of the products at this stage.

Affinity of mercury towards sulfur is much greater than the oxygen. This fact has been reflected from the reaction of bis(triphenyltin) sulphide with mercuric acetate which produces mercuric sulphide and triphenyltin acetate probably according to the following mechanism:



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PART-IV

ON THE PREPARATION OF SOME NEW ORGANOTIN CARBOXYLATE OXINATES AND ORGANOTIN COMPLEXES.

Introduction:

In this part, preparation of some organotin carboxylate oxinates have been attempted. They include the following types of compounds viz., PhSn(OCOR)Ox$_2$ and (OCOR)$_2$SnOX$_2$. The compound n-Bu$_2$Sn(OCOCH$_3$)Ox, reported by Huber and Kaiser (1) is probably the only example of organotin carboxylate oxinate.

Beside the preparation of organotin carboxylate oxinates, some other organotin complexes have been prepared and action of mercuric chloride/mercuric acetate/phenyl mercuric acetate on these complexes have been investigated.

A short description of known organotin oxinates and related complexes may be relevant here.

Organotin oxinate complexes:

Various types of organotin oxinates viz., R$_3$SnOx, R$_2$SnOx$_2$, R$_2$Sn(X)Ox and RSnOx$_3$, where R = organic group, Ox = oxinate and X = halogen, isothiocyanate, acetate, nitrate are described in the literature~~s~~ (1-12).

R$_3$SnOx, R$_2$SnOx$_2$ and RSnOx$_3$ are generally prepared by one of the following ways: (a) reaction of organotin halides with oxine (3,4), (b) reaction of organotin halides with sodium oxinate (2,10,14) and (c) reaction of organotin oxides with oxine (10,13), e.g.,

(a) $Me_2SnCl_2 + 4HOx \longrightarrow Me_2SnOx_2 + 2HOx.HCl$

(b) $n\text{-BuSnCl}_3 + 3\text{NaOx} \longrightarrow n\text{-BuSnOx}_3 + 3\text{NaCl}$

(c) $(\text{Ph}_3\text{Sn})_2\text{O} + 2\text{HOx} \longrightarrow 2\text{Ph}_3\text{SnOx} + \text{H}_2\text{O}$

Methyltintrioxinate was prepared by heating methyltin sesquisulphide with oxine, in a 1:3 molar ratio, in boiling toluene, while similar heating of butyltin sesquisulphide and oxine in a 1:2 molar ratio produced $(\text{BuSnOx}_2)_2\text{S}$ (15).

Martin and Ramaiah (16) prepared tintetraoxinate, Sn(Ox)_4 by heating Ph_2SnOx_2 with oxine at 300°. Tin tetraoxinate was formed by the Sn-C bond fission.

If a dihalide and oxine were allowed to react in a 1:1 molar ratio in the absence of a base, the haloxinates were produced (1,17).

$$\text{R}_2\text{SnCl}_2 + \text{HOx} \longrightarrow \text{R}_2\text{Sn(Cl)Ox} + \text{HCl}$$

These may also be prepared through disproportionation of a equimolar mixtures of a dihalide and a dioxinate in refluxing ethanol or benzene (1,14, 17-19):

$$\text{R}_2\text{SnCl}_2 + \text{R}_2\text{SnOx}_2 \longrightarrow 2\text{R}_2\text{Sn(Cl)Ox}$$

or by reaction between a dioxinate and a silver halide (1)

$$\text{R}_2\text{SnOx}_2 + \text{AgX} \longrightarrow \text{R}_2\text{Sn(X)Ox} + \text{AgOx}$$

These compounds may undergo disproportionation to yield more stable hexa coordinated R_2SnOx_2 (17).

Dialkyltin isocyanate oxinate and acetate oxinates have been prepared by disproportionation reactions as in the case with $R_2SnClOx$ (1).

Huber and his coworker (1) have also prepared dialkyltin nitrate oxinate and sulphate oxinate by the following methods:

$$R_2SnOx_2 + AgNO_3 \xrightarrow{CH_3OH} R_2Sn(NO_3)Ox + AgOx$$

$$2R_2Sn(Cl)Ox + Ag_2SO_4 \xrightarrow{CH_3OH} \left[R_2SnOx\right]_2SO_4 + 2AgCl$$

In other halogen substitution reactions the product disproportionates (19).

$$R_2Sn(Cl)Ox + I^- \longrightarrow \left[R_2Sn(I)Ox\right] + Cl^-$$

$$2\left[R_2Sn(I)Ox\right] \longrightarrow R_2SnI_2 + R_2SnOx_2$$

The oxinate group of triphenyltin oxinate may be exchanged by a number of anions such as halide ions, simply by shaking a solution of triphenyltin oxinate with the appropriate reagent. The halogen atom of penta coordinated tin halo oxinate undergoes ready exchange with groups such as butyl, alkoxy or even with chelates e.g., acetylacetonates (17, 19) which may disproportionate into diorganotin dioxinates. For example:

(1) $R_2Sn(Cl)Ox + Tl - OC_2H_5 \longrightarrow R_2Sn(OC_2H_5)Ox$

(2) $R_2Sn(Cl)Ox + NaI \longrightarrow R_2Sn(I)Ox \longrightarrow R_2SnOx_2 + R_2SnI_2$

$$\begin{tikzcd}
(3) \quad R_2Sn(Cl)Ox + n\text{-}BuLi \arrow[r] & R_2Sn(n\text{-}Bu)Ox \arrow[d] \\
& R_2SnOx_2 + (n\text{-}Bu)_2SnR_2
\end{tikzcd}$$

$$\begin{tikzcd}
(4) \quad R_2Sn(Cl)Ox + Tl\text{-}aCaC \arrow[r] & R_2Sn(aCaC)Ox \arrow[d] \\
& R_2SnOx_2 + R_2Sn(aCac)_2
\end{tikzcd}$$

Monoorganotin chloro dioxinate have generally been prepared by the reaction of organotin trichloride with oxine (17, 20). Phenyltin halodioxinates have also been prepared by reacting diphenyltin dioxinate with mercuric halides in ether at room temperature (21).

Dichlorotin dioxinate, Cl_2SnOx_2 (5) was prepared by the reaction of oxine on $SnCl_4$.Cl_2SnOx_2 has been found to be thermally stable upto 360°, insoluble in mineral acids and alkali solutions but soluble in concentrated sulphuric acid.

All the organotin oxinates and halo oxinates are yellow to orange crystals, having well defined melting points. These are usually soluble in common organic solvents and are monomeric in benzene solution (12).

Similar to those of various chelated metal oxinates which absorb at 370-430 mμ, the tin oxinates are characterised to have an electronic absorption spectrum in the region 360-430 mμ(12). This has been considered as an evidence for the presence of chelated ring in the molecule. The molar extinction coefficient depends on the number of oxinate groups present. For example, the extinction coefficient of dioxinate complexes are nearly double that of the monooxinate complexes and the extinction coefficient of the tin trioxinate complexes e.g., n-BuSnOx$_3$, is 2.5 times that of the monooxinate complexes (2).

Organotin dioxinates have been shown to have hexa coordinated tin atom by Okawara et al (22), the monooxinates and diorganotin halo oxinates are penta coordinated (12) while n-butyl tin trioxinate has been suggested to have a hepta coordinated tin atom (2).

The configuration of the penta coordinated complexes of the type R$_3$SnOx and R$_2$Sn(Cl)Ox has not yet been investigated. Although several studies of triphenyltin oxinate have been reported (6,12, 17), there is uncertainity as to whether this compound has structure (i) or (ii) (Fig. I)

(i)

(ii)

Fig. I.

Organotin complexes:

Si, Ge, Sn and Pb can extend their coordination number beyond four. I.R. Beattie (23) has attributed this fact to the availability of empty 'd' orbitals in these elements. However, these orbitals in a single atom are too difuse and hence the bond formation due to effective overlap is only possible when they contract sufficiently in the presence of highly electronegative ligands (24-26). From a number of investigations on bonding, it has been observed that an effective overlap between ligand 'p' orbitals and metal 'd' orbitals takes place to form π -bonds, in case of silicon compounds (27). Evidence for such pπ - dπ bonding is based largely on the analysis of bond characteristics e.g., bond lengths, bond angles, electric moments etc. The pπ - dπ bonding depends on the size of the central metal atom and availability of the 'd' orbitals as well. In particular, it has been observed that pπ -dπ bonding is of considerable importan~~ta~~ce for Ge-O bonds but it is very small or almost non existent for Sn-O bonds (loc.cit). Since the acceptor property of tin halides are well known (23), the probability of π bonding with atoms other than oxygen may not be ruled out.

Organotin halides form addition compounds with electron pair donors and are usually of the type $R_nSnX_{4-n}.2L$ (when n = 2, 3) (28) where R = Organic group, X = halogen and L = an electron pair donor.

The organotin monohalides usually form 1:1 adducts, $R_3SnX.L$. For trimethyltin chloride, a colorometric method of calculating the enthalpy of formation of adducts with Lewis bases has been reported (29).

The stability of the addition compounds depends on the number of organic groups present and for tetraorganotin compounds there is little evidence for Lewis acid behaviour. When the chlorine atoms of stannic chloride are replaced by relatively electropositive organic groups, the acceptor property of tin declines as follows $SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl$ (30), $Ph_3SnCl > Bu_3SnCl$ (31) and $PhSnCl_3 > MeSnCl_3 > BuSnCl_3$ (32). With different donating molecules, slight variation in the above sequence, however, is observed.

The stereochemistry of some of these complexes have been settled recently. Me_3SnOAc (33), R_3SnR' where R' is an unsaturated organic radical containing two nitrogen atoms in the 1,3 position such as imadozol (34) have been proposed to have penta coordinated tin atom. The presence of five coordinated tin atom in $Me_3SnCl.Py$ has been established conclusively by X-ray analysis (35) and the structure has been shown to be trigonal bipyramidal with the three methyl groups occupying the equatorial positions. $R_2SnX_2.2L$ and $RSnX_3.2L$ compounds have indicated the presence of hexa coordinated tin atom. Very recently Kitching et al (36-38) have prepared a number of complexes with diorganosulphoxides such as dimethyl sulphoxide (DMSO), dibenzylsulphoxide (DBzSO) diethylsulphoxide (DEtSO) etc. As because the Sn-O frequency in these complexes are lowered as compared to the free ligands, coordination through oxygen atom have been suggested. Both the penta and hexa coordinated environment of tin have been proposed for $R_3SnCl.L$ and $R_2SnCl_2.2L$ respectively.

In recent years, there have been growing interest for the preparation of organotin chelates. Complexes with chelating agents such as β-diketones (19, 39-44), 1,10 phenanthroline (22, 45, 46), bipyridyl (45-48), terpyridyl (47), 8-hydroxy quinoline (2-12), dithiocarbamate (49, 50), ethylene diamine tetracetic acid (51), tropolene (52), salicylaldehyde (44), picoline (42, 44), phthalocyanine (53), kojates (54) etc. have been reported. Similar to monodentate ligands, both penta and hexa coordinated complexes have been isolated with chelating agents. In addition, a few hepta and octa coordinated tin complexes are also known.

By the cleavage of Sn-Ph bonds (40), acetylacetone, benzyl acetone, dibenzyl acetone, salicylaldehyde, oxine etc. produce $Cl_2Sn(Ch)_2$ when reacted with Ph_2SnCl_2(HCh is the bidentate, monoprotic chelating agent). R_2SnCh_2 complexes, where R is an organic radical, may be prepared by the reaction of R_2SnCl_2 with thalium (41) or sodium (42) salt of the chelating agents.

Example of hepta and octa coordinated complexes of tropolonates and oxinates are known (52,10,14,16). The presence of seven and eight coordinated tin in these compounds have been deduced from various physical measurements such as UV spectra, molecular weight determinations, electrical conductivity etc.

Though rare, an interesting type of complex are the organotin mixed chelates. Westlake and Martin (19) prepared $Ph_2Sn\ (C_6H_5COCHCOC_6H_5)Ox$ as a pure compound. Dimethyltin oxinate tropolonate (7) has been prepared by the reaction of dimethyltin dioxinate and dimethyltin ditropolonate and has been characterised by IR and X-ray spectroscopy.

Scope, object and results:

As indicated in the beginning of this part the present investigation deals with the preparation of carboxylate of the type $PhSn(OCOR)Ox_2$ and $(ROCO)_2SnOx_2$ derivatives of organotin dioxinates. Prior to this work, only reported compound of this type was dibutyltinacetate oxinate prepared by Huber and Kaiser (1).

$PhSn(OCOR)Ox_2$ have been prepared by using two routes viz., (i) by reacting $PhSn(Cl)Ox_2$ with a slight excess of silver salt of carboxylic acids and (ii) by the reaction of Ph_2SnOx_2 with $PhHgOCOR$ in 1:1 molar proportions:

$$\text{(i)}\quad PhSn(Cl)Ox_2 + AgOCOR \longrightarrow PhSn(OCOR)Ox_2 + AgCl$$

$$\left[\text{where } R = -CH_3,\ -CH_2-CH_3 \text{ and } -CH_2Cl\right]$$

$$\text{(ii)}\quad Ph_2SnOx_2 + PhHgOCOR \longrightarrow PhSn(OCOR)Ox_2 + Ph_2Hg$$

$$\left[\text{where } R = -CH_3 \text{ and } -CF_3\right]$$

Where as all the $(ROCO)_2SnOx_2$ compounds have been prepared through the exchange reaction between Cl_2SnOx_2 and AgOCOR:

$$Cl_2SnOx_2 + 2AgOCOR \longrightarrow (ROCO)_2SnOx_2 + 2AgCl$$

$$\left[R = -CH_3, -CH_2CH_3 \text{ and } -CH_2Cl\right]$$

Since mercuric or phenylmercuric acetates can dearylate various organotin compounds, attempts are made to prepare carboxylate oxinates of tin by the use of these reagents. The reactions between Ph_3SnOx, $Ph_2Sn(Cl)Ox$ and mercuric and phenylmercuric acetates have been studied. In all cases $PhSn(OAc)Ox_2$ is one of the products. In the reaction of triphenyltin oxinate with mercuric acetate phenyltin acetate dioxinate, diphenyl mercury and polymeric phenyl stannoic acetate are the products:

$$Ph_3SnOx + Hg(OAc)_2 \longrightarrow PhSn(OAc)Ox_2 + Ph_2Hg + PhSn(O)OAc$$

on the other hand, the reaction of triphenyltin oxinate and phenylmercuric acetate in 1:1 molar proportion, produces the same products as above and fifty percent unreacted triphenyltin oxinate is isolated:

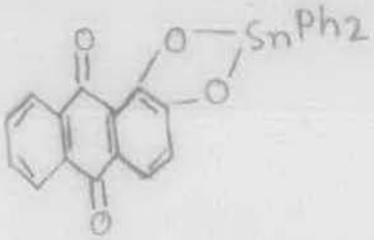
$$Ph_3SnOx + 2PhHgOAc \longrightarrow \tfrac{1}{2}PhSn(OAc)Ox_2 + 2Ph_2Hg + \tfrac{1}{2}PhSn(O)OAc$$

But in case of reaction between diphenyltin chlorooxinate and phenylmercuric acetate the reaction products are phenylmercuric chloride, diphenyl mercury, phenyltin acetate dioxinate and polymeric phenyl stannoic acetate.

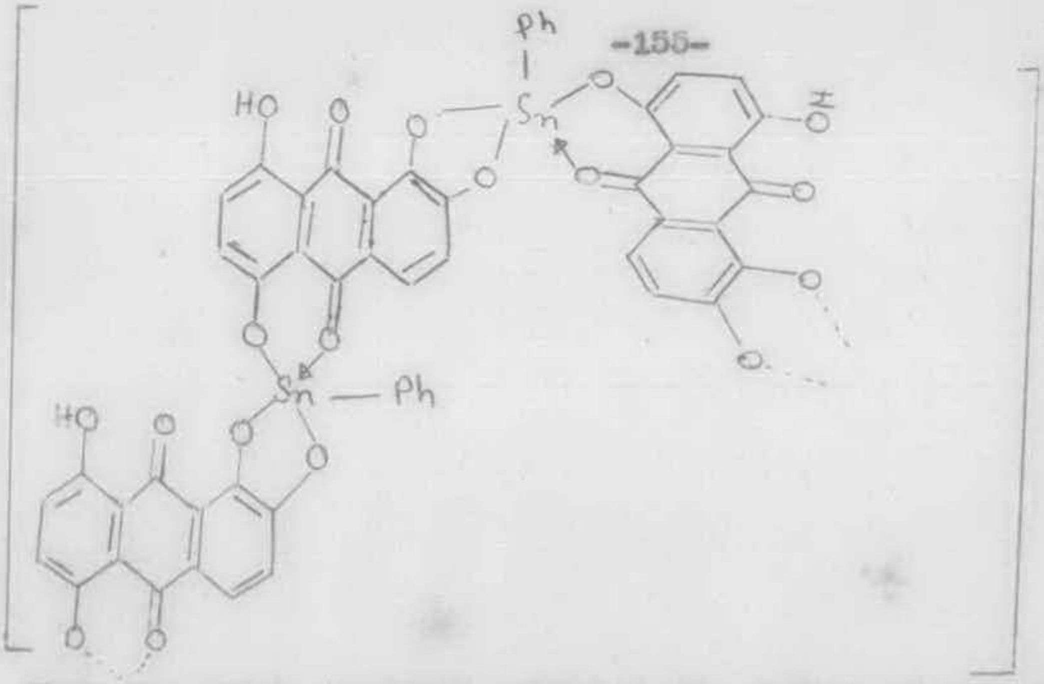
Apart from the above oxinate complexes, few other organotin chelates were also investigated.

Dearylation of triphenyltin salicylaldehyde with mercuric chloride produces triphenyltin chloride, phenyl mercuric chloride and a polymer of the type $Sn(OH)_4$ containing a very few chlorine/phenyl/salicylaldehyde groups in the terminal positions.

Reaction of triphenyltin hydroxide with alizarin (1,2 dihydroxy anthra quinone) produces a new compound which on the basis of elemental analysis and IR spectroscopy may be formulated as follows.



Quinalizarin (1,2,5,8 tetrahydroxy anthra quinone), on the other hand, reacts with triphenyltin hydroxide to produce a polymeric complex compound probably of the following type:



That the above compound contains two phenyl groups per molecule has been observed by isolating successively two equivalents of phenyl mercuric chloride, when treated with mercuric chloride in refluxing methanol.

PART- IV

EXPERIMENTAL

EXPERIMENTAL

All the solvents were purified and dried as mentioned in previous sections. The petroleum ether used had its boiling point 60-80°. Mercuric chloride (B.D.H), mercuric acetate (E.M) and phenylmercuric acetate (Riedel) were dried in an air oven at 105° for about 12 hr and kept in a desiccator for use. Triphenyltin chloride (Fluka A.G), diphenyltin dichlrodie (Fluka A.G), alizarin (E.M), quinalizarin (E.M) and silver carbonate (E.M.) were used without further purification. All melting points were uncorrected.

The various compounds used in the present investigation were prepared as follows:

1. Triphenyltin oxinate, Ph_3SnOx:

Triphenyltin oxinate was prepared by the reaction of hexaphenyldistannoxane with oxine in warm methanol. The product was recrystallised several times from methanol and dried in vacuum for 24 hr, m.p. 150° [lit. (8, 17) m.p. 145°-146.5°] (Found: C = 65.25%, H = 4.26%, N = 3.03%; Calcd. for $C_{27}H_{21}SnON$, C = 65.64%, H = 4.28%, N = 2.84%).

2. Diphenyltin dioxinate, Ph_2SnOx_2:

Diphenyltin dioxinate was prepared following the method of Nelson and Martin (41). The product was recrystallised several times from benzene, m.p. 252° [lit. (41) m.p. 250°-253°](Found: C = 64.36%, H = 3.85%, N = 4.79%; Calcd. for $C_{30}H_{22}SnO_2N_2$: C = 64.20%, H = 3.95%, N = 4.99%).

3. Diphenyltin chlorooxinate, $Ph_2Sn(Cl)Ox$:

Diphenyl tin chloro oxinate was prepared following the method of Westlake and Martin (19). The product was recrystallised several times from benzene and dried in vacuum, m.p. 160° [lit.(19) m.p. 155°-157°] (Found: C = 55.67%, H = 3.66%, N = 2.83%; Calcd. for $C_{21}H_{16}SnONCl$: C = 55.73%, H = 3.57%, N = 3.09%).

4. Phenyltinchloro dioxinate; $PhSn(Cl)Ox_2$:

Phenyltinchlorodioxinate was prepared by the reaction of triphenyltin oxinate with mercuric chloride in ether (21). The product after recrystallisation from benzene had its melting point 218° [lit. (20,21) m.p. 218°-219°] (Found: C = 55.43%, H = 3.04%, N = 5.24%; Calcd. for $C_{24}H_{17}SnO_2N_2Cl$: C = 55.50%, H = 3.30%, N = 5.39%).

5. Silver salts of carboxylic acids, AgOCOR:

The silver salts of carboxylic acids viz., acetic acid, monochloro acetic acid and propionic acid was prepared by treating silver carbonate with excess of the appropriate acid, washed thoroughly with water and dried in vacuum as described in the literature.

6. Phenylmercuric trifluoroacetate, $PhHgOCOCF_3$:

When phenylmercuric hydroxide [prepared from phenylmercuric acetate, lit. (55)] was treated with a slight excess of trifluoroacetic acid (E.M.) than required in ether, phenylmercuric trifluoroacetate was formed. The product after recrystallisation from ether furnished pure product, m.p. 124°-125° (Found: C = 24.52%, H = 1.23%; Calcd. for $C_8H_5HgO_2F_3$: C = 24.61%, H = 1.28%).

7. Triphenyltin salicylaldehyde; $Ph_3SnOC_6H_4CHO$-2 :

Triphenyltin salicylaldehyde was prepared by dissolving triphenyltin hydroxide in salicylaldehyde (E.M.). The green compound was recrystallised from ether, m.p. 170° [lit. (56) m.p. 167°-169°] (Found: C = 63.94%, H = 4.27%, Sn = 24.93%; Calcd. for $C_{25}H_{20}SnO_2$: C = 63.74%, H = 4.25%, Sn = 25.23%).

8. Dichlorotin dioxinate, Cl_2SnOx_2 :

Dichlorotin dioxinate was prepared by treating anhydrous stannic chloride (Fluka A.G.) with calculated amount of oxine in benzene. The product was thoroughly washed with benzene, methanol etc. (Found: C = 44.90%, H = 3.14%, N = 5.58%, Cl = 14.79%; Calcd. for $C_{18}H_{12}SnO_2N_2Cl_2$: C = 45.26%, H = 2.53%, N = 5.87%, Cl = 14.85%).

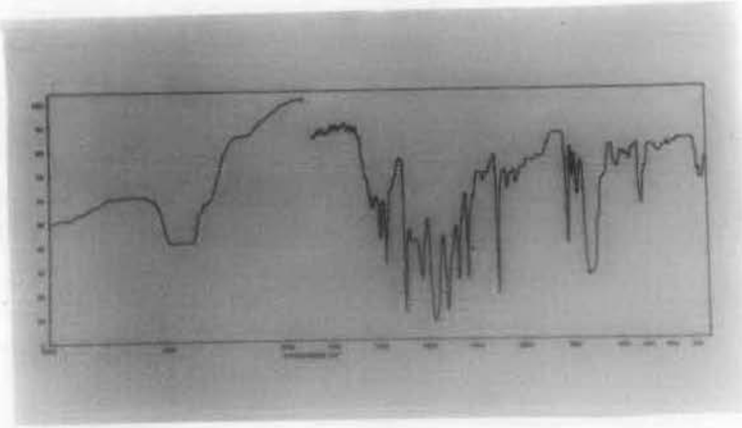


Fig. 4.1 IR spectrum of phenyltin acetate dioxinate, $PhSn(OCOCH_3)Ox_2$.

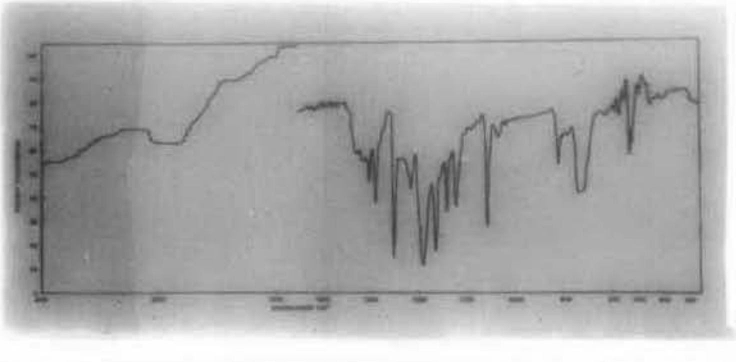


Fig. 4.2 IR spectrum of phenyltin propionate dioxinate, $PhSn(OCOCH_2CH_3)Ox_2$.

9.A. Preparation of phenyltinacetate dioxinate, $PhSn(OCOCH_3)Ox_2$ by the reaction of phenyltin chlorodioxinate with silver acetate:

1.30 gm of phenyltin chloro dioxinate and 0.42 gm of silver acetate were taken in a suspension of 200 ml of methanol and refluxed for 4 hr. The whole solution was evaporated and the residue was treated with warm benzene for several times. The benzene solution afforded a yellow crystalline compound when precipitated with petroleum ether. The yellow compound on several recrystallisation from benzene/petroleum ether mixture had its melting point 243°-244°, weighing 1.04 gm and was identified as phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$. (Found: C = 57.73%, H = 4.04%, Sn = 21.59%; Calcd. for $C_{26}H_{20}SnO_4N_2$: C = 57.56%, H = 3.70%, Sn = 21.87%).

IR and UV/vis spectra are shown in fig. 4.1 and figs. 4.8, 4.9 respectively.

9B. Preparation of phenyltin acetate dioxinate, $PhSn(OCOCH_3)Ox_2$ by the reaction of diphenyltin dioxinate with phenylmercuric acetate:

2.00 gm of diphenyltindioxinate and 1.20 gm of phenylmercuric acetate was taken in a suspension of 200 ml methanol and was refluxed for 5 hr. The solvent was evaporated off slowly and the yellow solid which remained was treated several times with hot petroleum ether. The petroleum ether soluble fraction afforded 1.20 gm of diphenyl mercury, m.p. 124° (m.m.p).

The petroleum ether insoluble solid was recrystallised several times from benzene/petroleum ether whereby pure phenyltin acetate dioxinate m.p. 243°-244° (m.m.p), 1.90 gm was afforded.

10. Preparation of phenyltin propionate dioxinate, PhSn(OCOCH$_2$CH$_3$)Ox by the reaction of phenyltin chlorodioxinate with silver propionate:

1.50 gm of phenyltin chloro dioxinate was taken in a suspension of 0.54 gm of silver propionate in 200 ml of methanol and was refluxed for 4 hr. After completion of the reaction the methanol was evaporated off and the residue was treated with warm benzene for several times. The benzene solution after concentration and precipitation by petroleum ether afforded yellow crystalline solid weighing 1.25 gm. This solid after several recrystallisation from benzene/petroleum ether afforded phenyltin propionate dioxinate, m.p. 222° (Found: C = 58.19%; H = 4.19%, N = 4.98%, Sn = 21.03%; Calcd. for $C_{27}H_{22}SnO_4N_2$: C = 58.20%, H = 3.95%, N = 5.03%, Sn = 21.32%).

The IR spectrum is shown in fig. 4.2 and UV/Vis. spectrum in figs. 4.8, 4.9.

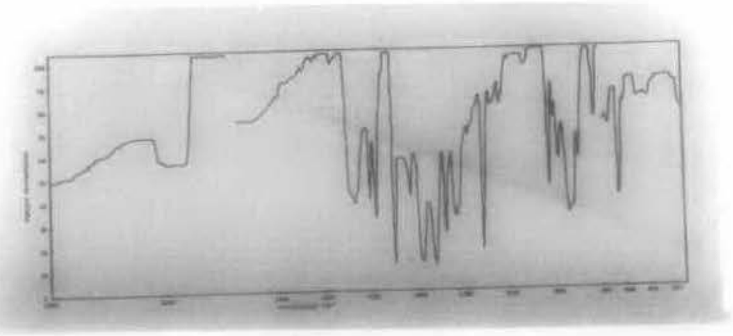


Fig. 4.3 IR spectrum of phenyltin monochloroacetate dioxinate, $PhSn(OCOCH_2Cl)Ox_2$.

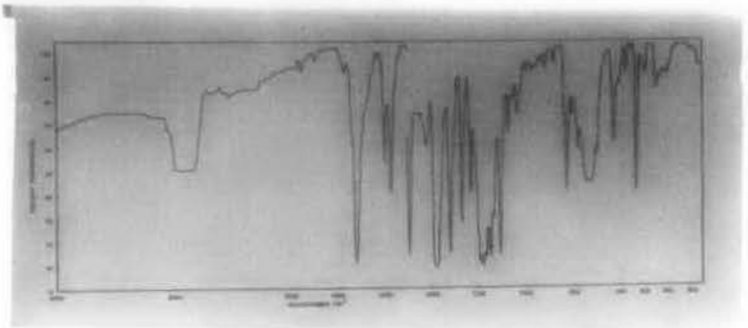


Fig. 4.4 IR spectrum of phenyltin trifluoroacetate dioxinate, $PhSn(OCOCF_3)Ox_2$.

11. Preparation of phenyltin monochloroacetate dioxinate, $PhSn(OCOCH_2Cl)Ox_2$ by the reaction of phenyltin chloro dioxinate with silver monochloroacetate:

1.40 gm of phenyltin chloro dioxinate and 0.60 gm of silver monochloroacetate was taken in 200 ml of methanol and the suspension was refluxed for 5 hr. The methanol was evaporated and the solid mass left was treated with benzene. The benzene soluble fraction on concentration and precipitation with petroleum ether yielded 1.16 gm of a yellow compound which on several recrystallisation from benzene/petroleum ether mixture was identified as phenyltin monochloroacetate dioxinate, m.p. 145°. (Found: C = 54.18%, H = 3.62%, N = 4.77%, Sn = 20.41%; Calcd. for $C_{26}H_{19}SnO_4N_2Cl$: C = 54.05%, H = 3.29%, N = 4.85%, Sn = 20.56%).

IR and UV/vis. spectra are shown in fig. 4.5 and figs. 4.8, 4.9 respectively.

12. Preparation of phenyltin trifluoroacetate dioxinate, $PhSn(OCOCF_3)Ox_2$ by the reaction of diphenyltin dioxinate with phenylmercuric trifluoroacetate:

1.30 gm of diphenyltin dioxinate and 0.90 gm of phenyl mercuric trifluoroacetate was taken in 300 ml of methanol and refluxed for 5 hr on a water bath. The solution became clear yellow after some time and then a yellow crystalline compound was precipitated in the solution during the reaction. After filtration, the yellow compound (0.80 gm) was recrystallised from a large volume of

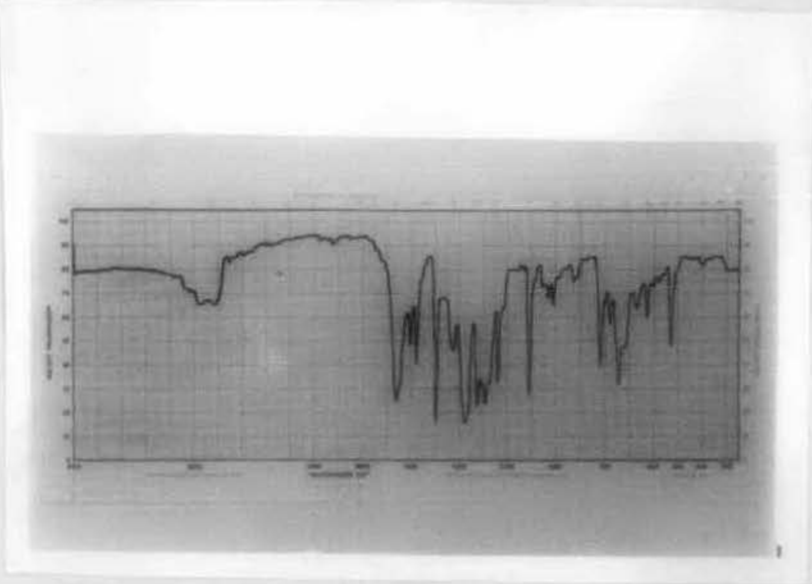
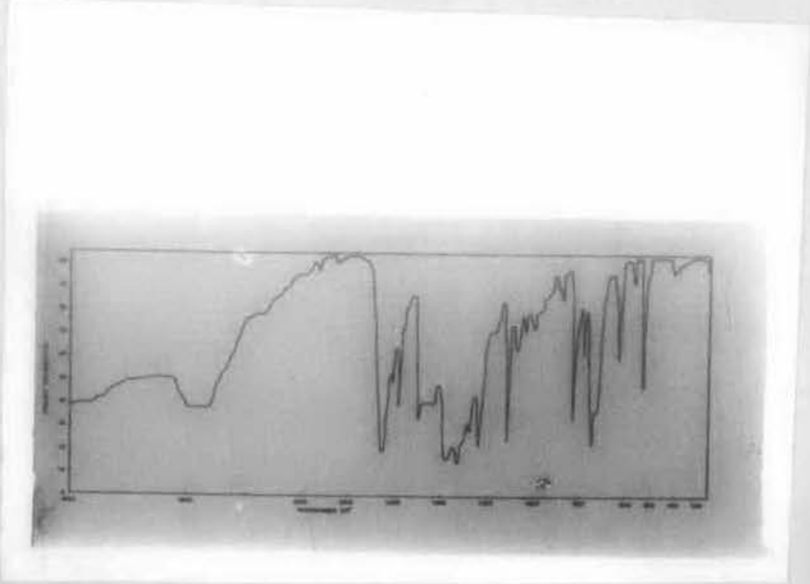


Fig. 4.5 IR spectrum of diacetatetin dioxinate, $(CH_3OCO)_2SnOx_2$.



ig. 4.6 IR spectrum of dipropionatetin dioxinate, $(CH_3CH_2OCO)_2$ $SnOx_2$.

tetrahydro furan/petroleum ether mixture which afforded compound of melting point 241°-242° and was identified as phenyltin trifluoroacetate dioxinate. (Found: C = 52.36%, H = 3.16%, N = 4.48%, Sn = 20.08%; Calcd. for $C_{26}H_{17}SnO_4N_2F_3$: C = 52.30%, H = 2.85%, N = 4.69%, Sn = 19.90%).

IR and UV/Vis spectra have been shown in fig. 4.4 and figs. 4.8, 4.9 respectively.

13. Preparation of diacetatetin dioxinate, $(CH_3COO)_2SnOx_2$ by the reaction of dichlorotin dioxinate with silver acetate:

1.20 gm of dichlorotin dioxinate and 0.90 gm of silver acetate were taken in 300 ml of methanol and the suspension was refluxed for 5 hr. The methanol was completely removed by evaporation after the reaction and the solid was treated with hot benzene. The benzene soluble portion gave 1.13 gm of a yellow compound after concentration. This on repeated recrystallisation from benzene/petroleum ether afforded pure diacetatetin dioxinate, m.p. 286°-287°. (Found: C = 49.75%, H = 3.45%, N = 5.21%, Sn = 22.31%; Calcd. for $C_{22}H_{18}SnO_6N_2$: C = 50.31%, H = 3.43%, N = 5.34%, Sn = 22.62%).

IR and UV/Vis spectra have been shown in fig. 4.5 and figs. 4.8, 4.9 respectively.

14. Preparation of dipropionatetin dioxinate, $(CH_3CH_2OCO)_2SnOx_2$ by the reaction of dichlorotin dioxinate with silver propionate:

1.50 gm of dichloridetin dioxinate and 1.20 gm of silver propionate were taken in 200 ml of methanol and the suspension was refluxed for 5 hr. The methanol was evaporated off after the reaction and the yellow solid left was treated with hot benzene. The benzene fraction was then concentrated which afforded 1.47 gm of a yellow compound. This compound on several recrystallisation from benzene was identified as dipropionatetin dioxinate, m.p. 266°-267°. (Found: C = 51.78%, H = 3.97%, N = 4.83%, Sn = 21.07%; Calcd. for $C_{24}H_{22}SnO_6N_2$: C = 52.12%, H = 3.98%, N = 5.07%, Sn = 21.48%).

IR and UV/vis spectra of this compound have been shown in fig. 4.6 and figs. 4.8, 4.9 respectively.

15. Preparation of bis monochloroacetatetin dioxinate, $(ClCH_2OCO)_2SnOx_2$ by the reaction of dichlorotin dioxinate with Silver monochloroacetate:

1.50 gm of dichlorotin dioxinate and 1.29 gm of silver mono chloroacetate were taken in 400 ml of methanol and the mixture was refluxed for 5 hr. The solvent was then removed by evaporation and the yellow solid left was treated with hot benzene. The benzene solution after concentration was mixed with sufficient volume of

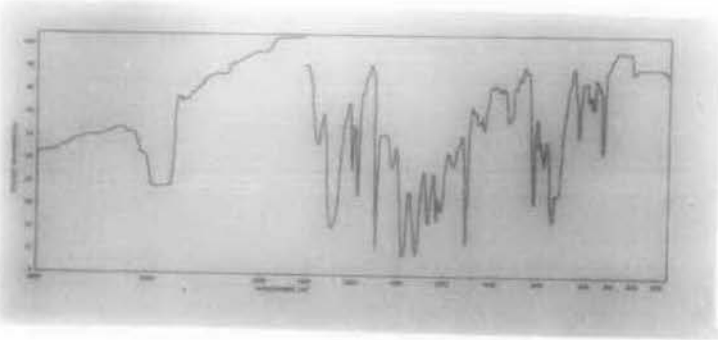


Fig. 4.7 IR spectrum of bis mono chloroacetatetin dioxinate, $(ClCH_2OCO)_2SnOx_2$.

petroleum ether whereby a yellow solid, 1.07 gm was precipitated. The solid on recrystallisation several times from benzene/petroleum ether mixture yielded pure bis monochloroacetatetin dioxinate, m.p. 205°-207°. (Found: C = 44.85%, H = 2.39%, N = 4.56%, Sn = 19.63%; Calcd. for $C_{22}H_{16}SnO_6N_2Cl_2$: C = 44.46%, H = 2.69%, N = 4.72%, Sn = 19.99).

IR and UV/Vis. spectra have been presented in fig. 4.7 and figs. 4.8, 4.9 respectively.

16. Reaction of diphenyltin chlorooxinate with potassium acetate:

2.22 gm of diphenyltin chloro oxinate and 0.65 gm of potassium acetate were taken in 400 ml of methanol and was refluxed for 6 hr. After complete evaporation of the solvent, the residue was extracted with benzene. The benzene soluble fraction afforded pure diphenyltin dioxinate, Ph_2SnOx_2, m.p. 248° (m.m.p) after several recrystallisation from benzene/petroleum ether mixture.

The benzene insoluble fraction was washed thoroughly with water and the water insoluble part after washing with methanol, benzene etc. dried in vacuum (0.74 gm). This compound was identified as polymeric diphenyltin oxide, Ph_2SnO on the basis of IR comparison with authentic spectrum. (Found: Sn = 40.87%; Calcd. for $C_{12}H_{10}SnO$: Sn = 41.11%).

The water solution was found to contain potassium chloride, KCl and excess potassium acetate, $KOOCCH_3$ by qualitative tests.

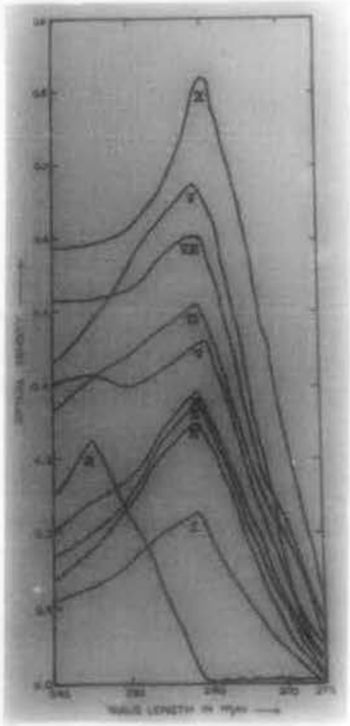


Fig. 4.8 Absorption spectra of the tin oxinates in the UV region:

I Phenyltin monochloroacetate dioxinate,

II Phenyltin acetate dioxinate,

III Phenyltin propionate dioxinate,

IV Phenyltin trifluoroacetate dioxinate,

V Dipropionatetin dioxinate,

VI Diacetatetin dioxinate,

VII Bis monochloroacetatetin dioxinate,

VIII Phenyltin chloro dioxinate,

X Diphenyltin dioxinate,

IX Dichlorotin dioxinate.

17. Reaction of triphenyltin oxinate with mercuric acetate:

2.97 gm triphenyltin oxinate was dissolved in 400 ml ether. To that, 1.91 gm mercuric acetate in 200 ml of ether was added and the suspension was stirred for 8 hr at room temperature and kept over night. The solvent was distilled off and the yellow residue was treated successively with petroleum ether and benzene. The petroleum ether fraction afforded 2.05 gm of a white solid, m.p. 120-123°, which on several recrystallisation from petroleum ether was identified as diphenyl mercury, m.p. 124°, by mixed melting point determination with an authentic sample of diphenyl mercury.

The benzene soluble fraction on slow evaporation afforded 1.39 gm of a yellow crystalline compound, m.p. 235-240°. This compound on several recrystallisation from benzene was identified as phenyltin acetate dioxinate, $PhSn(OAc)Ox_2$, m.p. 243-244°, identified by IR comparison and mixed melting point determination with authentic sample.

The petroleum ether and benzene insoluble fraction that remained was found to be insoluble in common organic solvents and was infusible even upto 360°. This white compound, 0.75 gm, was identified as polymeric phenyl stannoic acetate on the basis of IR comparison with authentic sample and preparation of oxine derivative, viz., phenyltin acetate dioxinate, by the method described in early chapters.

Liberation of acetic acid was detected during the course of reaction.

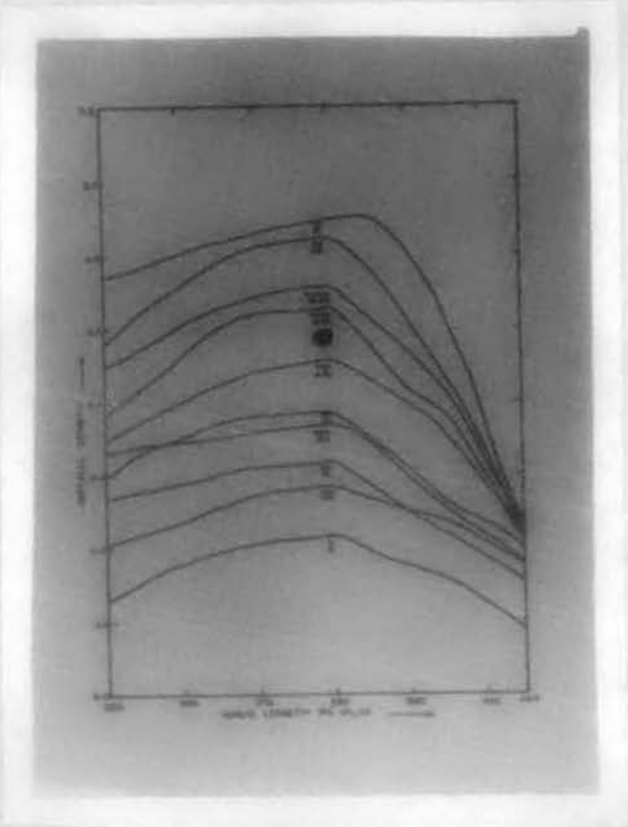


Fig. 4.9 Absorption spectra of the tin oxinates in the visible region:

I Phenyltin monochloroacetate dioxinate,

II Phenyltin acetate dioxinate,

III Phenyltin propionate dioxinate,

IV Phenyltin trifluoroacetate dioxinate,

V Dipropionatetin dioxinate,

VI Diacetatetin dioxinate,

VII Bis monochloroacetatetin dioxinate,

VIII Phenyltin chloro dioxinate,

IX Diphenyltin dioxinate,

X Dichlorotin dioxinate.

18. Reaction of triphenyltin oxinate with phenyl mercuric acetate:

To a solution of 4.42 gm of triphenyltin oxinate in 600 ml ether, 3.00 gm of phenyl mercuric acetate (1:1) in 200 ml of ether was added. The suspension was stirred for 8 hr and kept over night. The solvent was distilled off and the yellow residue was extracted successively with petroleum ether and methanol.

The petroleum ether fraction afforded on slow evaporation 3.10 gm of diphenyl mercury identified by mixed melting point determination with an authentic sample.

The methanol fraction on fractional crystallisation yielded 2.20 gm of unreacted triphenyltin oxinate (m.m.p) and 1.05 gm of phenyltin acetate dioxinate which was identified by IR comparison and mixed melting point determination with an authentic sample.

The petroleum ether and methanol insoluble fraction was identified as polymeric phenyl stannoic acetate by IR comparison and preparation of phenyltinacetate dioxinate by treatment with oxine.

It has been observed that when triphenyltin oxinate and phenyl mercuric acetate are reacted in 1:2 ratio no unreacted triphenyltin oxinate could be isolated. Thus 2.72 gm triphenyltin oxinate and 3.70 gm of phenyl mercuric acetate in ether yields 3.80 gm of diphenyl mercury, 1.31 gm phenyltin acetate dioxinate and 0.72 gm of polymeric phenyl stannoic acetate.

In both the reactions, the formation of acetate ions were detected by qualitative tests.

19. Reaction of diphenyltinchloro oxinate with phenyl mercuric acetate:

To a solution of 3.20 gm of diphenyltin chloro oxinate in 400 ml ether, 4.75 gm of phenyl mercuric acetate in 300 ml of ether was added. The mixture was stirred for 8 hr and kept over night. The solvent was distilled off and the residue was first treated with petroleum ether and then with hot methanol. The petroleum ether fraction afforded 2.5 gm of diphenyl mercury (m.m.p). The methanol fraction on fractional crystallisation afforded 2.18 gm of phenyl mercuric chloride, m.p. 251°, identified by mixed melting point determination with an authentic sample and 1.68 gm of phenyltin acetate dioxinate, identified by IR comparison and mixed melting point determination with authentic sample.

The petroleum ether and methanol insoluble fraction was identified as polymeric phenylstannoic acetate, 0.39 gm, by the procedure mentioned earlier.

The formation of acetate ion during the reaction was detected qualitatively.

20. Reaction of triphenyltin salicylaldehyde with mercuric chlorid

4.70 gm of triphenyltin salicylaldehyde was dissolved in 400 ml ether. To that, 2.71 gm of mercuric chloride in 200 ml of ether was added with stirring and the stirring continued for 7 hr The whole solution was then filtered whereby a polymeric compound 0.69 gm, infusible upto 360° and insoluble in common organic solvents was left as residue (18A).

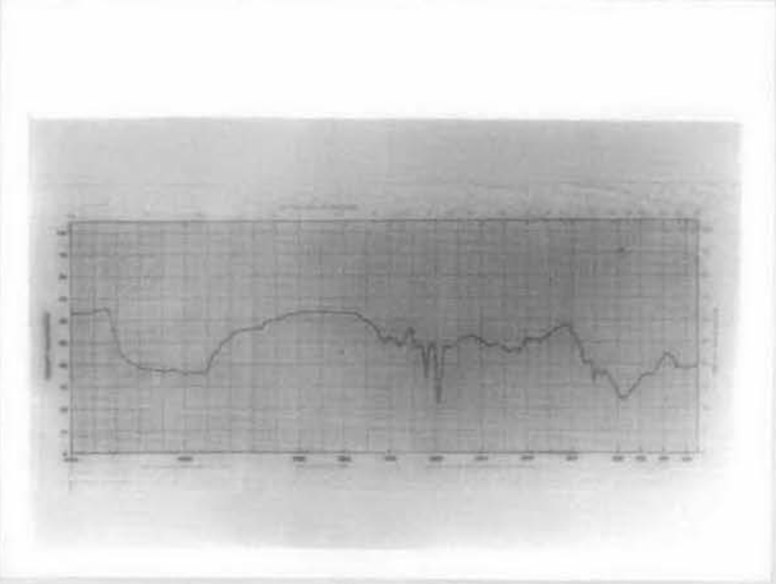


Fig. 4.10 IR spectrum of polymeric compound $Sn(OH)_4$ obtained from the reaction of triphenyltin salicylaldehyde and mercuric chloride.

The filtrate on working up following the procedure described in Chapter II yielded the following compounds:

1. Phenylmercuric chloride, 3.05 gm, m.p. 251° (m.m.p)
2. triphenyltin chloride, 2.41 gm, m.p. 105° (m.m.p)
3. salicylaldehyde- identified by qualitative tests and its boiling point, bp 197° (57)

The polymeric material from its elemental analysis and IR spectrum (fig. 4.10) was found to be essentially $Sn(OH)_4$ containing a few organic groups. (Found: C = 6.63%, H = 1.88%, Sn = 58.38%).

21. <u>Reaction of triphenyltin hydroxide with alizarin</u>:

3.63 gm of triphenyltin hydroxide (prepared from triphenyltin chloride and sodium hydroxide in ether/water mixture) and 2.35 gm of alizarin were mixed together in 400 ml methanol and refluxed for 6 hr. The whole solution was then filtered and the residue was treated with hot benzene. The benzene soluble fraction afforded tetraphenyltin, m.p. 224° (m.m.p). The residue (20A) thus obtained was found to be infusible upto 360°.

The original filtrate was evaporated to dryness and then treated with benzene. The benzene soluble fraction afforded a red needle shaped crystalline compound (20B), m.p. 232-234°, after several recrystallisation from benzene. The benzene insoluble frac tion was again an infusible compound (20C).

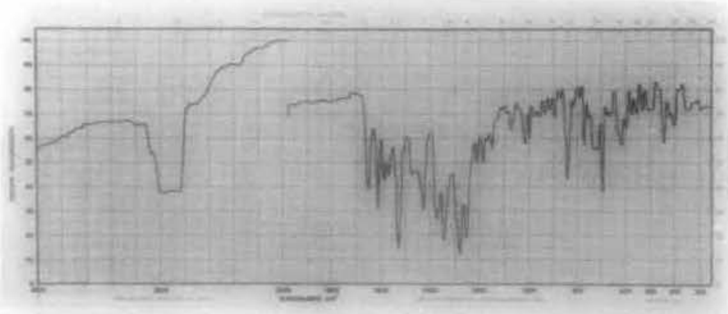


Fig. 4.11 IR spectrum of alizarin complex.

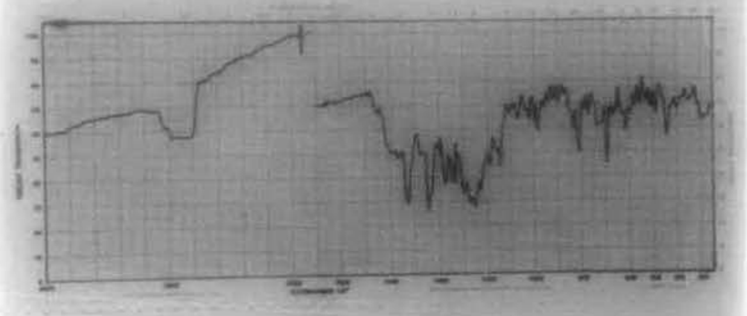
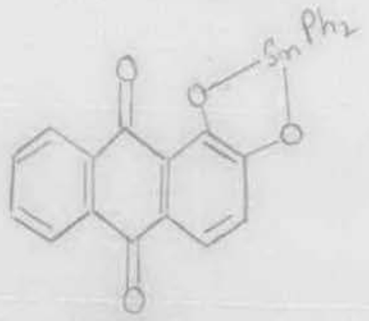


Fig. 4.12 IR spectrum of quinalizarin complex.

Characterisation of the compound 20B:

The red compound 20B was identified as a diphenyltin alizarin complex having the following formula; on the basis of elemental analysis and IR spectrum:



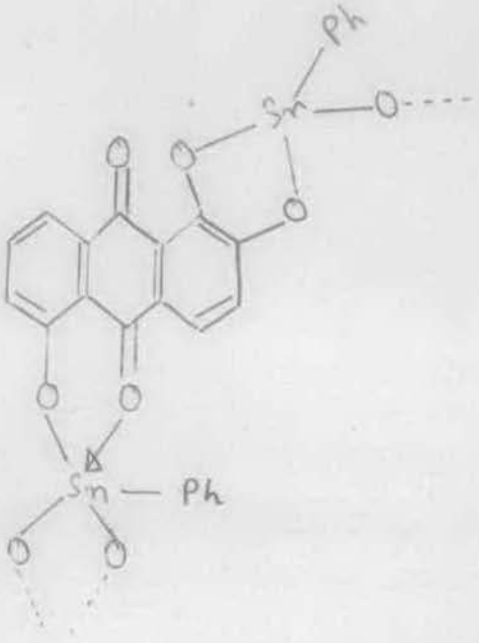
(Found: C = 60.78%, H = 3.32%, Sn = 22.7%; Calcd. for $C_{26}H_{16}SnO_4$: C = 60.98%, H = 3.32%, Sn = 23.2%).

The infrared spectrum (fig. 4.11) on comparison with the spectrum of alizarin showed the absence of any hydroxyl (-OH) band which signified that the two hydroxyl group of alizarin had been utilised in the complex formation. Beside this a new band was appeared at 1530 cm^{-1}. Although the origin of this band cannot be assigned with certainity but may be associated with carboxyl frequency which had been lowered through co-ordination.

The characterisation of the compounds 20A and 20C were not possible, however, this reaction is under further investigations.

22. Reaction of triphenyltin hydroxide with quinalizarin:

3.00 gm of triphenyltin hydroxide was treated with 2.25 gm of quinalizarin in 400 ml of methanol. The solution was refluxed for 6 hr and the solvent was carefully pumped off. The solid was then dried in vacuum and weighed 4.48 gm. The loss in weight due to the reaction indicated the formation of a volatile product. The volatile product had been identified as benzene by spectrophotometric technique described later on. The solid was washed thoroughly with benzene. The benzene soluble fraction was identified as unreacted quinalizarin (1.11 gm). The benzene insoluble fraction was recrystallised from a large volume of T.H.F. and petroleum ether and the violet compound which obtained appeared to be polymer from its poor solubility in common organic solvents and infusibility upto 360°. This compound on the basis of IR spectrum (fig. 4.12) and elemental analysis has been tentatively formulated having the following units:



(Found: C = 43.81%, H = 2.30%, Sn = 19.12%; Calcd. for $C_{26}H_{15}Sn_2O_9$: C = 44.68%, H = 2.15%, Sn = 19.67%).

That the compound contained two phenyl groups per molecule was verified by dearylation of the complex with mercuric chloride. Thus the complex yielded stepwise two equivalents of phenyl mercuric chloride when it was refluxed first with one equivalent of mercuric chloride in methanol and then with excess of the mercuric chloride.

Identification of the volatile product:

All the apparatus used were heated for 24 hr in an air oven. Methanol used in this investigation was of G.R./E.M. quality.

All materials were scrupulously checked for traces of benzene by ultral violet spectra in the region 230-270 mμ and were found to be free from benzene. A blank experiment was also made by refluxing 1.00 gm of triphenyltin hydroxide in 100 ml methanol for 6 hr. The distillate was again found to be benzene free by the same procedure.

1.00 gm of triphenyltin hydroxide and 0.75 gm quinalizarin was taken in 100 ml of methanol and was refluxed for 6 hr. The methanol was then distilled off from the mixture completely. After required dilution with methanol, the absorption spectrum in the region 230-260 mμ was carefully measured with a Beckman DU-2 spectrophotometer. The spectrum was completely identical with that of A.R.

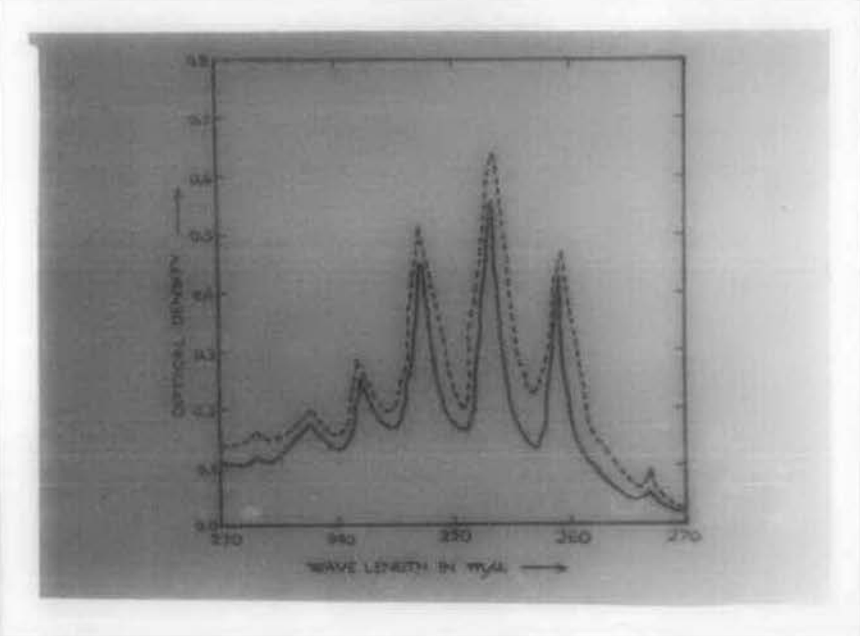


Fig. 4.13 Absorption spectrum of the distillate of the reaction of triphenyltin hydroxide and quinalizarin (solid line). The spectrum of pure benzene (dashed line) in the same solvent is shown for comparison.

benzene taken in the same solvent (fig. 4.13), thus demonstrating the formation of benzene in the reaction.

Separation of benzene by fractional distillation from methanol was not feasible because of the very low benzene content.

PART - IV

DISCUSSION

DISCUSSION

The reactions of $PhSn(Cl)Ox_2$ and Cl_2SnOx_2 with silver carboxylates, AgOCOR may be represented by the following exchange reactions:

$$PhSnClOx_2 + AgOCOR \longrightarrow PhSn(OCOR)Ox_2 + AgCl$$

$$Cl_2SnOx_2 + 2\ AgOCOR \longrightarrow (ROCO)_2SnOx_2 + 2AgCl$$

It is known that the electrophilic attack at carbon atom directly bonded to tin atom could cleave the tin carbon bond as have been demonstrated by the reactions of triorganotin carboxylates with mercury salts described in section II. By taking advantage of such type of reactions, organotin carboxylate oxinates have been prepared.

Thus :

$$Ph_2SnOx_2 + PhHgOCOR \longrightarrow PhSn(OCOR)Ox_2 + Ph_2Hg$$

(Where $R = CH_3,\ CF_3$)

The above reaction may be conveniently used as a route for the preparation of phenyltin carboxylate dioxinates.

Reaction of triphenyltin oxinate with mercuric acetate produces phenyltin acetate dioxinate; $PhSn(OCOCH_3)Ox_2$, diphenyl mercury; Ph_2Hg and polymeric phenyl stannoic acetate; $[PhSn(O)OAc]_n$. Considering the stoichiometry of the products obtained the following mechanism may be proposed:

$$\Delta \quad 2Ph_3SnOx + 2Hg(OAc)_2 \longrightarrow 2Ph_2Sn(OAc)Ox + 2PhHgOAc$$

$$2Ph_2Sn(OAc)Ox \longrightarrow Ph_2SnOx_2 + Ph_2Sn(OAc)_2$$

$$Ph_2SnOx_2 + PhHgOAc \longrightarrow PhSn(OAc)Ox_2 + Ph_2Hg$$

$$PhSn(OAc)_2 + PhHgOAc \longrightarrow PhSn(OAc)_3 + Ph_2Hg$$

$$PhSn(OAc)_3 + H_2O \longrightarrow PhSn(O)OAc + 2AcOH$$

The over all reaction is

$$2Ph_3SnOx + 2Hg(OAc)_2 \longrightarrow PhSn(OAc)Ox_2 + PhSn(O)OAc + 2Ph_2Hg + 2AcOH$$

Inspite of our best efforts, it has been observed that the reaction of diphenyltin chloro oxinate, $Ph_2Sn(Cl)Ox$ with potassium acetate produces only diphenyltin dioxinate, Ph_2SnOx_2 and diphenyltin oxide, Ph_2SnO instead of diphenyltin acetate oxinate, $Ph_2Sn(OAc)Ox$. Diphenyltin acetate oxinate is probably unstable and may redistribute as follows:

$$Ph_2Sn(Cl)Ox + KOCOCH_3 \longrightarrow Ph_2Sn(OAc)Ox + KCl$$

$$Ph_2Sn(OAc)Ox \longrightarrow \tfrac{1}{2}Ph_2SnOx_2 + \tfrac{1}{2}Ph_2Sn(OAc)_2$$

The overall reaction is, therefore,

$$Ph_2Sn(Cl)Ox + KOCOCH_3 \longrightarrow \tfrac{1}{2}Ph_2SnOx_2 + \tfrac{1}{2}Ph_2Sn(OAc)_2$$

Diphenyltin diacetate, $Ph_2Sn(OAc)_2$ thus produced undergoes hydrolysis to form Ph_2SnO. Formation of Ph_2SnOx_2 is also observed when silver acetate is used in place of potassium acetate. The postulation of the formation of diphenyltin dioxinate by the redistribution of $Ph_2Sn(OAc)Ox$ in the second step of the mechanism A may thus be justified . Phenyltin triacetate, $PhSn(OAc)_3$ hydrolyses to polymeric phenyl stannoic acetate, $[PhSn(O)OAc]_n$(58) as indicated in the last step of the mechanism A.

The various products viz., $[PhSn(O)OAc]_n$, $PhSn(OAc)Ox_2$ and Ph_2Hg as well as their relative amounts obtained from the reaction of triphenyltin oxinate and phenyl mercuric acetate (1:2) may similarly be explained by the sequence of reactions as suggested in mechanism A. In case of the reaction when equimolar proportions of the above reactants are used, the products are essentially same except that fifty percent unreacted triphenyltin oxinate could be recovered. This indicates that the above reaction always proceeds in 1:2 molar proportions of the reactants.

An interesting feature is observed in the reaction between diphenyltin chloro oxinate, $Ph_2Sn(Cl)Ox$ and phenyl mercuric acetate, $PhHgOAc$. In this case phenyl mercuric chloride, $PhHgCl$ is produced together with Ph_2Hg, $PhSn(OAc)Ox_2$ and $[PhSn(O)OAc]_n$. Considering the stoichiometry of the products obtained, the following mechanism may be proposed:

B

$$2Ph_2Sn(Cl)Ox + 2PhHgOAc \longrightarrow 2Ph_2Sn(OAc)Ox + 2PhHgCl$$

$$2Ph_2Sn(OAc)Ox \longrightarrow Ph_2SnOx_2 + Ph_2Sn(OAc)_2$$

$$Ph_2SnOx_2 + PhHgOAc \longrightarrow PhSn(OAc)Ox_2 + Ph_2Hg$$

$$Ph_2Sn(OAc)_2 + PhHgOAc \longrightarrow PhSn(OAc)_3 + Ph_2Hg$$

$$PhSn(OAc)_3 + 2H_2O \longrightarrow PhSn(O)OAc + 2AcOH$$

$$2Ph_2Sn(Cl)Ox + 4PhHgOAc + 2H_2O \longrightarrow PhSn(OAc)Ox_2 + PhSn(O)OAc + 2PhHgCl + 2Ph_2Hg$$

A number of reactions are known where $Ph_2Sn(Cl)Ox$ exchanges chlorine atom with a variety of anions (loc. cit). For this reason, to explain the formation of PhHgCl, chlorine-acetate exchange has been postulated in frist step of the mechanism B.

UV, Visible and IR spectra of $PhSn(OCOR)Ox_2$ and $(ROCO)_2SnOx_2$:

The electronic absorption spectra of the four phenyltin carboxylate dioxinate and three bis carboxylate tin dioxinate are shown in figs. 3.8 and 3.9. The spectra of $PhSn(Cl)Ox_2$, Ph_2SnOx_2 and Cl_2SnOx_2 have also been included in the figures for comparison. All these spectra are characterised by an intense absorption band in the region 245 mμ to 270 mμ and a broad band around 380 mμ. All the spectra have been measured in methanol solutions. The data are shown in table-I.

Table-1*

Compound	λ max (in mμ)
$PhSn(OCOCH_3)Ox_2$	259,380 (3.71)
$PhSn(OCOCH_2CH_3)Ox_2$	259,380 (3.74)
$PhSn(OCOCH_2Cl)Ox_2$	259,380 (3.71)
$PhSn(OCOCF_3)Ox_2$	260,380 (3.69)
$(CH_3OCO)_2SnOx_2$	259,380 (3.70)
$(CH_3CH_2OCO)_2SnOx_2$	259,380 (3.70)
$(ClCH_2OCO)_2SnOx_2$	259, 380 (3.70)
$PhSn(Cl)Ox_2$	259,380 (3.71)
Ph_2SnOx_2	260,380 (3.76)
Cl_2SnOx_2	245,385

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* Figures in the parenthesis indicate log ϵ max.

The close similarity in the spectra of the carboxylate dioxinates and diphenyltin dioxinates not only indicates hexa coordination around tin atom but also a general similarity in their structures. The spectra of Cl_2SnOx_2 is however, slightly different. Although detailed structures of Ph_2SnOx_2 and Cl_2SnOx_2 are not known, trans configuration has been suggested for the former on the basis of IR, NMR, dipole moment and optical resolution studies (40) and a cis configuration for the latter from IR studies (44). These considerations suggest trans configuration for the phenyltin carboxylate dioxinate, $PhSn(OCOR)Ox_2$ and cis for the bis carboxylatetin dioxinate, $(ROCO)_2SnOx_2$. However, the existence of rigorously defined cis and trans forms is probably meaningless in view of the recent structural determination of Me_2SnOx_2 by Schlemper (11). This compound which was believed to have a trans geometry from various physico chemical studies has been shown to possess a highly distorted structure where the terms cis and trans have little relevance. In fact, Schlemper (11) has interpreted the structure of Me_2SnOx_2 as derived from a distorted tetrahedral structure. The possibility of the variation in the angle between the planes of the two oxinate groups cannot be ruled out. Such a variation will alter the extent of interaction between the two oxinate groups resulting in slight changes in the UV and visible spectra.

The IR spectra have been shown in figures 4.1 - 4.7.

ν_{as}(OCO) frequencies in carboxylate oxinates in solid phase (nujol mull) together with the corresponding triphenyltin carboxylates are given in table-II.

Table-II

Compound	$\nu_{as}(OCO)^{a}$	$\nu_{as}(OCO)^{b}$
$Ph_3SnOCOCH_3$	1548	1640
$Ph_3SnOCOCH_2CH_3$	1535	1632
$Ph_3SnOCOCH_2Cl$	1576	1662
$Ph_3SnOCOCF_3$	1650	1722
$PhSn(OCOCH_3)Ox_2$	1645	
$PhSn(OCOCH_2CH_3)Ox_2$	1645	
$PhSn(OCOCH_2Cl)Ox_2$	1672	
$PhSn(OCOCF_3)Ox_2$	1725	
$(CH_3OCO)_2SnOx_2$	1660	
$(CH_3CH_2OCO)_2SnOx_2$	1650	
$(ClCH_2OCO)_2SnOx_2$	1700	

(a) solid in nujol

(b) $\nu_{as}(OCO)$ in CCl_4, taken from literatures (58,59).

νas (OCO) in triorganotin carboxylates are usually in the range 1548-1650 cm^{-1} and the lowering of νas (OCO) in solid phase has been attributed to the formation of intermolecular coordination (58) by the carboxylate groups. In contrast to this νas(OCO) in solid carboxylate oxinates are found in the region 1645-1725 cm^{-1} and are very nearly equal to νas (OCO) in the corresponding triorganotin carboxylates in CCl_4 solution. The large increase in νas(OCO) in going from solid to solution phase (by about 100 cm^{-1}) has been interpreted interms of breaking of the intermolecular coordination bonds and consequent formation of molecules with non bridging (or non chelating) carboxylate groups (comparable to ester type carboxylate groups) (58,59). The close correspondence between νas (OCO) in carboxylate oxinates in solid phase and those in simple carboxylates in solution thus indicates the absence of bridging or chelating carboxylate groups in the former. These compounds, therefore, contain hexacoordinated tin like the corresponding tin halo oxinates and dichlorotin dioxinate. The reluctance of the carboxylates to form intermolecular bridges in these compounds may be attributed to the comparatively weak donor property of the carbonyl oxygen as well as the acceptor property of already hexa coordinated tin atom.

The effect of substitution at the α -carbon atom of the carboxylate group in tin carboxylate oxinates is analogous to that observed in simple tin carboxylates (59). Thus νas (OCO) increases in the series:

$CH_3COO \gtrsim CH_3CH_2COO < ClCH_2COO < CF_3COO.$

This trend is therefore, due mainly to the inductive effect of the substituent groups; increase in the electronegativities of the substituent groups leads to a lower contribution by the polar structure  and therefore raises νas (COO).

The reaction of mercuric chloride with triphenyltin salicylaldehyde complex may be comparable to the corresponding reaction of triphenyltin acetate. Both of them are known to have a penta coordinated tin atom and therefore, likely to behave in a similar way towards the same reagent, mercuric chloride. Thus the formation of the products in the reaction between mercuric chloride and triphenyltin salicylaldehyde complex may be represented by the following sequence of reactions:

D

$$Ph_3SnSal + HgCl_2 \longrightarrow Ph_2Sn(Cl)Sal + PhHgCl$$

$$Ph_2Sn(Cl)Sal + Ph_3SnSal \longrightarrow Ph_3SnCl + Ph_2Sn(Sal)_2$$

$$Ph_2Sn(Sal)_2 + HgCl_2 \longrightarrow PhSn(Cl)Sal_2 + PhHgCl$$

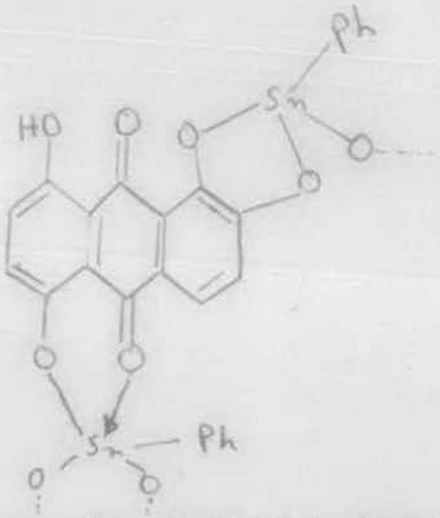
$$PhSn(Cl)Sal_2 + Ph_3SnSal \longrightarrow Ph_3SnCl + PhSn(Sal)_3$$

$$PhSn(Sal)_3 + HgCl_2 \longrightarrow Sn(Cl)Sal_3 + PhHgCl$$

$$Sn(Cl)Sal_3 + 4HOH \longrightarrow Sn(OH)_4 + 3SalH + HCl$$

(Where Sal = $-OC_6H_4CHO-2$).

Reaction of triphenyl hydroxide with alizarin (1,2 dihydroxy anthraquinone) produces among other products a new diphenyltin alizarin complex. Whereas the reaction between triphenyltin hydroxide and quinalizarin (1,2,5,8 tetrahydroxy anthraquinone) produces a polymeric organotin complex of quinalizarin whose formula has been tentatively assigned as follows on the basis of elemental analysis, chemical reactions and IR spectroscopy:



However, it may be mentioned that both of the above reactions are under investigation to characterise the products and their mode of formation with certainty. Nothing more can be said about these reactions at this stage.

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