PART- IV

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

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

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

1. Triphenyltin oxinate, Ph_3SnOx:

Triphenyltin oxinate was prepared by the reaction of hexaphenyldistannoxane with oxine in warm methanol. The product was recrystallised several times from methanol and dried in vacuum for 24 hr, m.p. 150° [lit. (8, 17) m.p. 145°-146.5°] (Found: C = 65.25%, H = 4.26%, N = 3.03%; Calcd. for $C_{27}H_{21}SnON$, C = 65.64%, H = 4.23%, N = 2.84%).

2. Diphenyltin dioxinate, Ph_2SnOx_2:

Diphenyltin dioxinate was prepared following the method of Nelson and Martin (41). The product was recrystallised several times

from benzene, m.p. 252° [lit. (41) m.p. 250°-253°](Found: C = 64.36%, H = 3.85%, N = 4.79%; Calcd. for $C_{30}H_{22}SnO_2N_2$: C = 64.20%, H = 3.93%, N = 4.99%).

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

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

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

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

5. Silver salts of carboxylic acids, AgOOCR:

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

6. Phenylmercuric trifluoroacetate, $PhHgOOCF_3$:

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

7. Triphenyltin salicylaldehyde: $Ph_3SnOC_6H_4CHO-2$:

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

8. Dichlorotin dioxinate, Cl_2SnOx_2 :

Dichlorotin dioxinate was prepared by treating anhydrous stannic chloride (Fluka A.G.) with calculated amount of oxine in benzene. The product was thoroughly washed with benzene, methanol etc. (Found: C = 44.90%, H = 3.14%, N = 6.58%, Cl = 14.79%; Calcd. for $C_{18}H_{12}SnO_2N_2Cl_2$: C = 45.26%, H = 2.53%, N = 5.87%, Cl = 14.85%).

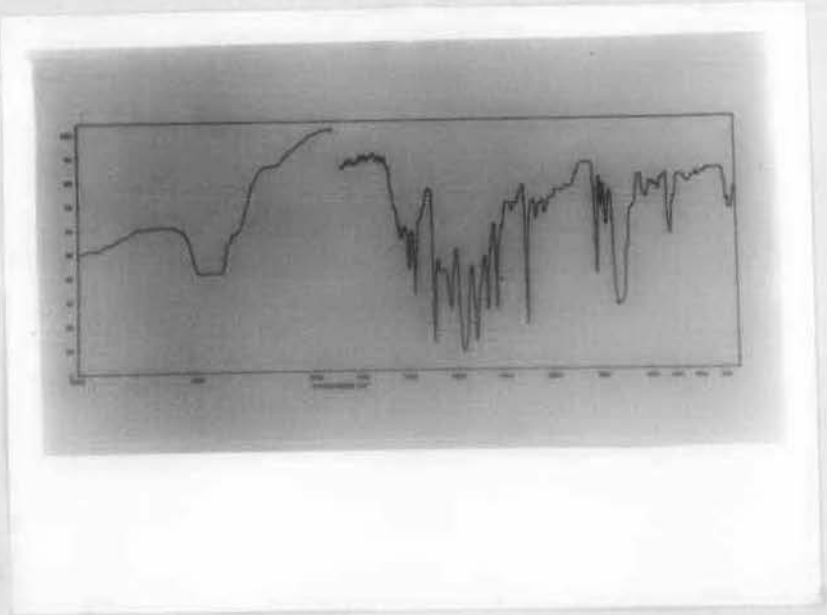


Fig. 4.1 IR spectrum of phenyltin acetate dioxinate, $PhSn(OCOCH_3)Ox_2$.

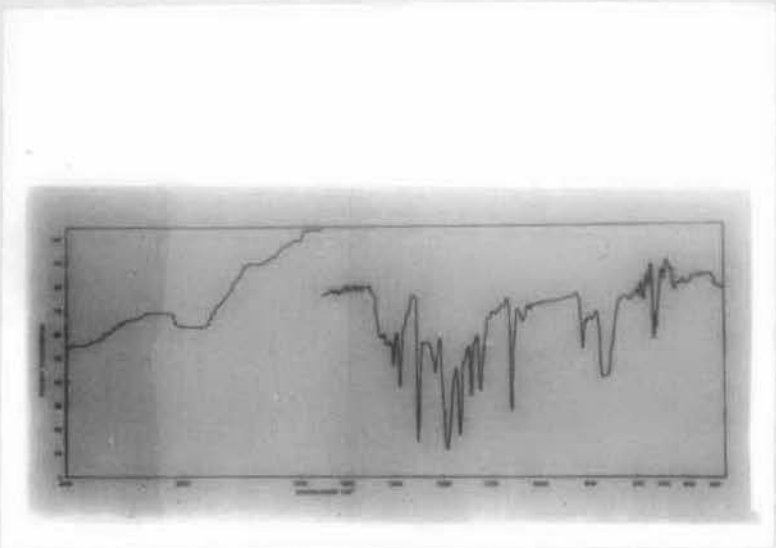


Fig. 4.2 IR spectrum of phenyltin propionate dioxinate, $PhSn(OCOCH_2CH_3)Ox_2$.

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

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

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

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

2.00 gm of diphenyltindioxinate and 1.20 gm of phenylmercuric acetate was taken in a suspension of 200 ml methanol and was refluxed for 5 hr. The solvent was evaporated off slowly and the

yellow solid which remained was treated several times with hot petroleum ether. The petroleum ether soluble fraction afforded 1.20 gm of diphenyl mercury, m.p. 124° (m.m.p).

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

10. Preparation of phenyltin propionate dioxinate, $PhSn(OOCH_2CH_3)Ox_2$ by the reaction of phenyltin chlorodioxinate with silver propionate:

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

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

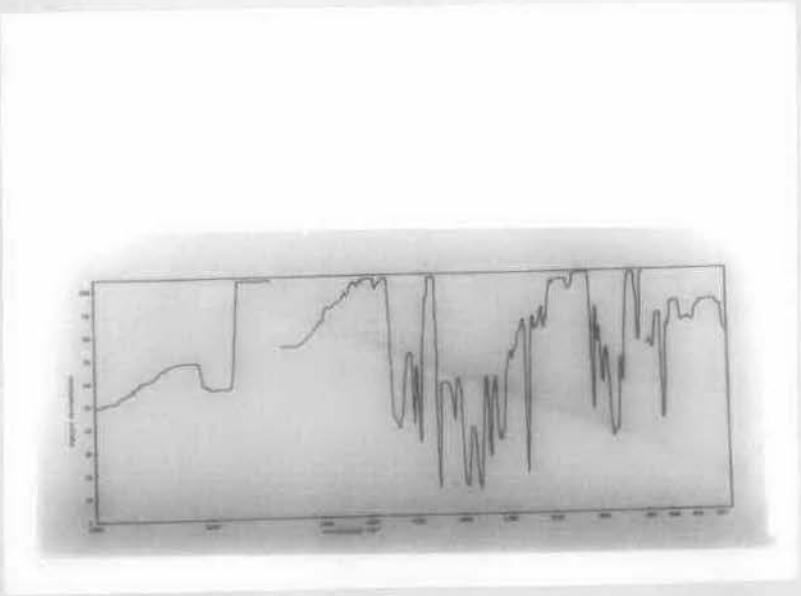


Fig. 4.3 IR spectrum of phenyltin monochloroacetate dioxinate, $PhSn(OCOCH_2Cl)Ox_2$.

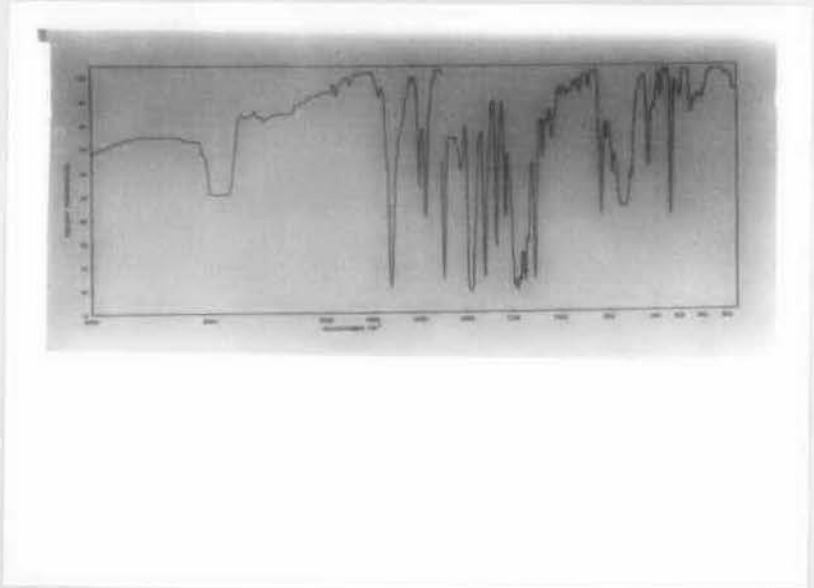


Fig. 4.4 IR spectrum of phenyltin trifluoroacetate dioxinate, $PhSn(OCOCF_3)Ox_2$.

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

1.40 gm of phenyltin chloro dioxinate and 0.60 gm of silver monochloroacetate was taken in 200 ml of methanol and the suspension was refluxed for 5 hr. The methanol was evaporated and the solid mass left was treated with benzene. The benzene soluble fraction on concentration and precipitation with petroleum ether yielded 1.16 gm of a yellow compound which on several recrystallisation from benzene/petroleum ether mixture was identified as phenyltin monochloroacetate dioxinate, m.p. 145°. (Found: C = 54.18%, H = 3.62%, N = 4.77%, Sn = 20.41%; Calcd. for $C_{26}H_{19}SnO_4N_2Cl$: C = 54.06%, H = 3.29%, N = 4.85%, Sn = 20.56%).

IR and UV/vis. spectra are shown in fig. 4.3 and figs. 4.8, 4.9 respectively.

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

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

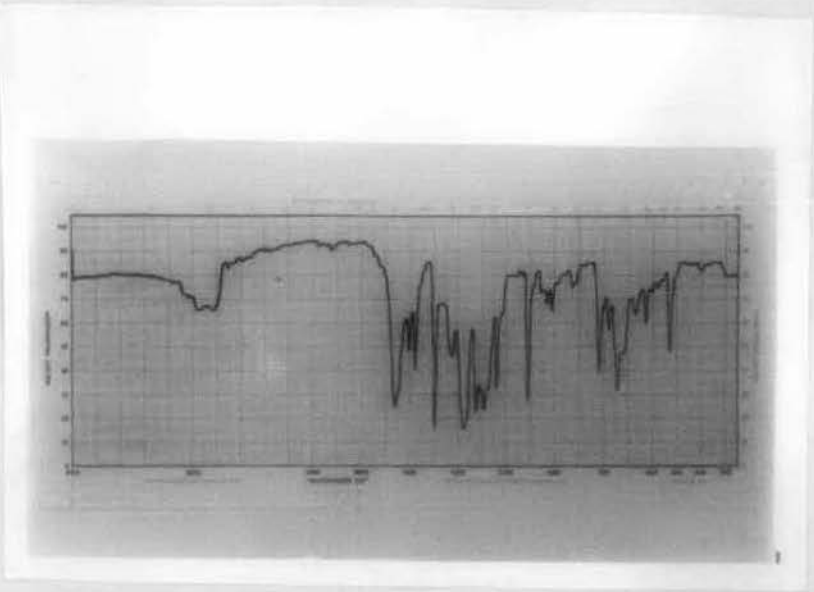
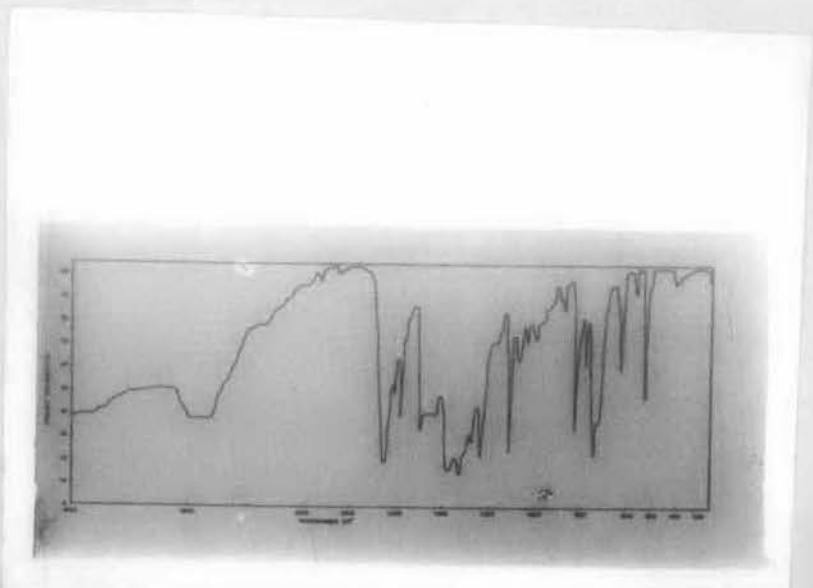


Fig. 4.5 IR spectrum of diacetatetin dioxinate, $(CH_3OCO)_2SnOx_2$.



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

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

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

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

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

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

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

1.50 gm of dichloridetin dioxinate and 1.20 gm of silver propionate were taken in 200 ml of methanol and the suspension was refluxed for 5 hr. The methanol was evaporated off after the reaction and the yellow solid left was treated with hot benzene. The benzene fraction was then concentrated which afforded 1.47 gm of a yellow compound. This compound on several recrystallisation from benzene was identified as dipropionatetin dioxinate, m.p. 266°-267°. (Found: C = 51.78%, H = 3.97%, N = 4.83%, Sn = 21.07%; Calcd. for $C_{24}H_{22}SnO_8N_2$: C = 52.12%, H = 3.98%, N = 5.07%, Sn = 21.48%).

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

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

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

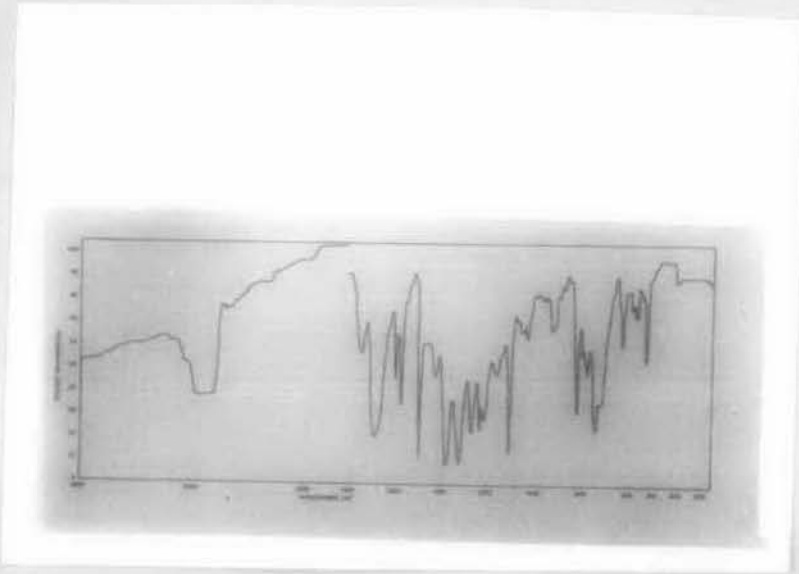


Fig. 4.7 IR spectrum of bis mono chloroacetatetin dioxinate, $(ClCH_2OCO)_2SnOx_2$.

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

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

16. Reaction of diphenyltin chlorooxinate with potassium acetate:

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

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

The water solution was found to contain potassium chloride, KCl and excess potassium acetate, $KOOCH_3$ by qualitative tests.

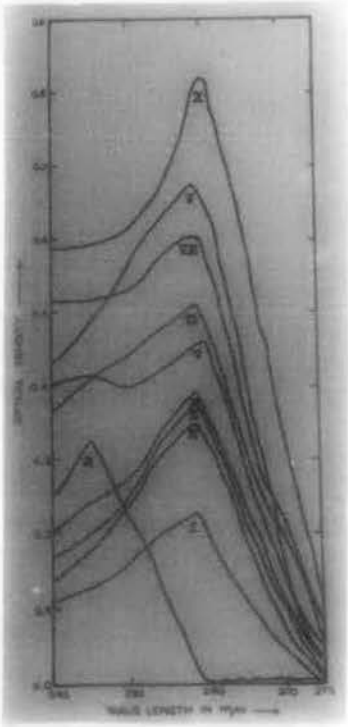


Fig. 4.8 Absorption spectra of the tin oxinates in the UV region:

I Phenyltin monochloroacetate dioxinate,

II Phenyltin acetate dioxinate,

III Phenyltin propionate dioxinate,

IV Phenyltin trifluoroacetate dioxinate,

V Dipropionatetin dioxinate,

VI Diacetatetin dioxinate,

VII Bis monochloroacetatetin dioxinate,

VIII Phenyltin chloro dioxinate,

X Diphenyltin dioxinate,

IX Dichlorotin dioxinate.

17. Reaction of triphenyltin oxinate with mercuric acetate:

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

The benzene soluble fraction on slow evaporation afforded 1.39 gm of a yellow crystalline compound, m.p. 235-240°. This compound on several recrystallisation from benzene was identified as phenyltin acetate dioxinate, $Ph_3Sn(OAc)Ox_2$, m.p. 243-244°, identified by IR comparison and mixed melting point determination with authentic sample.

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

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

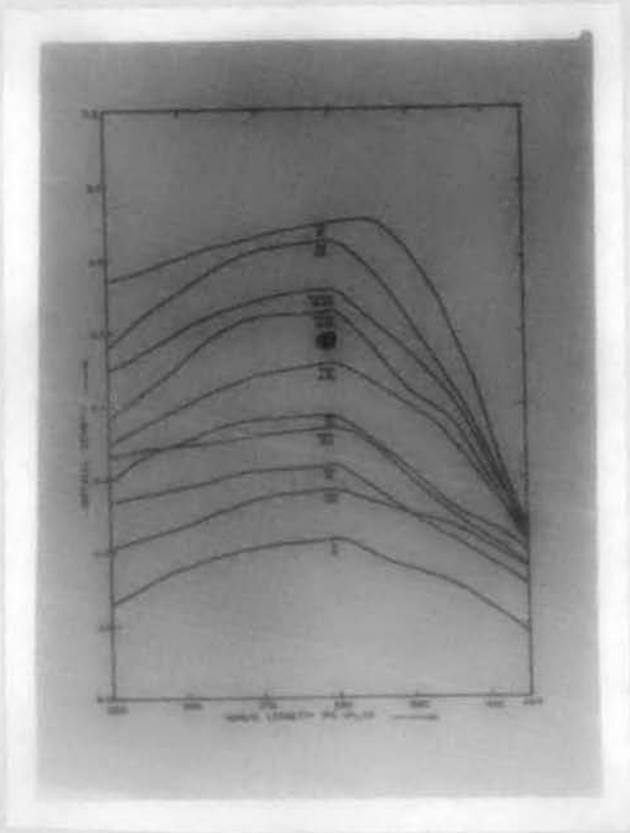


Fig. 4.9 Absorption spectra of the tin oxinates in the visible region:

I Phenyltin monochloroacetate dioxinate,

II Phenyltin acetate dioxinate,

III Phenyltin propionate dioxinate,

IV Phenyltin trifluoroacetate dioxinate,

V Dipropionatetin dioxinate,

VI Diacetatetin dioxinate,

VII Bis monochloroacetatetin dioxinate,

VIII Phenyltin chloro dioxinate,

IX Diphenyltin dioxinate,

X Dichlorotin dioxinate.

18. Reaction of triphenyltin oxinate with phenyl mercuric acetate:

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

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

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

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

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

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

19. Reaction of diphenyltinchloro oxinate with phenyl mercuric acetate:

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

The petroleum ether and methanol insoluble fraction was identified as polymeric phenylstannoic acetate, 0.89 gm, by the procedure mentioned earlier.

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

20. Reaction of triphenyltin salicylaldehyde with mercuric chloride

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

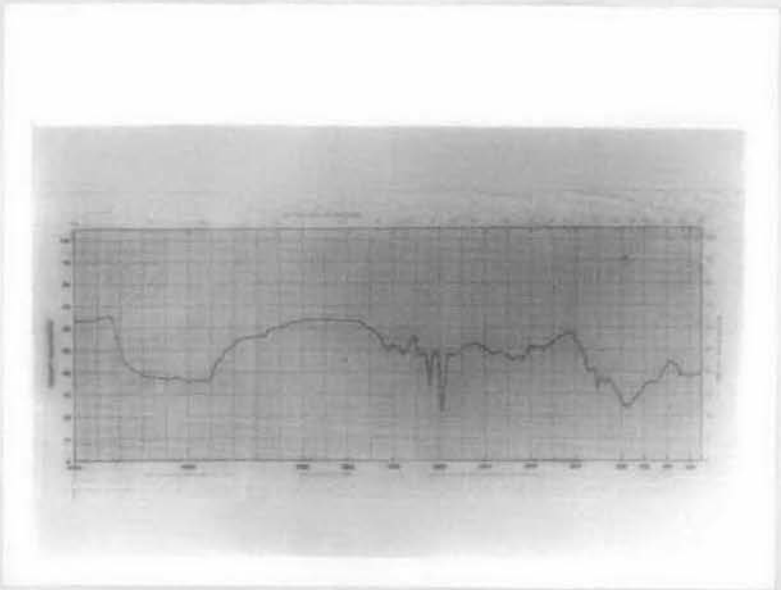


Fig. 4.10 IR spectrum of polymeric compound $Sn(OH)_4$ obtained from the reaction of triphenyltin salicylaldehyde and mercuric chloride.

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

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

The polymeric material from its elemental analysis and IR spectrum (fig. 4.10) was found to be essentially $Sn(OH)_4$ containing a few organic groups. (Found: C = 6.63%, H = 1.83%, Sn = 58.38%).

21. Reaction of triphenyltin hydroxide with alizarin:

3.63 gm of triphenyltin hydroxide (prepared from triphenyltin chloride and sodium hydroxide in ether/water mixture) and 2.36 gm of alizarin were mixed together in 400 ml methanol and refluxed for 6 hr. The whole solution was then filtered and the residue was treated with hot benzene. The benzene soluble fraction afforded tetraphenyltin, m.p. 224° (m.m.p). The residue (20A) thus obtained was found to be infusible upto 360°.

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

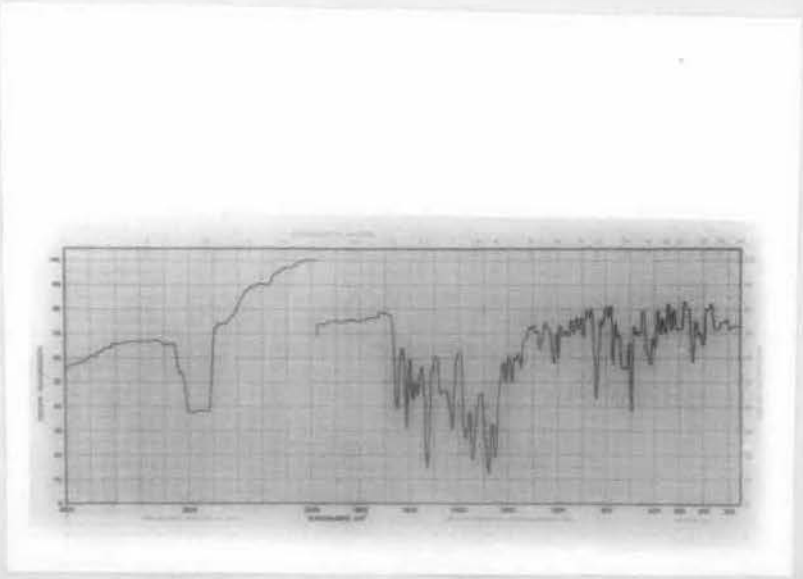


Fig. 4.11 IR spectrum of alizarin complex.

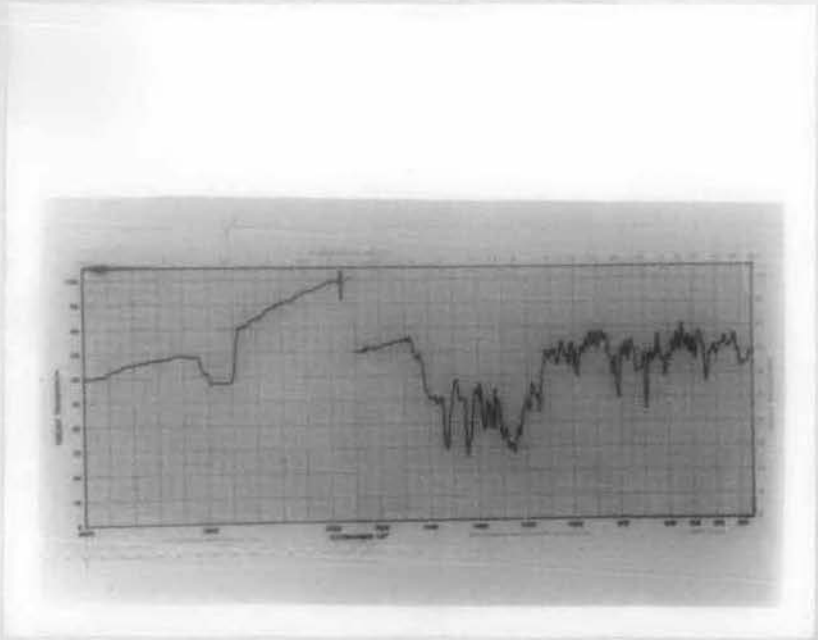
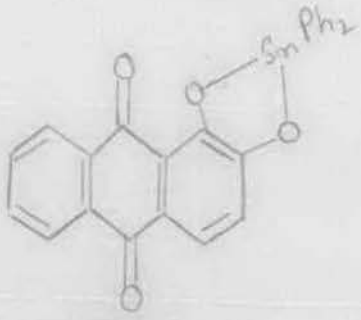


Fig. 4.12 IR spectrum of quinalizarin complex.

Characterisation of the compound 20B:

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



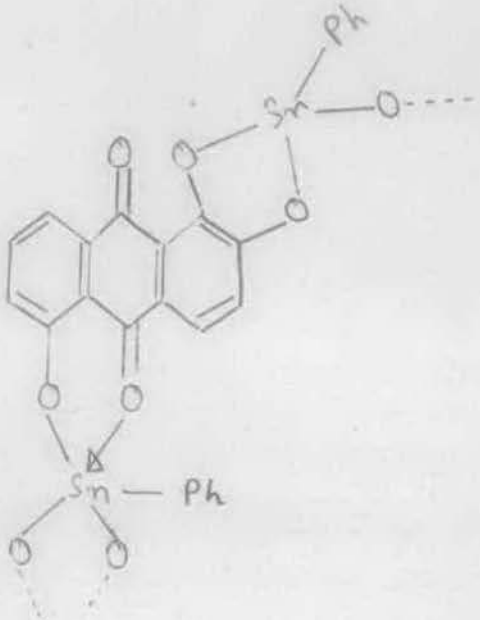
(Found: C = 60.78%, H = 3.32%, Sn = 22.7%; Calcd. for $C_{26}H_{16}SnO_4$: C = 60.98%, H = 3.32%, Sn = 23.2%).

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

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

22. Reaction of triphenyltin hydroxide with quinalizarin:

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



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

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

Identification of the volatile product:

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

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

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

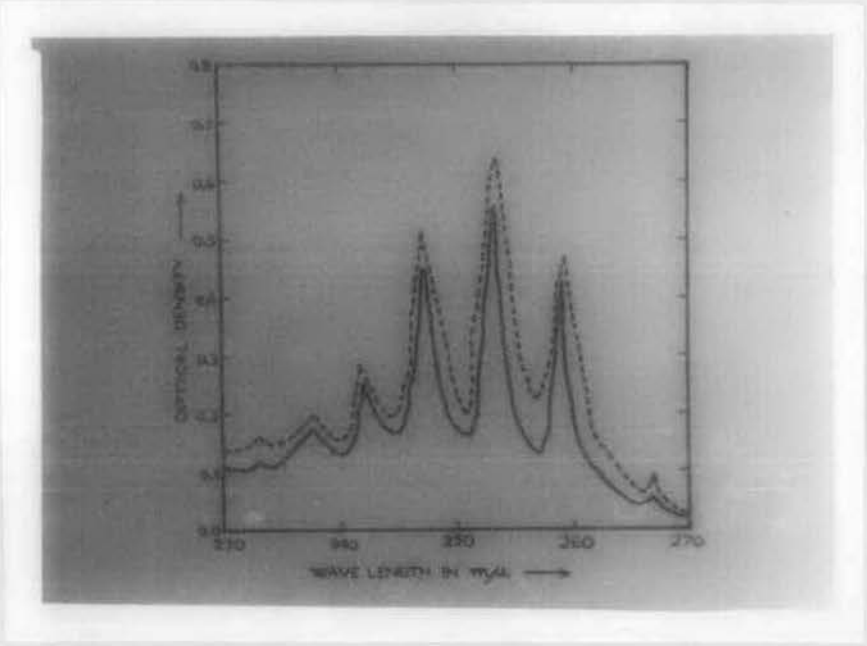


Fig. 4.13 Absorption spectrum of the distillate of the reaction of triphenyltin hydroxide and quinalizarin (solid line). The spectrum of pure benzene (dashed line) in the same solvent is shown for comparison.

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

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

PART - IV

D I S C U S S I O N

D I S C U S S I O N

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

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

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

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

Thus :

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

(Where R = CH_3, CF_3)

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

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

$$\text{A}\quad 2Ph_3SnOx + 2Hg(OAc)_2 \longrightarrow 2Ph_2Sn(OAc)Ox + 2PhHgOAc$$

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

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

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

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

The over all reaction is

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

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

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

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

The overall reaction is, therefore,

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

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

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

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

B

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

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

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

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

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

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

$$PhSn(O)OAc + 2PhHgCl + 2Ph_2Hg$$

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

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

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

the spectra have been measured in methanol solutions. The data are shown in table-I.

Table-I*

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

* Figures in the parentheses indicate log ϵ max.

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

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

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

Table-II

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

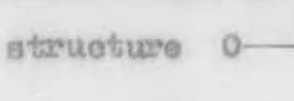
(a) solid in nujol

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

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

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

$CH_3COO \approx CH_3CH_2COO < ClCH_2COO < CF_3COO$.

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

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

R

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

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

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

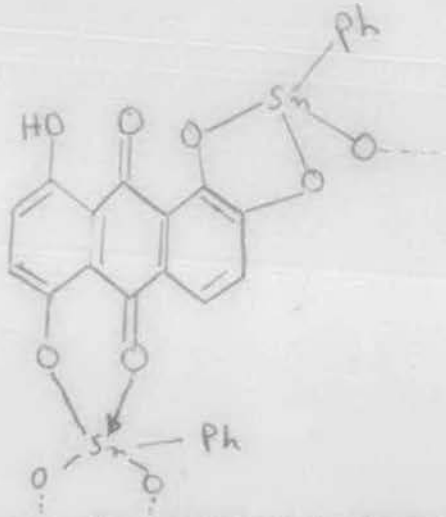
$$PhSn(Cl)Sal_2 + Ph_3SnSal \longrightarrow Ph_3SnCl + PhSn(Sal)_3$$

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

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

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

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



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

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