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: $R_3SnOOCR'$, $R_2Sn(OOCR')_2$ and $RSn(OOCR')_3$ 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 azeotropic distillation or alternatively be removed by refluxing the reaction at higher temperatures (16).

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

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 tetraacetate, 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.

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

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

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

$$2Bu_2SnH(OAc) \longrightarrow Bu_2Sn(OAc) - SnBu_2(OAc)$$

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

$$2Bu_2SnH_2 + (C_6H_5COO)_2 \longrightarrow Bu_2Sn(OOCC_6H_5) - SnBu_2(OOCC_6H_5) + 2H_2$$

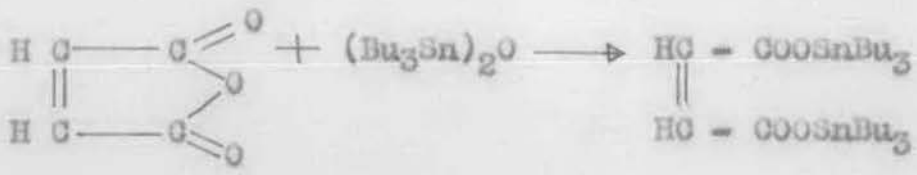
Halo carboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular propertion of dihalide and a dicarboxylate in an inert solvent (30, 31)

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

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.(°C/mm)	M.P.(°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).

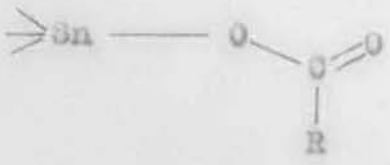
Structure of organotin carboxylates:

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 more 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)

Fig. I

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

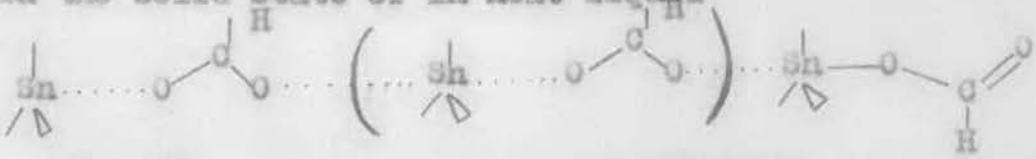


Fig. II

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 α-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 infrared 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,

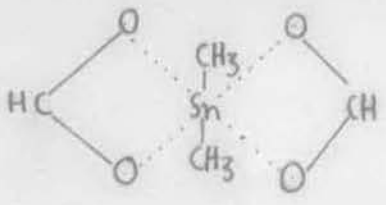


Fig. III

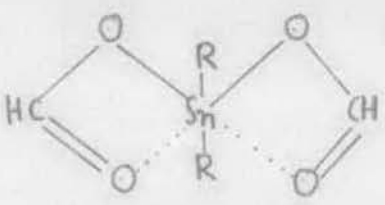


Fig. IV

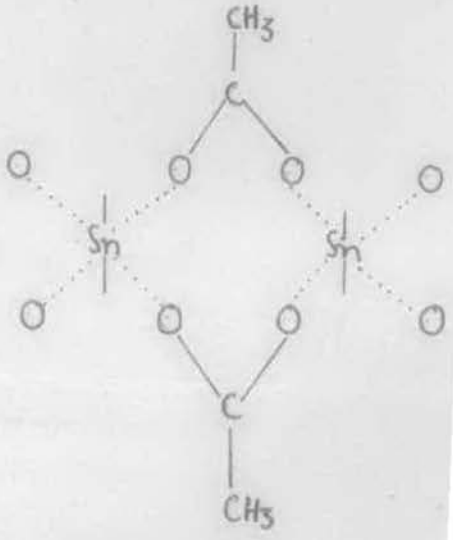


Fig. V

due to the presence of an additional band at ~1560 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).

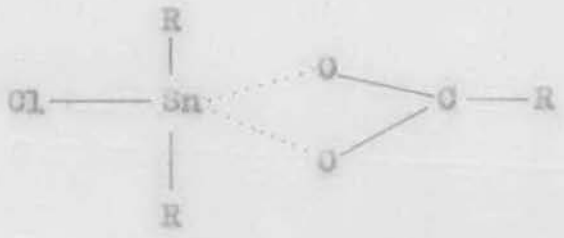


fig. VI

Allock and Timms (58) 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).

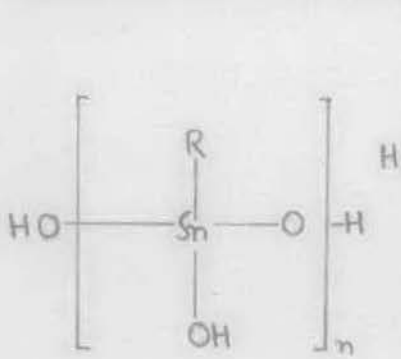


Fig. VII

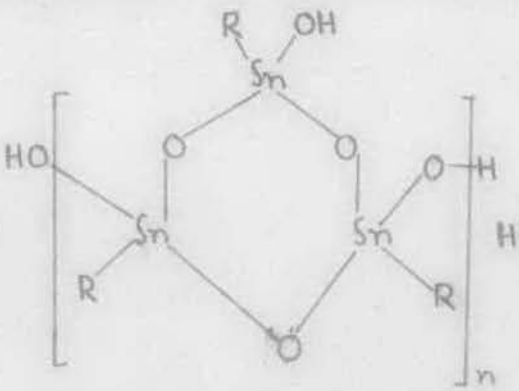


Fig. VIII

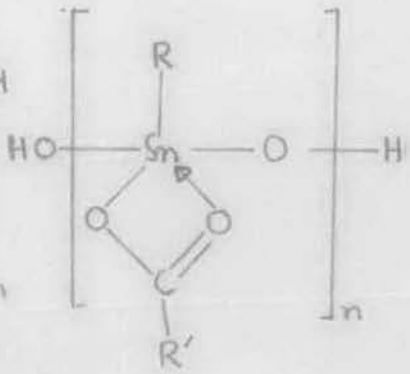


Fig. IX

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

.C.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 $\left[RSn(O)OCOR'\right]_n$ of the stannoic acids $\left[RSn(O)OH\right]_n$ 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	1.62 - 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 (18,45).

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 characteristics 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 νas (Sn-O-Sn) stretching in mono and dialkyl poly stannoxanes (70-72). Assignment of the νas (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).

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

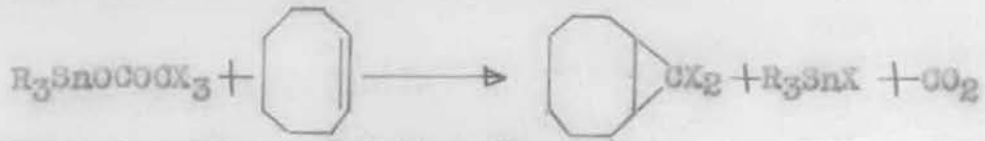
[Where R' = C_6H_5 or SnR_3]

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

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

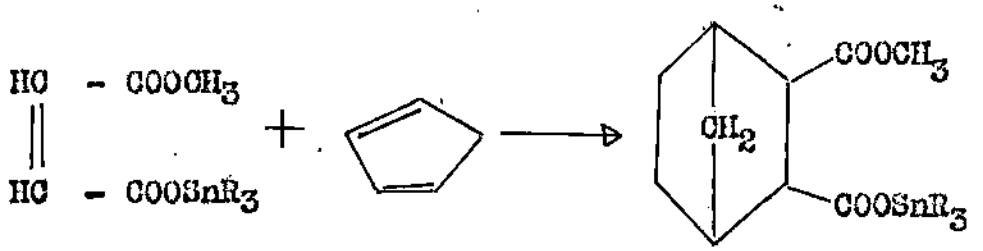
[R = n - C_3H_7, n - C_4H_9]

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. Hufti and R.C.Poller (32) with organotin carboxylates and dienes.



[R = n-C_4H_9; C_6H_5]

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).

$$Bu_3SnOAc + Ti(OBu)_4 \longrightarrow Bu_3SnOTi(OBu)_3$$

$$\downarrow (HOCH_2CH_2)_3N$$

$$Bu_3SnOTi(OCH_2CH_2)_3N$$

Diorganotin dicarboxylates undergo redistribution with diorganotin dihalides, dialkoxides and dihydrides to produce mixed carboxylates of the type $R_2SnX(OOCR')$, 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).

$$Bu_2Sn(OMe)OAc + CCl_3CHO \longrightarrow Bu_2Sn(OAc)OCH(CCl_3)OMe$$

$$Bu_2Sn(OAc)_2 + Bu_2Sn\left[OCH(CCl_3)OMe\right]_2 \nearrow$$

1,3 tetrabutyl 1,3 diacetoxy distannoxane reacts with ^tBuOOH to give $(^tBuOO)Bu_2SnOSnBu_2(OOBu^t)$ (17,81).

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

Oligomeric acetate is usually formed when a dialkyltin diacetate and a dialkyltin dialkoxide are heated at 180° 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).

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

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).

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

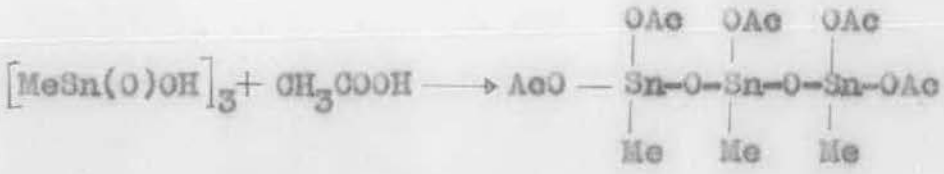
[Where X = Cl]

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.

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

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).



Recently Sams et al (13) 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 (35,36),

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:

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

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 $\rightleftharpoons$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 $\left[RSn(OH)_2OCOR'\right]_n$,

$\left[RSn(O)OH\right]_n$, $\left[Sn(OH)_4\right]_n$ 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 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, $\left[PhSn(O)OAc\right]_n$. 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

E X P E R I M E N T A L

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 (B.M.), mercuric iodide (B.M.), mercuric acetate (B.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 [illegible] Sams et al (18). It was then recrystallised from benzene/petroleum ether 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. Reaction of triphenyltin formate with mercuric chloride:

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°(d) was found insoluble. The benzene soluble fraction was evaporated and 2.00 gm of solid material (10B), m.p. 247-249° was obtained. The filtrate was slowly concentrated and the following fractions were obtained:

1) Shining leafy crystals, 1.00 gm, m.p. 249-250°(10C)
2) Crystalline solid, 1.55 gm, m.p. 227-247°, (10D)
3) Crystalline solid, 2.06 gm, m.p. 100-102° (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.

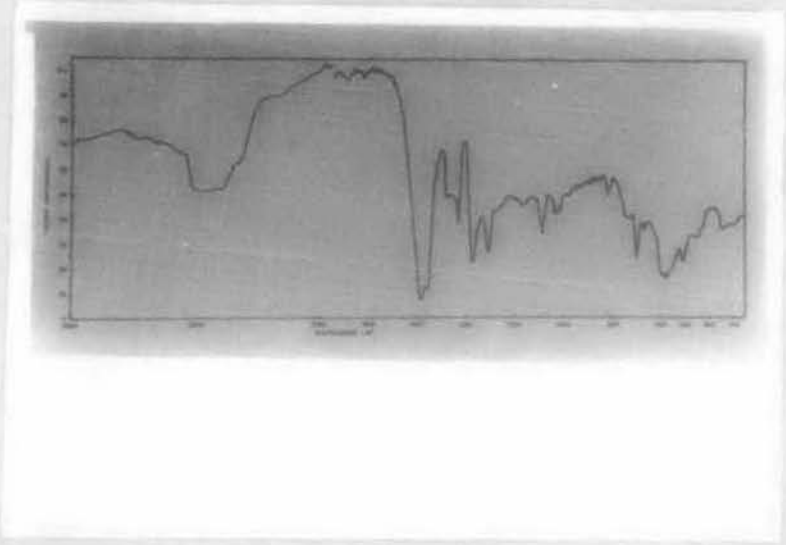


Fig. 2.1 IR spectrum of polymeric compound phenyltin dihydroxy formate, $PhSn(OH)_2OCOH$ obtained from the reaction of triphenyltin formate and mercuric chloride.

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:

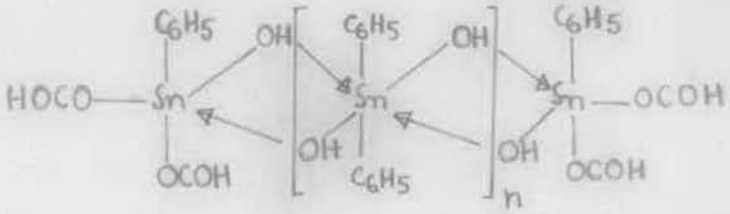
1) Insolubility in almost all common organic solvents*
2) Decomposes at 270°.
3) The IR spectrum (fig. 2.1) showed the following major bands.

ν(OH) = 3540 cm^{-1}; 3370 cm^{-1}

ν_{as}(OCO) = 1575 cm^{-1}; 1550 cm^{-1}

ν_{as}(Sn-O-Sn) = 560 cm^{-1}

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



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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.

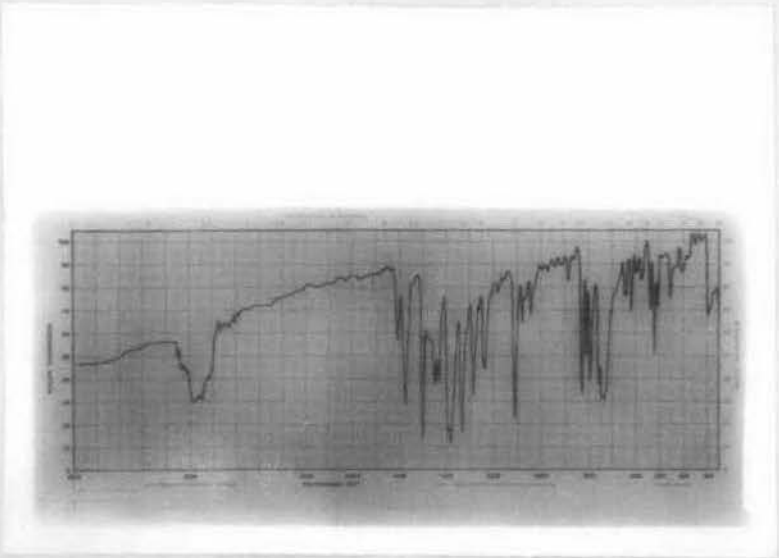

Fig. 2.2 IR spectrum of phenyltin trioxinate, $PhSn(Ox)_3$.

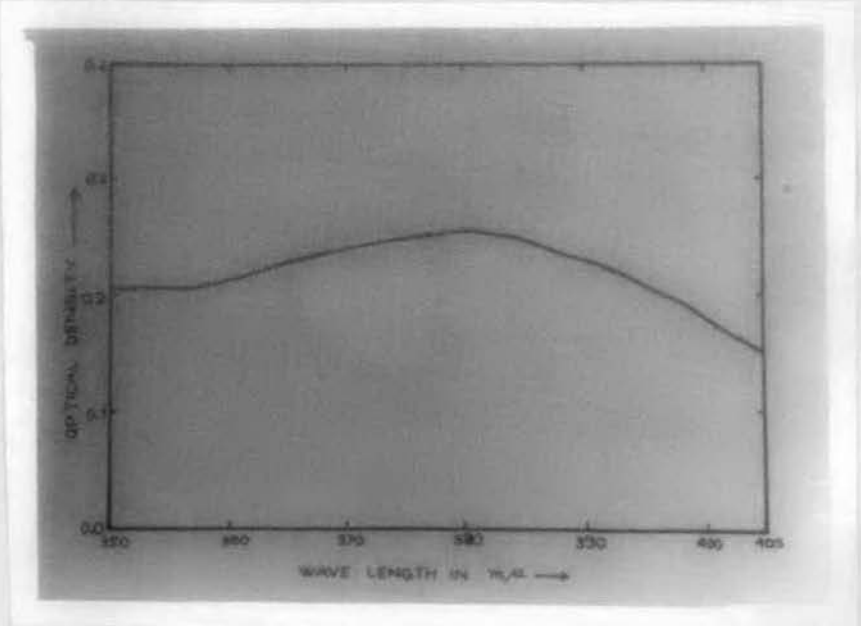

Fig. 2.2A Absorption spectrum of phenyltin trioxinate, $PhSn(Ox)_3$ in the visible region.

(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 whereby 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 390 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

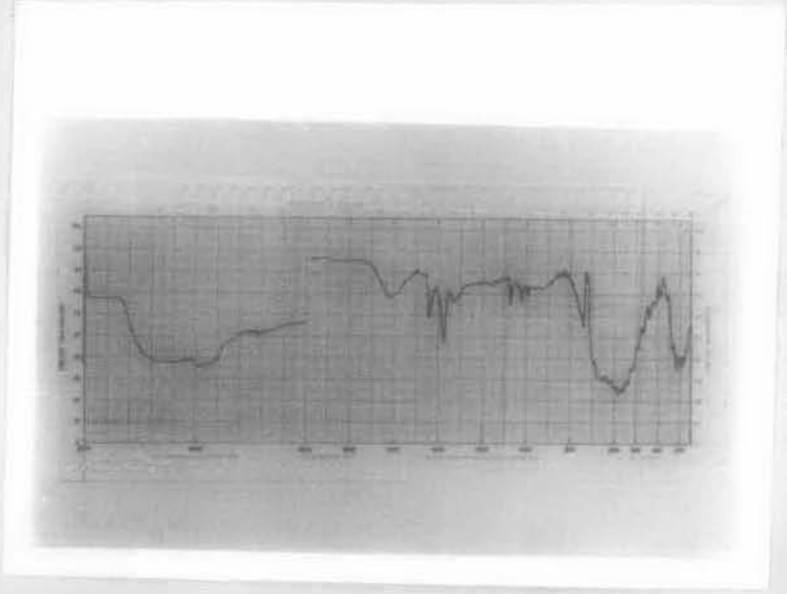

Fig. 2.3 IR spectrum of polymeric phenyl stannoic acid, PhSn(O)OH.

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, $\left[C_6H_5Sn(O)OH\right]_n$ 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 $\left[C_6H_5Sn(OH)_2OCOH\right]_n$ for about a year in a glass tube stoppered with bark cork, it decomposed to polymeric $\left[C_6H_5Sn(O)OH\right]_n$ 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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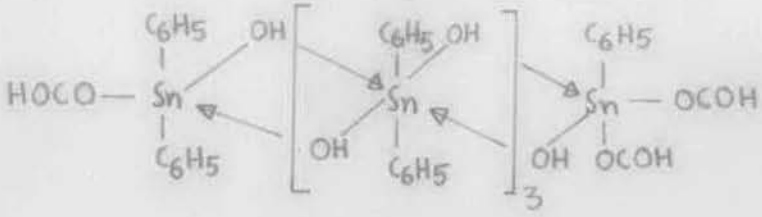
* The same procedure have been adopted to detect the formation of carboxylate/halide ions during the latter reactions.

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.

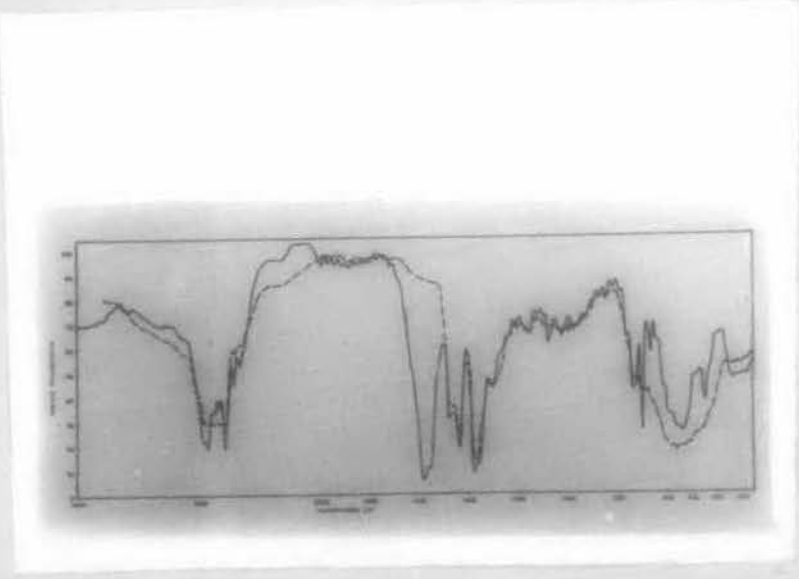


Fig. 2.3A IR spectrum of the compound obtained by heating phenyltin dihydroxy formate, $PhSn(OH)_2OCOH$ (dashed line). The spectrum of phenyltin dihydroxy formate (solid line) is shown for comparison.

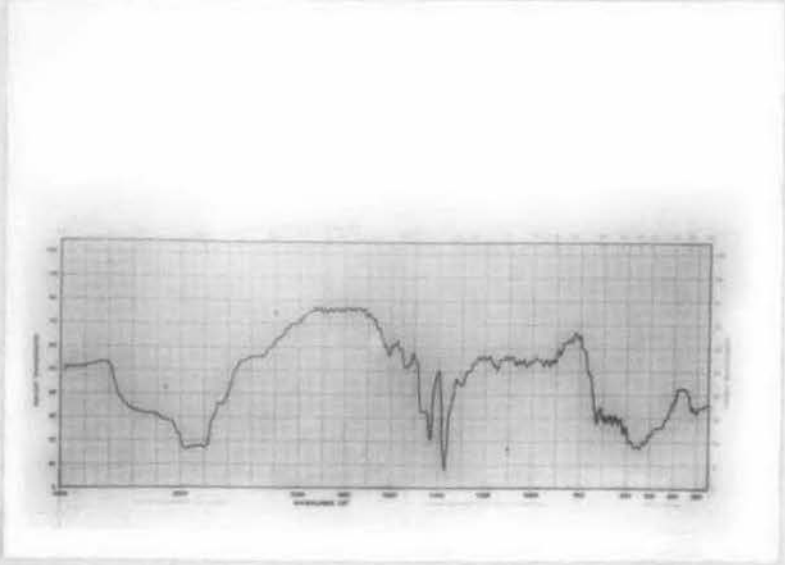


Fig. 2.4 IR spectrum of the compound $\left[Sn(OH)_4\right]_n$ containing few organic groups obtained by boiling phenyltin dihydroxy formate in dimethyl formamide.

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. $\left[C_6H_5Sn(OH)_2OCOH\right]_n$ 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 $\left[C_6H_5Sn(OH)_2OCOH\right]_n$ 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 $\left[Sn(OH)_4\right]_n$ 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%).

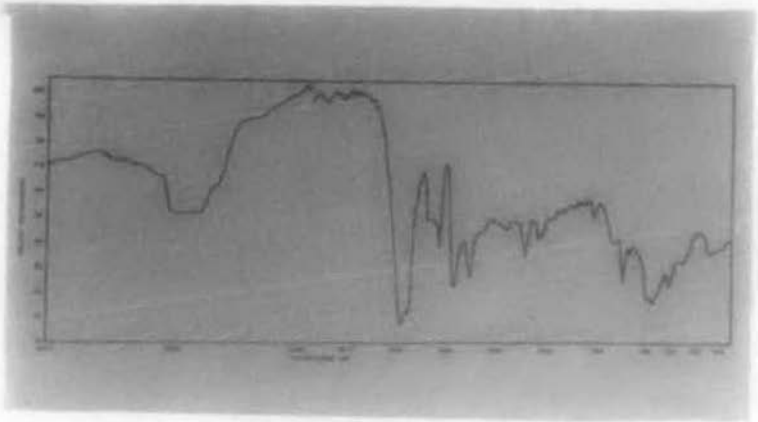
12. Reaction of triphenyltin formate with mercuric iodide:

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 800 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°].

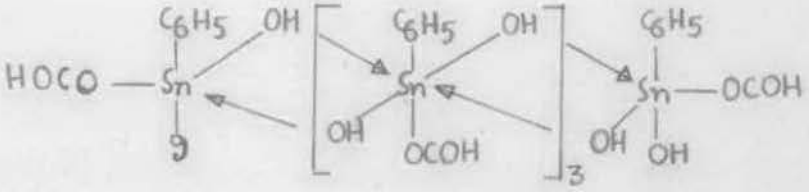


ig. 2.5 IR spectrum of polymeric compound phenyltin dihydroxy formate, $PhSn(OH)_2OCOH$ obtained from the reaction of triphenyltin formate and mercuric iodide.

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

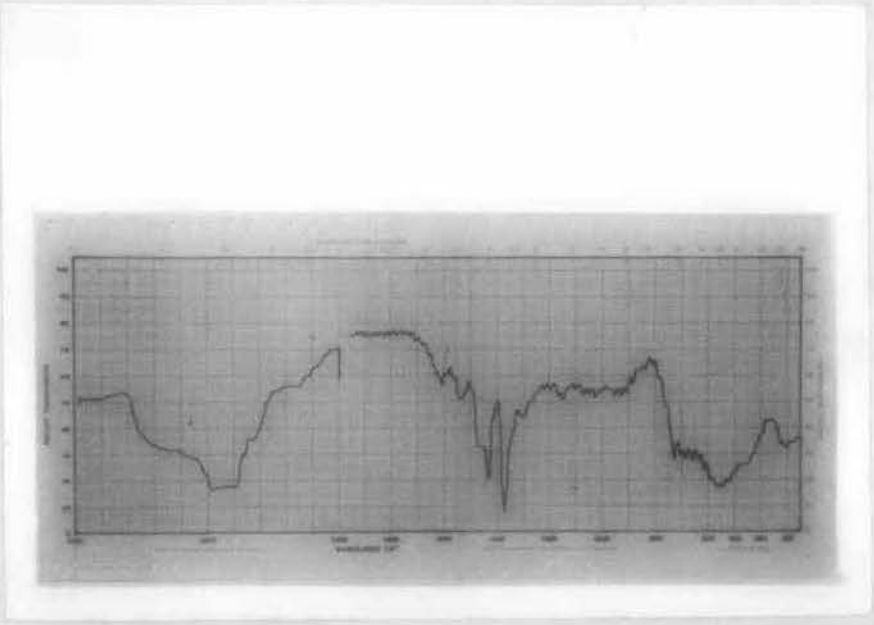


Fig. 2.6 IR spectrum of polymeric compound $\left[Sn(OH)_4\right]_n$ containing a few halogen/organic groups obtained from the reaction of triphenyltin acetate and mercuric chloride.

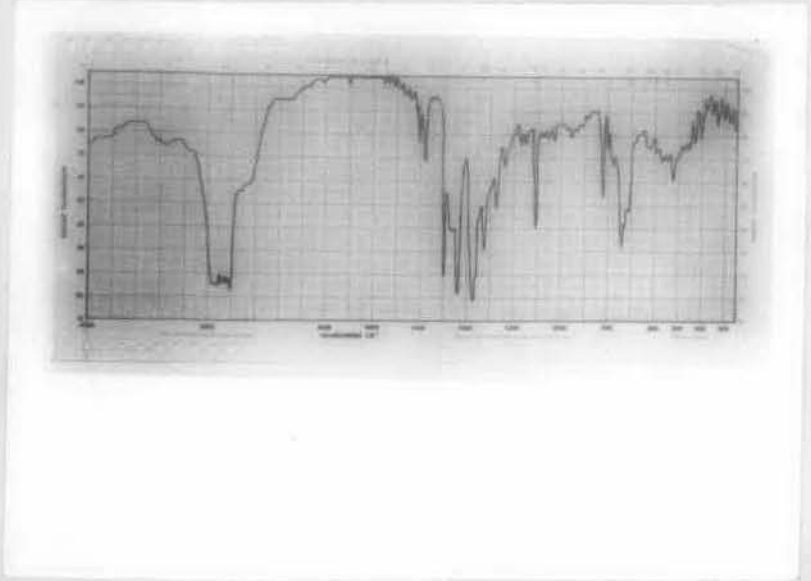
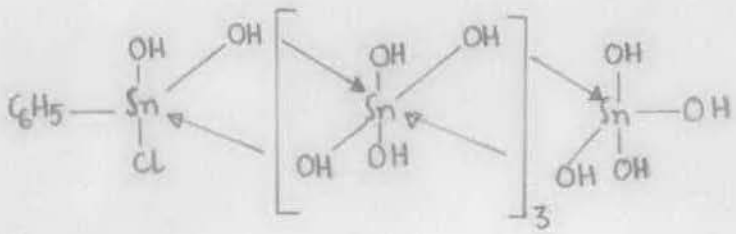


Fig. 2.7 IR spectrum of $(HO)_6Sn_2Ox_2$.

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)[ν(O-H) = 3400 cm^{-1}, ν_{as}(Sn-O-Sn) = 550 cm^{-1}] and preparation of oxine derivatives this compound was identified essentially as polymeric $[Sn(OH)_4]_n$ 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

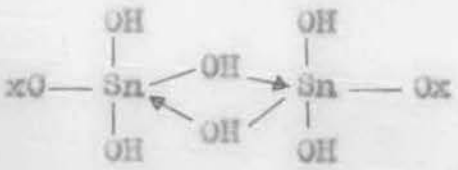
$C_6H_{23}Sn_5O_{18}Cl$: C = 7.11%, H = 1.78%, Sn = 58.65%, Cl = 3.51%).

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 = 32.96%, 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

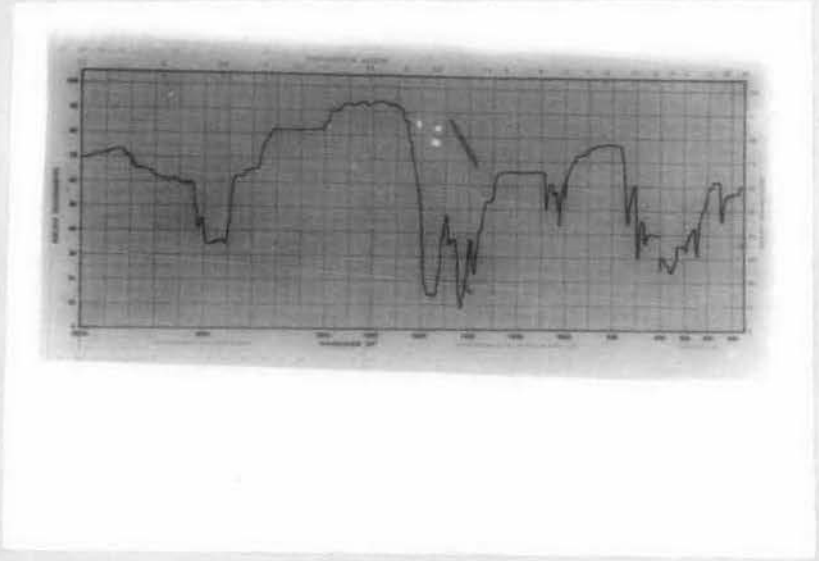


Fig. 2.8 IR spectrum of polymeric compound phenyltin dihydroxy acetate, $PhSn(OH)_2OCOCH_3$ obtained from the reaction of triphenyltin acetate and mercuric bromide.

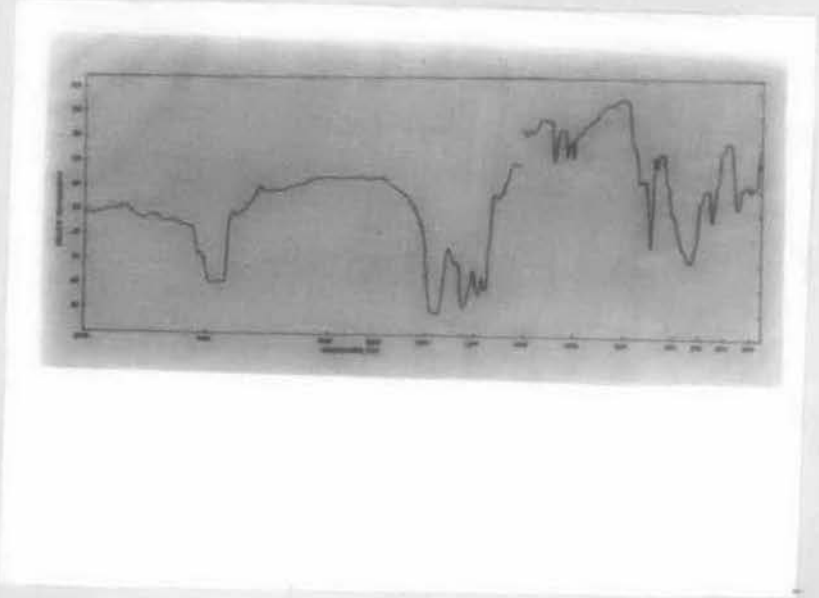


Fig. 2.9 IR spectrum of polymeric compound phenyltin dihydroxy propionate, $PhSn(OH)_2OCOCH_2CH_3$ obtained from the reaction of triphenyltin propionate and mercuric bromide.

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. 2.8)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:

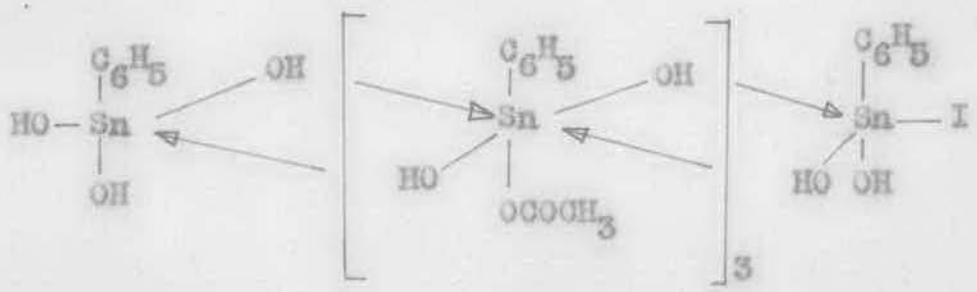
To a solution of 4.69 gm of triphenyltin acetate in 400 ml of ether, a solution of 5.21 gm of mercuric iodide in 1200 ml of ether was added slowly with constant stirring at room temperature. The stirring was continued for 8 hr and kept over night. After the filtration of the whole solution, 1.44 gm of 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° (m.m.p) [lit (86) m.p. 212°] and 0.30 gm of phenyltin trioxinate, $PhSnOx_3$, m.p. 302-303° (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° 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° 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° 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 $\left[Sn(OH)_4\right]_n$ with a few phenyl propionate as terminal groups. (Found : C = 1.79%, H = 1.67%, Sn = 62.80%; Calcd. for H_4SnO_4 : Sn = 63.89%). 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.

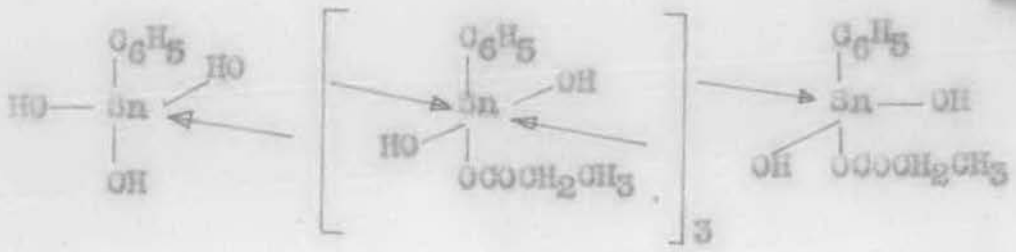
17. Reaction of triphenyltin propionate with mercuric bromide:

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 triphenyltin bromide after several recrystallisation from petroleum ether, m.p. 122° (m.m.p). The petroleum ether insoluble fraction, 1.02 gm, m.p. 265-270° was identical with fraction (17C) (m.m.p) and were mixed

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

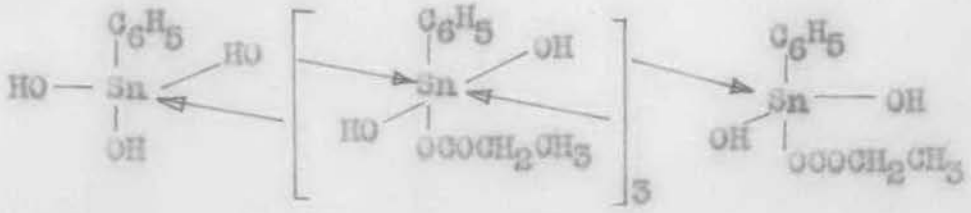
overnight. A white precipitate was formed and was filtered off. The residue, 1.95 gm (18A), was digested with benzene in a soxhlet for 12 hr whereby a white benzene insolube compound, 1.00 gm was obtained (18B). This was found to be a polymeric compound from its infusible nature upto 360° and insolubility 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 2.00 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 $C_{42}H_{56}Sn_3O_{19}$: 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. Reaction of tributyltin acetate with mercuric chloride:

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, ether 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°]

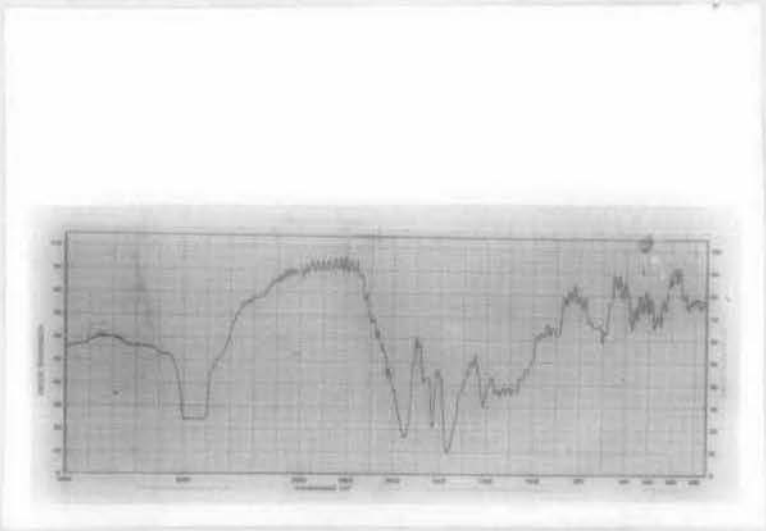


Fig. 2.10 IR spectrum of polymeric compound butyltin dihydroxy acetate, $BuSn(OH)_2OOCCH_3$ obtained from the reaction of tributyltin acetate and mercuric chloride.

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, $\left[BuSn(OH)_2OAc\right]_n$ (Found: C = 26.57%, H = 5.83%, 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. 278°].

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, $\left[PrSn(OH)_2OAc\right]_n$ (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° (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 2.38 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° 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° (22C).

The original filtrate on concentration yielded 1.99 gm of a compound, m.p. 266-270° 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° (m.m.p).

Identification of the solid 22B:

The solid (22B), from superimposible 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%).

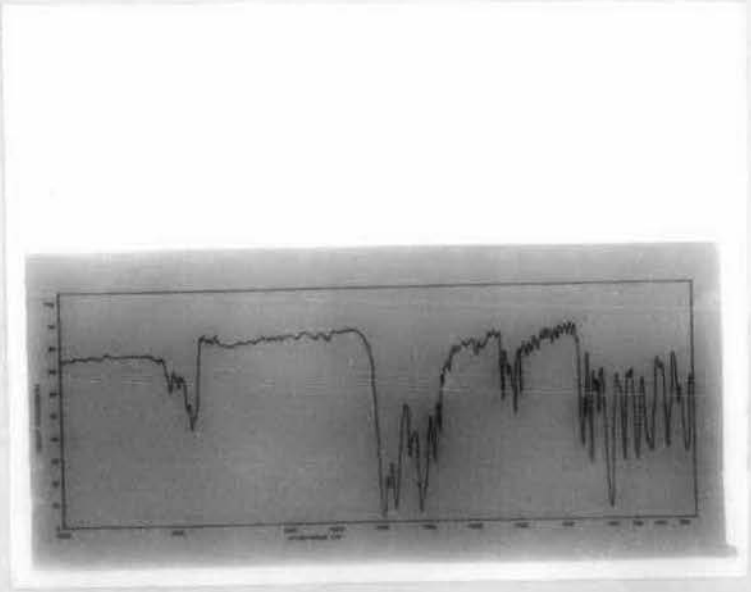


Fig. 2.11 IR spectrum of phenyl stannoic acetate, $PhSn(O)OCOCH_3$.

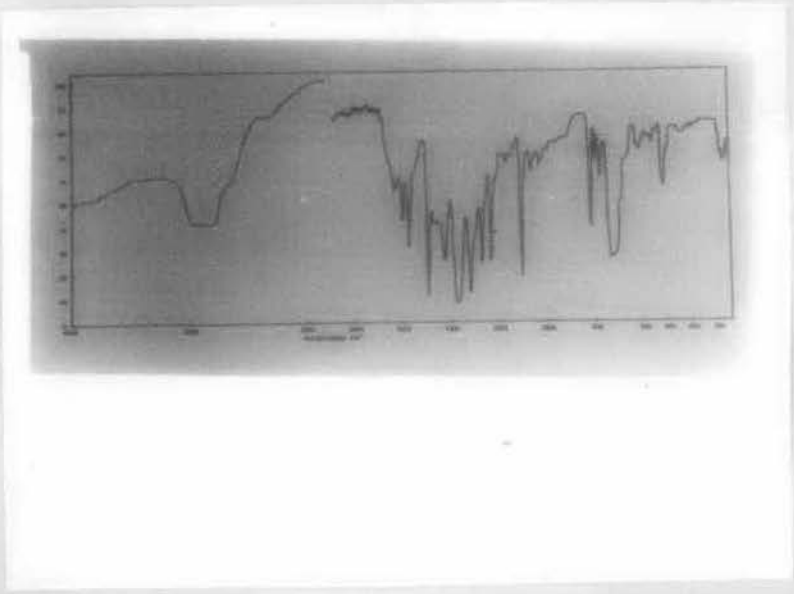


Fig. 2.12 IR spectrum of Phenyltin acetate dioxinate, $PhSn(OCOCH_3)Ox_2$.

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 throughly 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° obtained as petroleum ether insoluble fraction, after several recrystallisation from benzene/petroleum ether mixture afforded a yellow crystalline compound, m.p. 243-244°. 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 thoroughly 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 ether.

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, $\left[PhSn(O)OAc\right]_n$.

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 mercuric 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

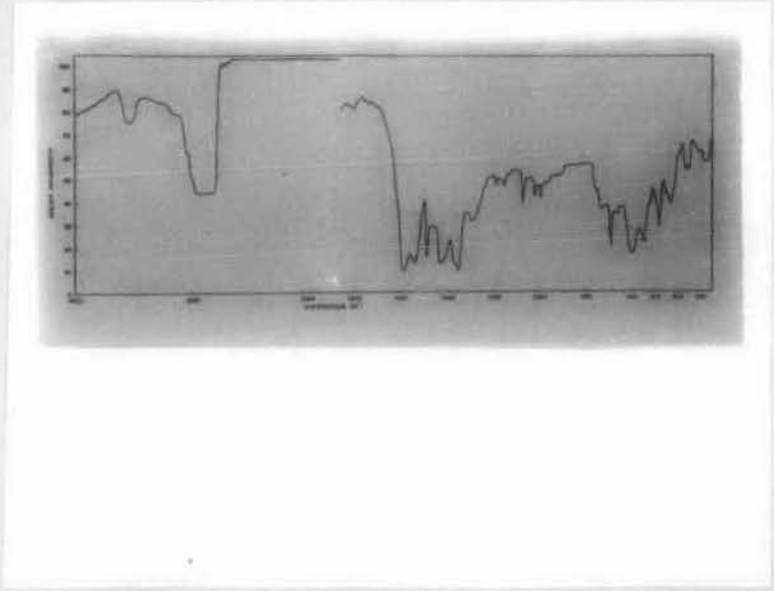
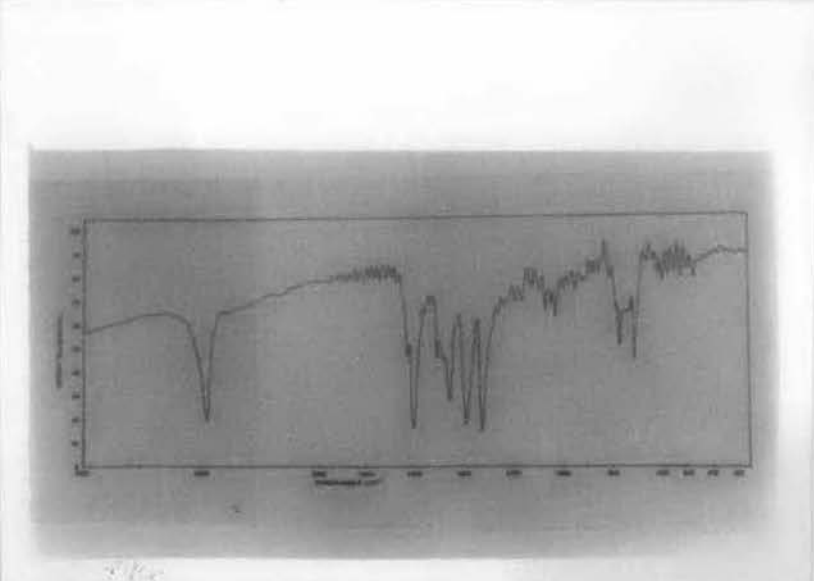


Fig. 2.13 IR spectrum of 1,3 dibenzyl 1,3 dihydroxy 1,3 diacetoxy distannoxane, BzAcO(OH)Sn(OH)OAcBz.



ig. 2.15 IR spectrum of benzylmercuric acetate, $BzHgOOCCH_3$.

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 $Bz_2Sn<$ 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 etheral 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 etheral 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-

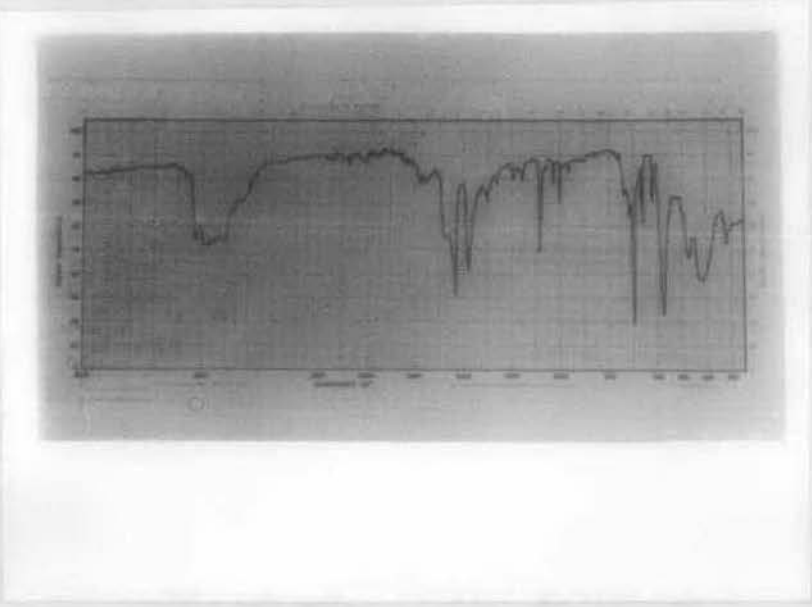


Fig. 2.14 IR spectrum of diphenyltin oxide, Ph_2SnO.

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	νB_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		
$Ph_3SnOOCCH_3$ + $HgBr_2$	$Ph_3SnOOCCH_3$ + 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	
1540 s	1550 s	ν_{as}(OCO)
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	ν_{as}(SnOSn)
500 m	500 m	
450 m	450 w	ν_{B_1}
340 m	340 w	
270 vw	275 vw	ν_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 $\left[Sn(OH)_4\right]_n$ containing few Ph/halogen/carboxylate groups:

Products obtained from the reactions of $Ph_3SnOCOCH_3$ + $HgCl_2$	$Ph_3SnOCOCH_3$ + $HgBr_2$ 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	
680 w	680 w	
570 m	560 w,b	ν_{as}(SnOSn)
470 w		
440 w	380 m	C-C-C asym. deform.
330 w	335 w	

PART - II

D I S C U S S I O N

D I S C U S S I O N

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. $(R_3Sn)_2O + HgX_2 \longrightarrow R_2Sn(X)-O-Sn(OH)R_2 + RHgX + BzH$

[Where R = Bz; 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. $R_3SnOCOR' + HgX_2 \longrightarrow R_3SnX + [Sn(OH)_4]_n + RHgX$

[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. $R_2SnX(OCOR') + R_3SnOCOR' \longrightarrow R_2Sn(OCOR')_2 + R_3SnX$

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. $R_3SnOCOR' + HgX_2 \longrightarrow R_2SnX(OCOR') + RHgX$

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

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

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

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

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

The overall reaction is therefore,

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

[Where 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 oximates (86) where the following mechanism has been proposed to account for the products obtained:

C.

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

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 quinolineto, X = Cl, Br, I]

Since, the triorganotin carboxylates are penta coordinated like triorganotin oximates, 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 oximates 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 hydro-

lysis 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 $R_3SnX(OCOR')_2$ 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 cut 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:

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

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 stoichiometry obtained in the reaction, the following mechanism may be proposed:

1. $Ph_3SnOAc + Hg(OAc)_2 \longrightarrow Ph_2Sn(OAc)_2 + PhHgOAc$

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

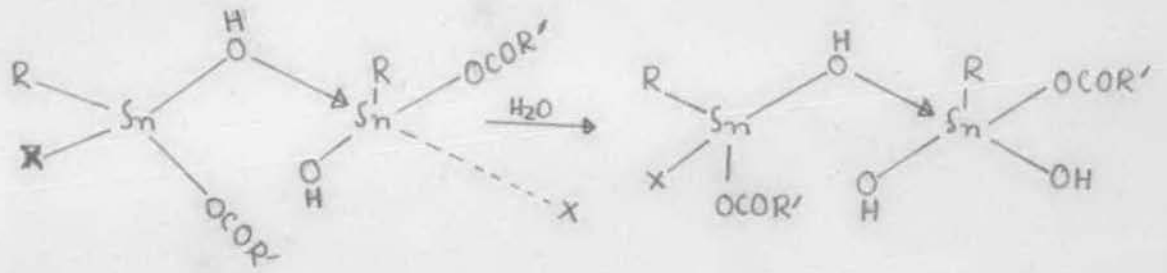
3. $PhSn(OAc)_3 + HOH \longrightarrow PhSn(O)OAc + 2AcOH$

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

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

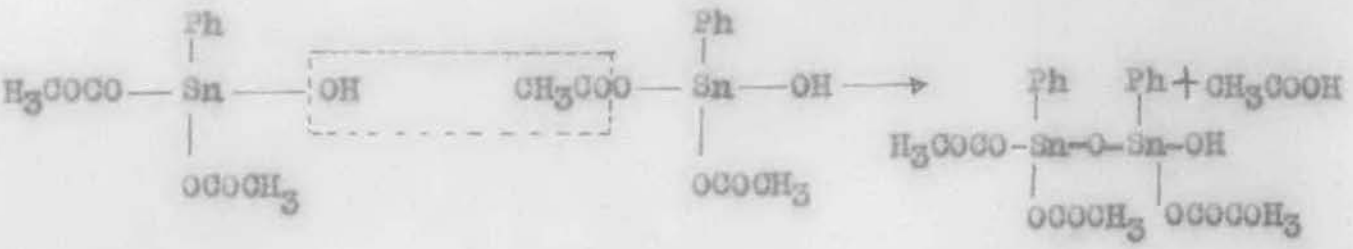
the greater reactivity of phenyl mercuric acetate with organotin carboxylates than the corresponding organo mercuric halides. It has been observed that phenyl mercuric acetate reacts readily with triphenyltin acetate at room temperature to produce diphenyl mercury and phenyl stannoic acetate polymer. Secondly, the polymeric products (except for triphenyltin acetate and propionate with mercuric chloride) obtained in the former reactions are mostly of the type $RSn(OH)_2OOCR'$ while that obtained from the later reaction is of the type $PhSn(O)OOOCH_3$. These two polymers probably owe their formation to the hydrolysis of $RSnX(OOCR')_2$ and $PhSn(OOOCH_3)_3$ respectively as suggested in the mechanisms. One possible reasons for this difference ~~is~~ in hydrolysis behaviour may be the difference in coordination numbers of tin atom in two intermediates. Thus in case of $RSnX(OOCR')_2$ (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 pentm coordinated $RSnX(OOCR')OH$. 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:

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



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:

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



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

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

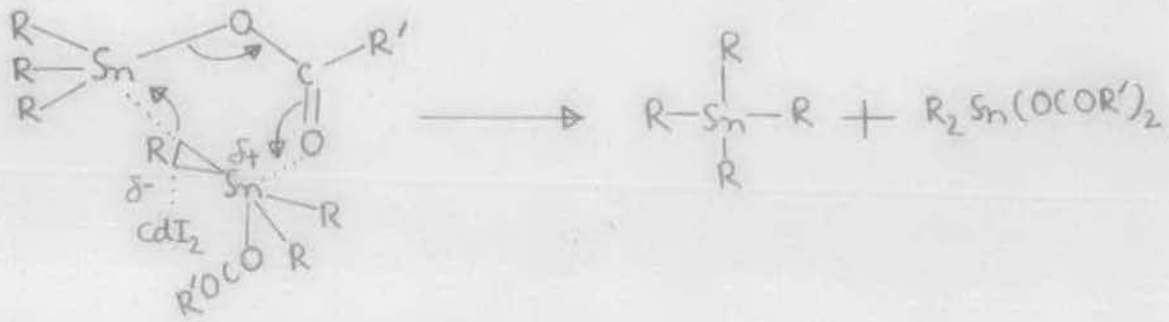
Isolation of benzylmercuric acetate, BzHgOAc, signifies that this compound is stabler than its phenyl analogue. For the same reason as with the hydrolysis of $PhSn(OAc)_3$, $BzSn(OAc)_3$ as postulated in the mechanism E, will then probably be converted to the distannoxane isolated. Few dimeric benzyl 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:

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

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,

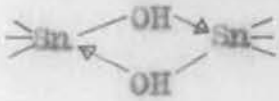
it produces one of these types of polymer and may be used as a very convenient route for the preparation of these polymeric compounds in good yield.

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

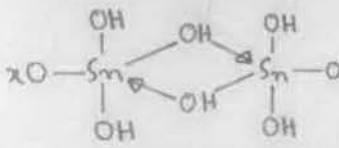


group (104).

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).

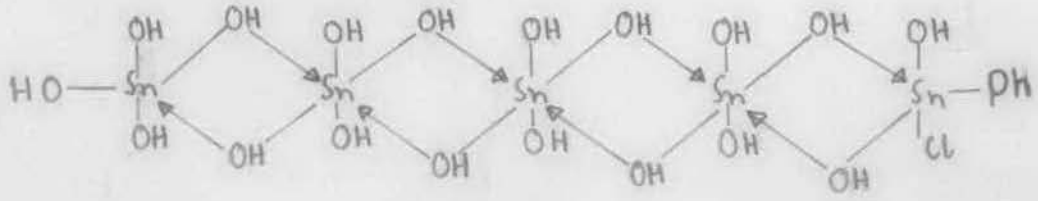
Because of the mode of preparation of this type of polymer, there remains a probability that a few phenyl/acetate/chlorine group to be used as terminal groups of the large polymer. This is supported by the presence of a very weak band at 1570-1540 cm^{-1} (OCO stretch) and very weak absorption at 725 cm^{-1} which may be assigned to out of plane C-H vibration of phenyl ring. The Sn-Cl stretching band generally appears at 385-318 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

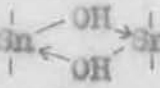
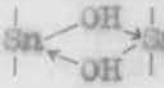


in 1:2 proportion. The isolation of $PhSnClOx_2$ reasonably indicates the presence of  group in the polymer. The stoichiometry of the products obtained signifies that every fifth tin atom contains a phenyl and chlorine group which might act a

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 characteresatics of the O-H stretching mode of  group (104) and hence  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.

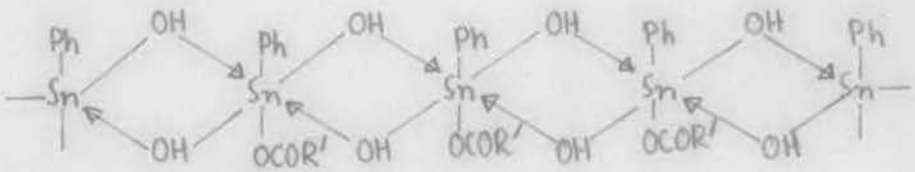
M.C.Henry and J.G.Noltes have assigned the 1080 cm^{-1} band to the C-H in plane deformation mode and to be the characteristic of phenyl group bonded to tin atom. The presence of a ~1080 cm^{-1} band indicates the presence of such group in these polymers.

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 νas(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 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 occure 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)OOR' 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 $\rangle Sn\langle^{Ph}_{OAc}$ 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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