PART - III

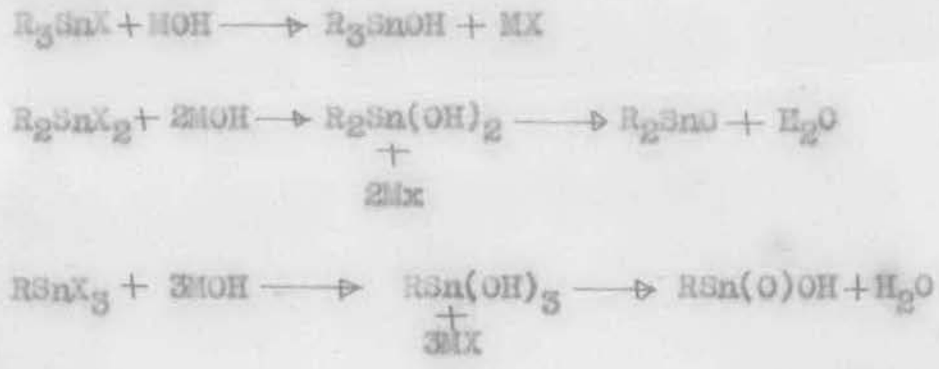
ACTION OF MERCURIC ACETATE ON HEXAORGANO DISTANNOXANES AND SOME RELATED REACTIONS.

Introduction:

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

Preparation of Organotin hydroxides and stannoxanes:

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



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

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

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

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

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

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

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

Physical properties of organotin hydroxides and organo stannoxanes:

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

Table-I

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

Contd..

Table-I (Contd.)

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

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

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

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

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

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

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

Chemical properties of organo stannoxane and organotin hydroxide:

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

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

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

$$Et_3SnOH \longrightarrow Et_2SnO + C_2H_6$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$R_2SnO + 2HOx \longrightarrow R_2SnOx_2 + H_2O$$

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

Scope, object and result:

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

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

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

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

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

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

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

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

EXPERIMENTAL

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

1. Preparation of hexaphenyl distannoxane:

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

2. Preparation of tribenzyltin chloride:

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

3. Preparation of hexabenzyl distannoxane:

Hexabenzyl distannoxane was prepared (65) by shaking an etheral solution of tribenzyltin chloride with 30% aqueous solution of potassium hydroxide. The product was recovered from ether layer and finally crystallised from acetone, m.p. 118-122° [lit (65) m.p. 120°]. (Found: C = 62.91%, H = 5.12%, Calcd. for $C_{42}H_{42}Sn_2O$: C = 63.06%, H = 5.28%).

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

4. Preparation of bis(triphenyltin) sulphide:

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

5. Preparation of polymeric diphenyltin oxide:

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

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

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

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

Identification of solid 6A:

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

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

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

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

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

8. Reaction of diphenyltin oxide with phenyl mercuric acetate:

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

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

9. <u>Reaction of hexapropyl distannoxane with mercuric acetate</u>:

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

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

10. <u>Reaction of hexa butyl distannoxane with mercuric acetate</u>:

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

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

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

11. Reaction of hexabenzyl distannoxane with mercuric acetate:

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

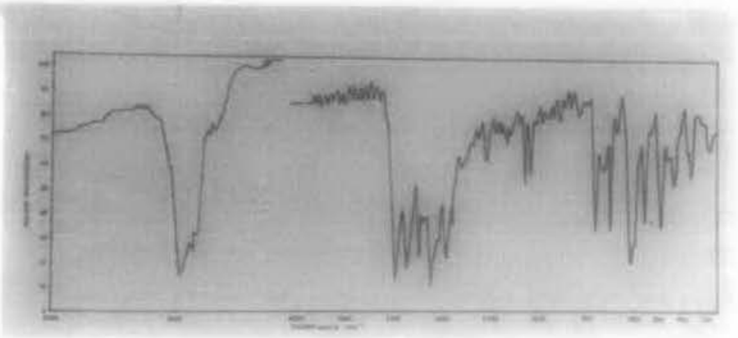


Fig. 3.1 IR spectrum of 1,3 dibenzyl 1,1,3,3 tetracetoxy distannoxane, $Bz(OAc)_2SnOSn(OAc)_2Bz$.

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

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

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

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

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

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

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

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

PART - III

DISCUSSION

DISCUSSION

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

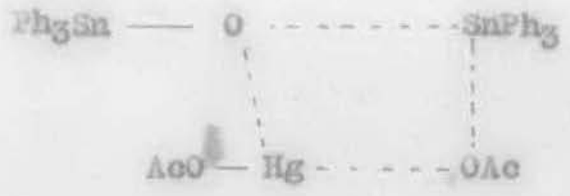
Considering the stoichiometry of the overall reaction, the reaction of mercuric acetate with hexaphenyl distannoxane in 1:1 ratio may be formulated as follows:

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

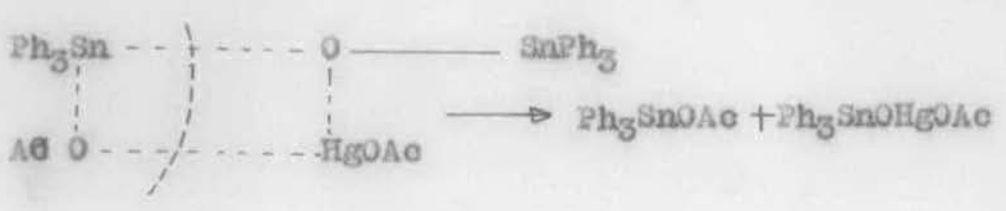
$$Ph_2SnO + PhHgOAc \longrightarrow PhSn(O)OAc + Ph_2Hg$$

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

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



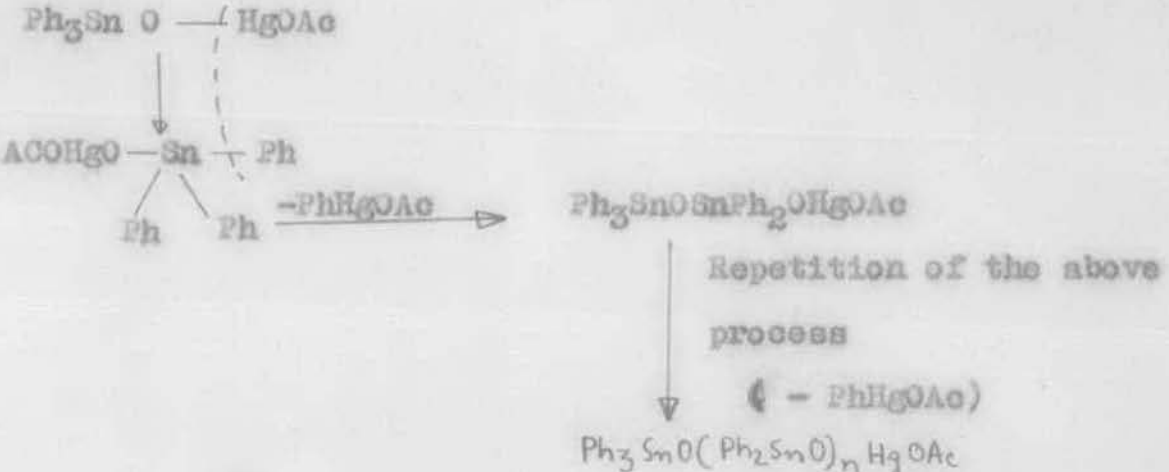
This transition state is expected to break as below:



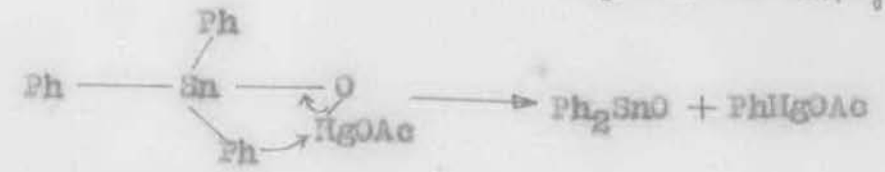
$Ph_3SnOHgOAc$, however, could not be isolated from this reaction probably because of its highly unstable nature.

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

(I)



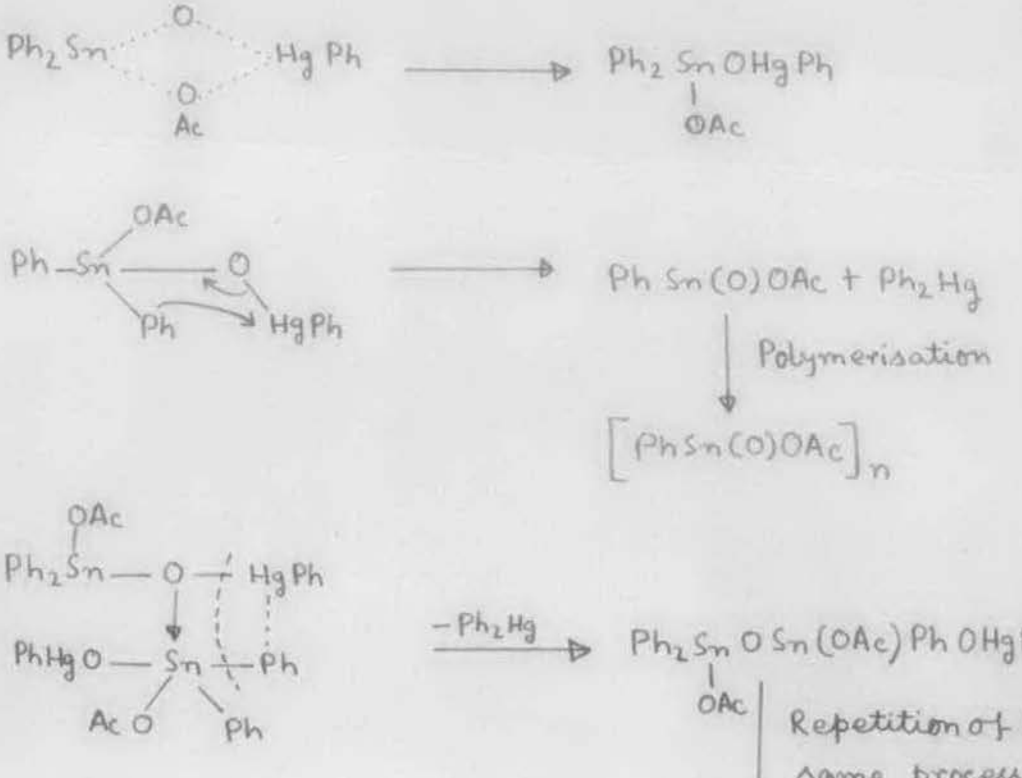
(II)



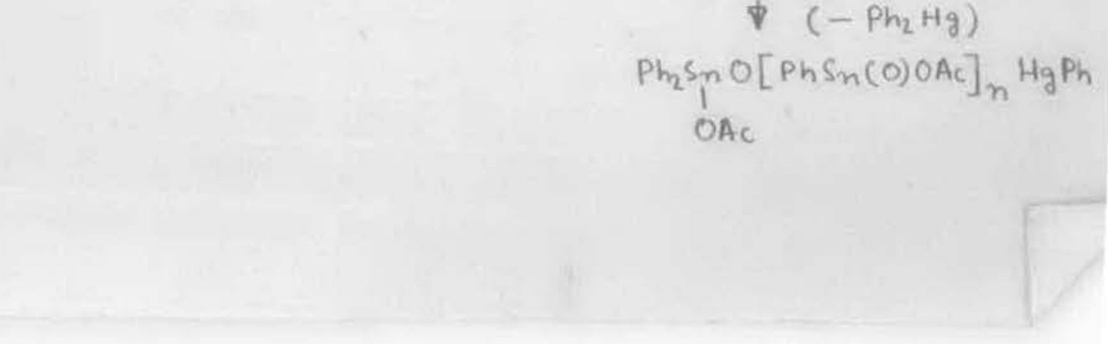
Davies et al (60) have recently reported the formation of $Bu_2\underset{Cl}{\underset{|}{Sn}}OHgPh$ by the reaction of Bu_2SnO with $PhHgCl$. From the isolation of phenyl stannoic acetate; $PhSn(O)OAc$ and diphenyl mercury; Ph_2Hg instead of Ph_2SnO and $PhHgOAc$ in the reaction of $(Ph_3Sn)_2O$ with

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

(III)



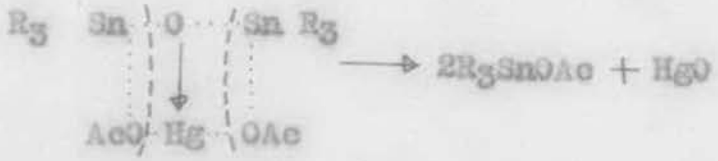
(IV)



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

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

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



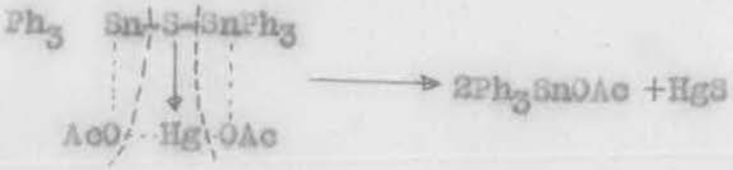
(R = Pr, Bu).

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

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

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

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



$$\underset{\text{AcO---Hg---OAc}}{Ph_3\,Sn{-}S{-}SnPh_3} \longrightarrow 2Ph_3SnOAc + HgS$$

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PART-IV

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

Introduction:

In this part, preparation of some organotin carboxylate oxinates have been attempted. They include the following types of compounds viz., $PhSn(OCOR)Ox_2$ and $(OCOR)_2SnOX_2$. The compound $n\text{-}Bu_2Sn(OCOCH_3)Ox$, reported by Huber and Kaiser (1) is probably the only example of organotin carboxylate oxinate.

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

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

Organotin oxinate complexes:

Various types of organotin oxinates viz., R_3SnOx, R_2SnOx_2, $R_2Sn(X)Ox$ and $RSnOx_3$, where R = organic group, Ox = oxinate and X = halogen, isothiocyanate, acetate, nitrate are described in the literature~~s~~ (1-12).

R_3SnOx, R_2SnOx_2 and $RSnOx_3$ are generally prepared by one of the following ways: (a) reaction of organotin halides with oxine (3,4), (b) reaction of organotin halides with sodium oxinate (2,10,14) and (c) reaction of organotin oxides with oxine (10,13), e.g.,

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

(b) $n\text{-}BuSnCl_3 + 3NaOx \longrightarrow n\text{-}BuSnOx_3 + 3NaCl$

(c) $(Ph_3Sn)_2O + 2HOx \longrightarrow 2Ph_3SnOx + H_2O$

Methyltintrioxinate was prepared by heating methyltin sesquisulphide with oxine, in a 1:3 molar ratio, in boiling toluene, while similar heating of butyltin sesquisulphide and oxine in a 1:2 molar ratio produced $(BuSnOx_2)_2S$ (15).

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

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

$$R_2SnCl_2 + HOx \longrightarrow R_2Sn(Cl)Ox + HCl$$

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

$$R_2SnCl_2 + R_2SnOx_2 \longrightarrow 2R_2Sn(Cl)Ox$$

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

$$R_2SnOx_2 + AgX \longrightarrow R_2Sn(X)Ox + AgOx$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

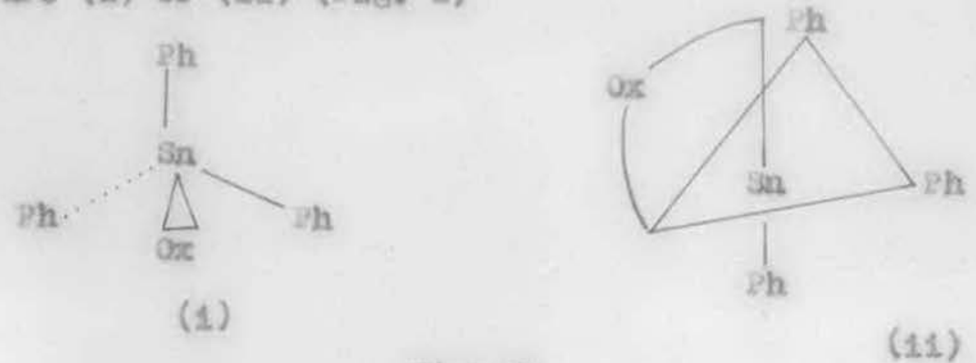
Dichlorotin dioxinate, Cl_2SnOx_2 (5) was prepared by the reaction of oxine on $SnCl_4$.Cl_2SnOx_2 has been found to be thermally stable upto 360^0, insoluble in mineral acids and alkali solutions but soluble in concentrated sulphuric acid.

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

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

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

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



(i)

(ii)

Fig. I.

Organotin complexes:

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

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

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

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

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

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

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

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

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

Scope, object and results:

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

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

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

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

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

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

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

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

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

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

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

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

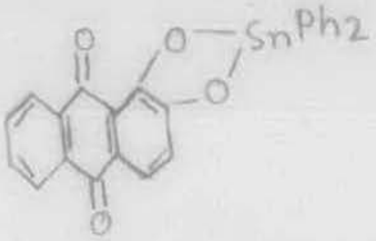
$$Ph_3SnOx + 2PhHgOAc \longrightarrow \tfrac{1}{2}PhSn(OAc)Ox_2 + 2Ph_2Hg + \tfrac{1}{2}PhSn(O)OAc$$

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

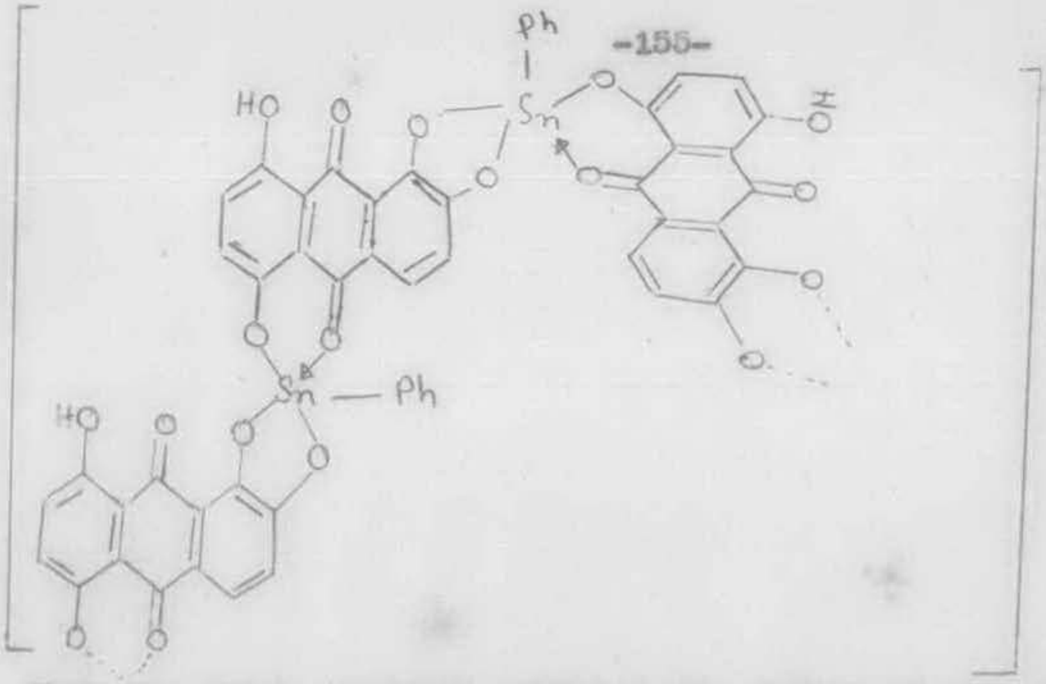
Apart from the above oxinate complexes, few other organotin chelates were also investigated.

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

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



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



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