## CHAPTER - IV

On preparation of organotin carboxylates by the reaction of organotin hydroxides with esters.

IV A Introduction :

Despite the tremendous amount of work already done on organotin carboxylates, interest in compounds containing - $OCOSnR_3$ group still continues. This is partly due to the growing importance of diffent types of organotin carboxylates in the industry and agriculture, and partly due to the variety of structural features found in organotin carboxylates.

Organotin carboxylates are generally prepared by the reaction of organotin oxides or hydroxides with carboxylic acids and their anhydrides (1-10) :

$$R_3SnOSnR_3 + 2R'COOH \rightarrow 2R_3SnOCOR' + H_2O \quad (1)$$

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

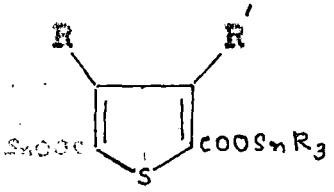
$$R_2SnO + 2\,R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \quad (3)$$

The water produced in these reactions is removed usually be azeotropic distillation or alternatively by refluxing at higher temperature

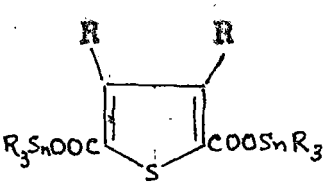
(II)

$$Bu_3SnOSnBu_3 + \text{(o-hydroxybenzoic acid)} \xrightarrow{100 - 110^{\circ}C} 2\ \text{(o-hydroxybenzoic acid, tributyltin ester)} \quad (4)$$

Recently a number of tin thiophene carboxylates (35) of the type I and II have been prepared from thiophene carboxylic acids and $R_3SnOH$ or $(R_3Sn)_2O$.




(Ia)




(Ib)

R = Ph, H;
R' = Bu, Me etc.

Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halide with the alkali metal or silver salt of carboxylic acids either by stirring the reactants in mixtures of organic/ aqueous medium at room temperature or by refluxing the mixture (9,12-14). This method represented as

$$R_3SnX + R'COOM \longrightarrow R_3SnOCOR' + MX \qquad (5)$$

M = Na, K, Ag; X = Halogen

is frequently used for its simplicity.

The ability of carboxylic acids to cleave metal carbon bonds is the basis of yet another method for the preparation of organotin carboxylates (15,16)

$$R_4Sn + R'COOH \longrightarrow R_3SnOCOR' + RH \qquad (6)$$

The cleavage of organic groups depends on the acid strength, nature of the groups R and R′ and also on temperature (17 - 19). Vinyl groups are cleaved more readily than normal alkyl groups but less readily than phenyl groups. $Pb(OAc)_4$ has also been used for acylation of $R_3SnH$, $R_2SnH_2$ , $(R_3Sn)_2$ , $R_4Sn$ and $(R_3Sn)_2O$ (20).

Kuivila (21) showed that the reaction of organotin hydrides with carboxylic acids produces carboxylates according to following equations :

$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2 \qquad (7)$$

$$R_2SnH_2 + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2H_2 \qquad (8)$$

$$R_2Sn(OCOR')_2 + R_2SnH_2 \rightarrow 2R_2SnH(OCOR') \qquad (9)$$

with di n - butyl tin dihydride, the intermediate hydride acetate decomposes to tetra n - butyl diacetate.

$$2\,Bu_2SnH_2 + 2\,CH_3COOH \longrightarrow 2\,Bu_2SnH(OAc) + 2H_2 \qquad (10)$$

$$2\,Bu_2SnH(OAc) \longrightarrow Bu_2Sn(OAc)-(OAc)SnBu_2 + H_2 \qquad (11)$$

Using similar methods 1,2 dicarboxylates have been prepared (22 - 24)

$$2\,R_2SnH_2 + 2\,R'COOH \longrightarrow R\,Sn(OCOR)-(OCOR)SnR + 3H_2 \qquad (12)$$

The nature of the products sometimes depends on the carboxylic acid. Action of benzoyl peroxide on di-n-butyl tin dihydride also produces the 1,2 dibenzoate (25).

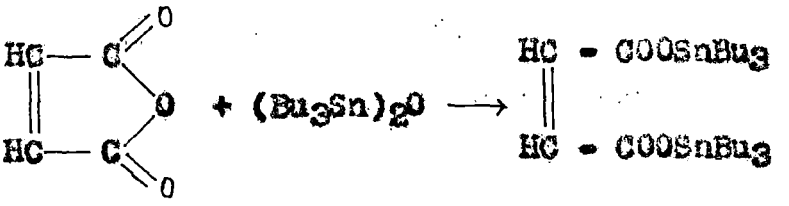
Halo carboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular mixture of the dihalide and the carboxylate in an inert solvent (26,27)

$$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \rightarrow 2Bu_2SnBr(OAc) \qquad (13)$$

These may be prepared by the following reactions also (28,29)

$$Bu_2SnCl_2 + KOOCR' \rightarrow Bu_2SnCl(OCOR') + KCl \qquad (14)$$

Anhydrides of an unsaturated acid e.g. maleic anhydride forms disubstituted organotin esters when reacted with hexabutyl distannoxane (30)




(15)

A novel method of preparation of trialkyl tin acetate by electrochemical method using $R_4Sn$ (where R = Me, Et, Pr, Bu) and Hg(1) acetate have been described by Tagliavini and his co-workers (31).

Tricarboxylates derivatives of the type $RSn(OCOR')_3$ are usually prepared from the corresponding trichloride by the action of silver salts of carboxylic acids (32).

Anderson (33) has shown that triethyltin carboxylates can be prepared in good yields by the following reaction :

$$(Et_3Sn)_2O + RCOOEt \longrightarrow Et_3SnOCOR + Et_3SnOEt \qquad (16)$$

clearly, organotin hydroxides would undergo similar reaction according to the equation;

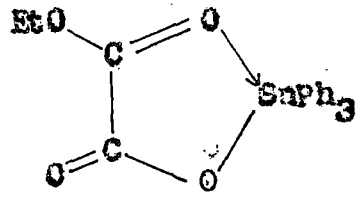
$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH \qquad (17)$$

Since the organotin hydroxides can be easily prepared from the corresponding halides by shaking an ethereal solution with aqueous sodium hydroxide, and since no drying of the product is necessary unlike $(R_3Sn)_2O$, it was decided to investigate the scope and suitability of the method for preparation of different types of organotin carboxylates. The results of this investigation are presented in this chapter.

## IV B Results and discussion

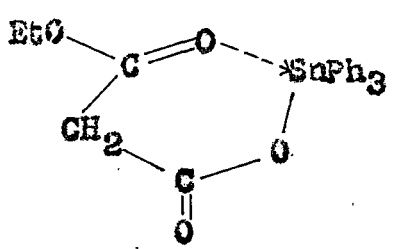
A summary of the reactions studied are given in table 1. As can be seen saturated carboxylates like formate and acetate are

obtained in almost quantitative yield. With functionally substituted esters like $ClCH_2COOEt$ and $CNCH_2COOEt$ the yield are fairly high. Further, no side products or polymeric products are generally formed. The method is extremely suitable for the preparation of half esters of dicarboxylic acids of the type $R_3SnOCO(CH_2)_nCOOH$. Attempts to prepare $Ph_3SnOCOCOOH$ by the reaction of triphenyl tin chloride with sodium hydrogen oxalate (mono sodium derivative in 1:1 mole ratio) always led to the formation of $Ph_2Sn(OOC)_2H_2O$. Even, the reaction of $Ph_3SnCl$ with $(COONa)_2$ in 1:1 mole ratio produced diphenyl tin oxalate through cleavage of Sn - Ph bond instead of the desired $Ph_3SnOOC.COONa$. However, the half ester $Ph_3SnOOC.COOEt$ could be easily prepared in good yield by stirring triphenyl tin hydroxide with diethyl oxalate with an excess of the latter. Half esters of diethyl malonate could also be obtained similarly. It is worth mentioning here that $\nu as(OCO)$ of the ester group in (triphenyl tin) mono ethyl oxalate $Ph_3SnOCo.COOC_2H_5$ occurs at 1680 $cm.^{-1}$ This value is considerably lower than that observed in normal esters (1720 - 40 $cm^{-1}$). The lowering of $\nu as(OCO)$ is indicative of co-ordination by the - C = O group of the ester. As such (triphenyl tin) mono ethyl oxalate is most probably intramolecularly co-ordinated as shown in structure II.




(II)

On the contrary, (triphenyl tin) mono ethyl malonate absorbs at 1730 $cm^{-1}$ and 1550 $cm^{-1}$ indicating the presence of unco-ordinated ester group probably intermolecularly bridged Sn–O–C(=O)–Sn – as in triorganotin formates, acetates etc. where $\nu as(OCO)$ occurs at about 1550 $cm^{-1}$. The reason for this difference between the molanate and the oxalate derivatives are not clear. However, it may be that the 5-membered Sn containing ring in structure II is probably more stable than 6-membered ring (III) which would be required to be formed in the malonate derivative if intramolecular co-ordination takes place. In that case inter molecular co-ordination may be more favourable in the malonate derivative.




III

The method however fails with benzoates and substituted benzoates. Thus no organotin derivative could be obtained with p - amino - or p - nitro benzoate. This is probably due to the facile hydrolysis of triphenyl tin benzoates by the water presnet with the organotin hydroxides.

It may be said in conclusion that the method seems to be preferable where pure derivatives are required, particularly when there is a tendency for the formation of polymeric products in the reaction between the organotin halides and the sodium or potassium carboxylates.

## IV C Experimental

The summary of the reactions of organic esters with organotin hydroxides is given in the table-I

### Table - I

| Triorgano-tin hydroxides (1) | Esters of carboxylic acids (2) | Conditions of reaction (3) | Products formed (4) | Melting point °C (5) | Yield of the products (6) |
|---|---|---|---|---|---|
| $Ph_3SnOH$ | $HCOOC_2H_5$ | Stirred at room temperature for eight hours | $HCOOSnPh_3$ | 202° | Almost quantitative |
| $Ph_3SnOH$ | $CH_3COOC_2H_5$ | Stirred for eight hours at room temperature | $CH_3COOSnPh_3$ | 121° | Almost quantitative |
| $Ph_3SnOH$ | $CH_3COOC_4H_9$ | Stirred at room temperature for eight hours | $CH_3COOSnPh_3$ | 121° | Almost quantitative |
| $Ph_3SnOH$ | $ClCH_2COOC_2H_5$ | Refluxed for 5 hours in benzene | $ClCH_2COOSnPh_3$ | 135° | Almost quantitative |

Table - I Contd.

| (1) | (2) | (3) | (4) | (5) | (6) |
|---|---|---|---|---|---|
| $Ph_3SnOH$ | $CNCH_2COOC_2H_5$ | Refluxed for five hours in benzene | $CNCH_2COOSnPh_3$ | 141° | 60% |
| $Ph_3SnOH$ | $C_2H_5OCOCOOC_2H_5$ | Refluxed for five hours in benzene | $C_2H_5OCOCOOSnPh_3$ | 127° | 80% |
| $Ph_3SnOH$ | $C_2H_5OCOCH_2COOC_2H_5$ | Refluxed for five hours in benzene | $C_2H_5OCOCH_2-COOSnPh_3$ | 139° | Almost quantitative |
| $Bu_3SnOH$ | $CH_3COOC_2H_5$ | Refluxed for five hours | $CH_3COOSnBu_3$ | 80-81° | Almost Quantitative |
| $Bu_3SnOH$ | $HCOOC_2H_5$ | Refluxed for five hours | $HCOOSnBu_3$ | 127-30°/ 3mm | Almost quantitative |
| $Bu_3SnOH$ | $CH_2=CHCOOCH_3$ | Strried at room temperature for eight hours | $CH_2=CHCOOSnBu_3$ | 63° | Almost quantitative |
| $Ph_3SnOH$ | $C_6H_5COOC_2H_5$ | No easter formed | | | |
| $Ph_3SnOH$ | $p\text{-}NH_2C_6H_4COOC_2H_5$ | No easter formed | | | |
| $Ph_3SnOH$ | $p\text{-}NO_2C_6H_4COOC_2H_5$ | No easter formed | | | |

Ph - $C_6H_6$ - ; Bu - $C_4H_9$ -

(1) Purification of ethyl formate, ethyl acetate, butyl acetate, diethyl oxalate and diethyl malonate : The esters, ethyl formate (b.p.53°), ethyl acetate (b.p. 76 - 77°), butyl acetate (b.p. 125°), diethyl oxalate (b.p. 182°) and diethyl malonate (b.p. 198°)

were thoroughly washed first with saturated sodium bicarbonate solution and then repeatedly with water. They were dried over anhydrous $MgSO_4$ and finally distilled. The last two esters were distilled under reduced pressure.

(2) Preparation of ethyl chloro acetate :

Ethyl chloro acetate was prepared by refluxing chloroacetic acid with ethyl alcohol in presence of concentrated sulphuric acid. The water produced in this reaction was removed by azeotropic distillation, the residue left in the distilling flask was added to water when the ester separated as an oily layer. The layer was separated, washed with saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and finally distilled when pure ethyl chloro acetate, b.p. $141^{o}$, was obtained.

(3) Preparation of ethyl cyano acetate :

Ethyl cyano acetate was prepared according to the method described by Vogel (34)

(4) Preparation of tri phenyl tin hydroxide :

$Ph_3SnOH$ was prepared by shaking an ethereal solution of tri phenyl tin chloride with 2N aqueous solution of sodium hydroxide. The white solid precipitated was filtered and washed thoroughly with water to remove sodium hydroxide and then with ether to remove any unchanged triphenyltin chloride or bis (triphenyl tin) oxide, which may be formed during the reaction $Ph_3SnOH$ was dried in air.

(5) Preparation of tributyl tin hydroxide :

$Bu_3SnOH$ was prepared by shaking tributyl tin chloride in ethereal solution with 2N aqueous NaOH. The ethereal solution was washed thoroughly with water. This solution was used in the reactions with esters after drying over anhydrous calcium chloride.

(6) Reaction of triphenyl tin hydroxide with ethyl formate 3.6 gms of triphenyl tin hydroxide was stirred in 10 ml ethyl formate for eight hours. Addition of excess of petroleum ether to the solution precipitated 0.5 gms of a white solid. The filtrate furnished 3.3 gms of the same compound on evaporation nearly to dryness and cooling. The product was crystallised from petroleum ether (m.p 201°), and identified as triphenyl tin formate by mixed melting point and IR spectrum.

(7) Reaction of tributyl tin hydroxide with ethyl formate :

3.2 gms of tributyl tin chloride was converted to tributyl tin hydroxide. The ethereal solution of the latter was refluxed with 15 ml of ethyl formate for five hours. Unreacted ethyl formate was evaporated off, the residue was treated with petroleum ether and filtered. The petroleum ether was evaporated off and the liquid was purified by distillation under reduced pressure (B.P. 127°-30°/3 mm). The distillate was identified as tributyl tin formate by comparison of IR spectrum with that of an authentic sample.

(8) Reaction of triphenyl tin hydroxide with ethyl acetate :

3.6 gms of triphenyl tin hydroxide was stirred in 10 ml ethyl acetate for eight hours. The solution was evaporated nearly to dryness when 3.95 gm of a white crystalline compound separated. The compound was purified by recrystallisation from petroleum ether (m.p 121°). The compound was identified as triphenyl tin acetate by mixed melting point and IR spectrum.

(9) Reaction of tributyl tin hydroxide with ethyl acetate :

3.2 gms of tributyl tin chloride was converted to tributyl tin hydroxide. The ethereal solution of the latter was refluxed with 15 CC ethyl acetate for five hours. The solution on evaporation furnished 3.3 gms of the crude product. On recrystallisation from petroleum ether pure tributyl tin acetate, m.p. 80-81° was obtained. The product was identified by mixed melting point with authentic sample.

(10) Reaction of triphenyl tin hydroxide with butyl acetate :

3.6 gms of triphenyl tin hydroxide was stirred with 10 ml butyl acetate. The solution was evaporated to dryness when 3.9 gms of a white solid was obtained which was recrystallised twice from petroleum ether to furnish pure triphenyl tin acetate, m.p. 121 -122°.

(11) Reaction of triphenyl tin hydroxide with ethyl mono chloro acetate.

3.6 gms of triphenyl tin hydroxide was refluxed with 3 ml carefully purified ethyl mono chloro acetate for 5 hours in 16 ml dry benzene.

The solution on concentration to a small volume and cooling in ice furnished 4.2 gms of a needle shaped crystalline solid. The solid was recrystallised twice from benzene petroleum ther mixture.

The compound was identified as triphenyl tin mono chloro acetate from its melting point (135°) and mixed melting point with authentic sample.

(12) Reaction of triphenyl tin hydroxide with ethyl cyano acetate :

3.6 gms of triphenyl tin hydroxide was refluxed with 3 ml of pure ethyl cyano acetate in 15 ml benzene for five hours. 0.72 gms of a white polymeric solid (m.p $>360^{\circ}$) was filtered off. The filtrate on concentration under reduced pressure furnished 1.1 gms of a polymeric compound ( m.p $>360^{\circ}$) again. The filtrate was evaporated to dryness under reduced pressure then recrystallised from benzene when 2.3 gms of triphenyl tin cyano acetate (m.p.141°, no depression in mixed melting point determination) was obtained.

(13) Reaction of tributyl tin hydroxide with methyl acrylate :

1.5 gms of tributyl tin chloride was converted to tributyl tin hydroxide. Theethereal solution of the latter was stirred with 10 ml of methyl acrylate for eight hours. A small amount of white solid formed was filtered off. The filtrate on concentration gave a semi-solid mass which furnished 1.3 gms of a crystalline solid by cooling in ice. The solid was crystallised twice from petroleum ether when pure tributyl tin methacrylate (m.p. 63°, lit. value 63°) was obtained.

(14) Reaction of triphenyl tin hydroxide with diethyl oxalate :

3.6 gms of triphenyl tin hydroxide was refluxed with 4ml of purified diethyl oxalate in 15 ml of benzene for five hours. The insoluble polymeric solid (m.p $>360^{\circ}$) was filtered off. The filtrate was evaporated nearly to dryness when 3.5 gms of a white compound crystallised out. It was purified by recrystallization twice from benzene - petroleum ther mixture (m.p. $127^{\circ}$)

Identification of the compound :

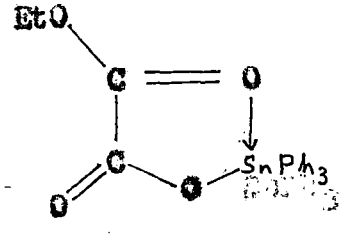
(i) Elemental analysis corresponds to (triphenyl tin) mono ethyl oxalate, $C_2H_5OCO.CO.OSnPh_3$

Analysis found : C = 55.42% ; H = 4.18% ; Sn = 24.39%

Calculated for

$C_{22}H_{20}O_4Sn$ : C = 56.56% ; H = 3.86% ; Sn = 25.43%

(ii) The presence of two non equivalent - COO groups in the molecule is shown by $\nu$ as(OCO) absorptions at 1680 $cm^{-1}$ and 1610 $cm^{-1}$. The 1610 $cm^{-1}$ absorption can be attributed to - $COOSnR_3$ while the 1680 $cm^{-1}$ absorption is certainly due to the - COOEt group. However, the lowering of $\nu$as(OCO) in the tin derivative compared to its position in normal esters ( $\sim$ 1720 - 40 $cm^{-1}$) is indicative of intramolecular co-ordination as shown below :



(15) Reaction of triphenyl tin hydroxide with diethyl malonate:

3.6 gms of triphenyl tin hydroxide and 4 ml of diethyl malonate was refluxed in 15 ml benzene for five hours. The solution was heated to evaporate off benzene and the unreacted diethyl malonate was distilled off at 83-85° under reduced pressure. The residue (4.9 gm)was recrystallised from benzene when a white solid, m.p.139° was obtained.

Identification of the solid :

(i) Elemental analysis corresponds to (triphenyl tin mono ethyl malonate, $Ph_3SnOCO.CH_2COOC_2H_5$.

Analysis found : C = 57.26% ; H = 4.75% ; Sn = 24.38%

Calculated for

$C_{23}H_{22}O_4Sn$ : C = 57.42% ; H = 4.5% ; Sn = 24.70%

(ii) IR spectrum shows the presence of - $COOC_2H_5$ group (1730cm$^{-1}$) and a carboxy group bonded to tin (1550 cm$^{-1}$). Unlike the oxalate derivative, no lowering of $\nu as(OCO)$ of the ester group is observed here indicating the absence of co-ordination by the - $COOC_2H_5$ group.

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