CHAPTER - II

ORGANOTIN CARBOXYLATES

IIA. Introduction:

Organotin carboxylates comprise one of the most important class of interesting research in the field of compounds in organotin chemistry. Apart from the academic interests (theoretical and structural) organotin carboxylates are finding more and more industrial and agricultural applications.

The compounds containing -OCOR groups bonded to tin which may be either monomeric or polymeric are of three general types viz., $R_3SnOCOR$ $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$ where R and R' may be same or different groups. Tin titra-carboxylates, $Sn(OCOR)_4$ are not organotin compounds in the rigid sense of the term, inspite of that they are sometimes included in the discussion of organotin carboxylates for the sake of comparison. A number of discussions with varying degree of details are available on these compounds (1-3) and as such only the more important aspects will be discussed here.

IIB. Preparation:

A variety of methods have been applied for the preparation of organotin carboxylates. These are generally prepared by the reaction between organotin oxides and hydroxides and carboxylic acids or their anhydrides (74-81, 3,40).

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

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

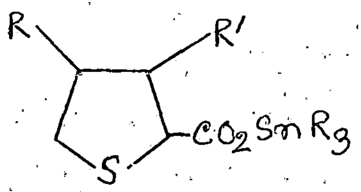
$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O .$$

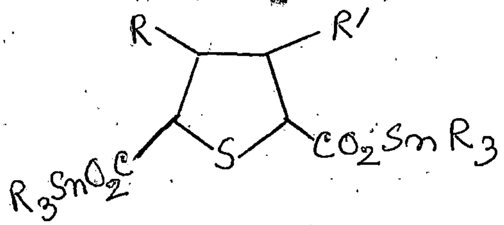
The water produced in these reactions is removed usually by azeotropic distillation or alternatively by refluxing at higher temperature (4).

$$Bu_3SnOSnBu_3 + 2o-OHC_6H_4COOH$$

$$\xrightarrow{100 - 110^0C} 2Bu_3SnOCOC_6H_4OH-o + H_2O$$

Recently a number of their thiophene carboxylates (5) of the type I & II have been prepared from the thiophene carboxylic acids and R_3SnOH or $(R_3Sn)_2O$.



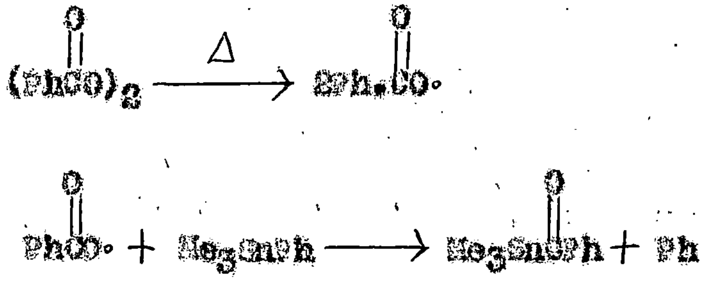


I

II

R = PhH; R' = Bu, Me, Cyclo C_6H_{11} etc.

Trimethyl tin benzoate has been prepared by the thermal decomposition of benzoyl peroxide in presence of trimethylphenyl tin (6).



$$(Ph\overset{\overset{O}{\|}}{C}O)_2 \xrightarrow{\Delta} 2Ph.\overset{\overset{O}{\|}}{C}O\cdot$$

$$Ph\overset{\overset{O}{\|}}{C}O\cdot + Me_3SnPh \longrightarrow Me_3SnO\overset{\overset{O}{\|}}{C}Ph + Ph$$

The triphenyl tin carboxylates Ph_3SnO_2CR ($R = C_6H_5$, p-$MeOC_6F_4$, p-$EtOC_6H_4$ or O-HOC_6H_4), p-$(Ph_3SnO_2C)_2C_6F_4$. H_2O and o-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ have been prepared by the reaction of triphenyl tin hydroxide with the appropriate polyfluorocarboxylic acids in MeOH (7).

Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halides with the alkali metal or silver salts of carboxylic acids either by stirring the reactants in mixture of organic/aqueous medium at room temperature or by refluxing the mixture (8-11). This method represented as

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

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

is generally used for its simplicity.

The ability of carboxylic acids to cleave M – C bonds is the basis of another method for the preparation of organotin carboxylates (12,13).

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

The cleavage of organic groups depends on the acid strength, nature of groups R and R' and also on the temperature (14-16). Vinyl groups are cleaved more rapidly than normal alkyl groups but less readily than phenyl groups. $Pb(CH_3COO)_2$ has also been used for acytation of R_3SnH, R_2SnH_2, $R_3(Sn)_2$, R_4Sn and $(R_3Sn)_2O$ (17).

Organotin hydrides react with carboxylic acids resulting in the formation of carboxylates (35).

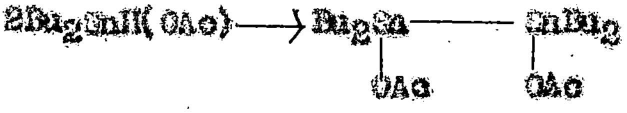
$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2$$

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

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

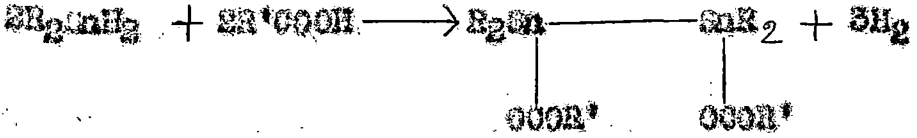
With di n-butyl tin dihydride, the intermediate hydride carboxylate decomposes to tetra-n-butyl 1,2, diacetate.

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



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

Similarly, 1,2 dicarboxylates have also been prepared (23-25).



$$2R_2SnH_2 + 2R'COOH \longrightarrow \underset{OOCR'}{\underset{|}{R_2Sn}} - \underset{OOCR'}{\underset{|}{SnR_2}} + 3H_2$$

Halo carboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular mixture of the dihalide and the dicarboxylate in an inert solvent (18,19).

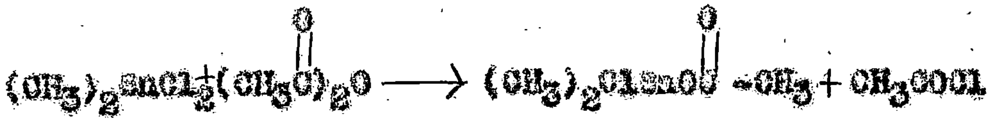
$$Bu_2SnBr_2 + Bu_2Sn(OAc)_2$$

$$\longrightarrow 2Bu_2SnBr(OAc)$$

These compounds may also be synthesised by the reaction (20, 21).

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

(=) Dimethyl tin chloride acetate, has been prepared by Okawara and Rochow by the reaction of acetic anhydride on dimethyl tin dichloride.

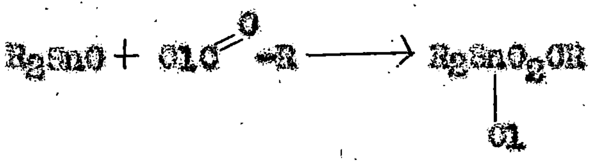


$$(CH_3)_2SnCl_2 + (CH_3\overset{O}{\overset{\|}{C}})_2O \longrightarrow (CH_3)_2ClSnO\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COCl$$

A number of dialkyl tin halide acetates have been prepared according to reactions (24):

$$2(R_2ClSn)_2O + 2CH_3COOH \longrightarrow 2R_2ClSnO_2CCH_3 + H_2O$$

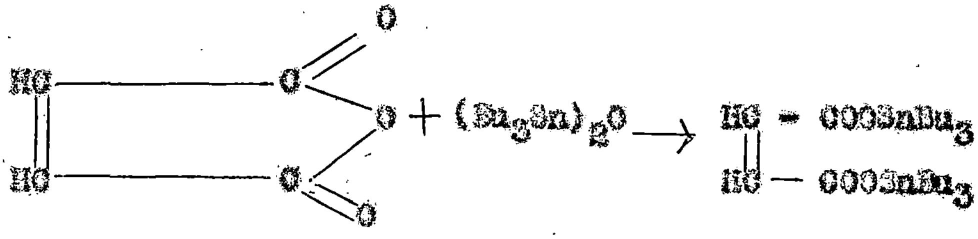
$$(R_2ClSn)_2O + (CH_3CO)_2O \longrightarrow 2R_2ClSnO_2CCH_3$$



$$R_2SnO + ClC\overset{O}{\diagup}-R \longrightarrow \underset{\underset{Cl}{|}}{R_2Sn}O_2CR$$

Thermodynamic data are reported 1/1 adducts of $Ph_2Sn(OCOMe)_2$, $Bu_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$ with pyridine, 4-methylpyridine, NBu_3, PBu_3, N,N,N',N' - Tetramethyl-1-2-diamino ethane and 1,10, phenanthroline have been reported (22).

Anhydride of an unsaturated acid (e.g., maleic anhydride) produces disubstituted organotin esters when reacted with hexabutyl distannoxane (23).



A novel method of preparation of trialkyl tin acetate by electrochemical method using R_4Sn (R = Me, Et, Pr, Bu) and Hg(I), acetate have been described by Tagliavini et al (25).

Organotin carboxylates may also be prepared from carboxylates may also be prepared from carboxylic esters by the following reactions (26,27):

$$(R_3Sn)_2O \;+\; R'COOEt \longrightarrow R_3SnOOCR' \;+\; R_3SnOEt$$

$$R_3SnOH \;+\; R'COOEt \longrightarrow R_3SnOOCR' \;+\; EtOH$$

Tricarboxylate derivatives of the type $RSn(COOR')_3$ are generally synthesised from the corresponding trichloride by the action of silver salts of carboxylic acids (28).

IIC. Physical properties of organotin carboxylates

The Sn-O bond in organotin carboxylates is essentially covalent but undergoes polar reactions depending on the solvents and the attacking groups. This is the reasons for the higher solubility of the carboxylates with the small organic groups in alcohol, ether etc. than in water (29). Many of the carboxylates have low melting points indicating these to be covalent compounds.

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

The physical properties of some representatives carboxylates are given in Table I.

Table - 1

Compound	Type	B.P. (°C/mm)	M.P. (°C)
Trimethyl tin Acetate	$R_3SnOCOR'$	—	196.5 -197.5
Triphenyl tin formate	"	—	202 - 205
Tricyclohexyltin acetate	"	—	62 - 63
Tripropyl tin trifluoroacetate	"	89-90/1	—
Dibutyl tin diacetate	$R_2Sn(OCOR')_2$	142-145/10	—
Diphenyl tin diacetate	"	—	116 - 117
Diethyl chlorotin acetate	$R_2SnX(OCOR')$	—	94
Dibutyl bromotin acetate	"	—	67 - 68.5
Butyltin triacetate	$RSn(OCOR')_3$	117 - 119/1	—
Ethyltin Tribenzoate	"	171 - 173/1	—

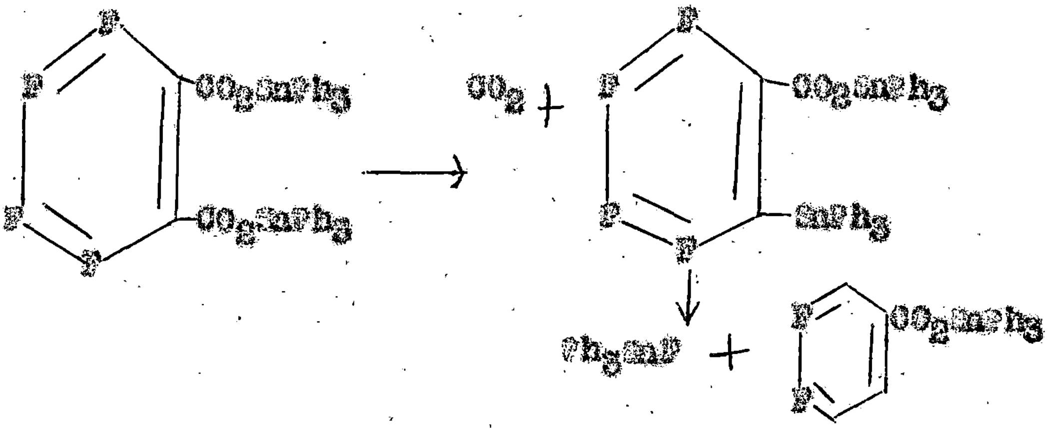
p-(Methylphenyl isopropyl stannyl) benzaldehyde has been prepared and resolved methyl carbazate in ethanol, $[\alpha]_D^{20}$ - 34.6°. Functional exchange with acetone of the less soluble diastereomer catalysed by traces of p-toluenesulphonic acid yields the optically active aldehyde with $[\alpha]_{436}^{20} + 0.350$ (33).

IID. Chemical properties of the organotin carboxylates

Decarboxylation and disproportionation reactions are the most interesting features of the organotin carboxylates. A cyanomethyl derivative is formed when triphenyl cyanoacetate is heated under vacuum (34).

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

$p\text{-}(Ph_3SnO_2C)_2C_6F_4$ is readily decarboxylated to $p\text{-}(Ph_3Sn)_2C_6F_4$. Ph_3SnO_2CR (where R = $p\text{-}CH_3OC_6F_4$ or $p\text{-}C_2H_5OC_6F_4$) undergoes disproportionation reaction resulting in the formation of Ph_4Sn and $Ph_2Sn(O_2CR)_2$. Thermal decomposition of bis (triphenyltin) tetrafluorothalate give an insoluble high melting solid, Ph_3SnF.



Thermal decomposition of Ph_3SnO_2CR in boiling pyridine give the corresponding polyfluorophenyl triphenyl tin Ph_3SnR (7).

Trialkyl tin carboxylate of unsaturated acids gives tetrasubstituted organotin compounds after decarboxylation (36,37).

$$R_3SnOCOC \equiv CR' \longrightarrow R_3SnC \equiv CR' + CO_2$$

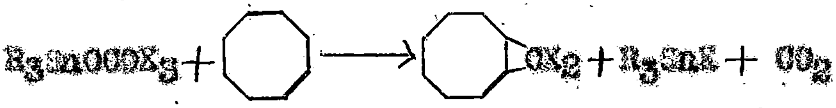
$$[\ R' = C_6H_5 \text{ or } SnR_3\ ]$$

Thermal decomposition of triorganotin formate yields the corresponding hydride and this reaction is useful for the preparation of hydrides (38).

$$R_3SnOCOH \longrightarrow R_3SnH + CO_2$$

$$[\ R = n\text{-}C_3H_7,\ n\text{-}C_4H_9\ ]$$

Seyferth et al (39) have used the reaction of triorganotin carboxylates of the halogen substituted carboxylic acids with cyclooctene as a carbene transfer reaction.



[$R = CH_3$, C_6H_5, $X = Cl$, Br]

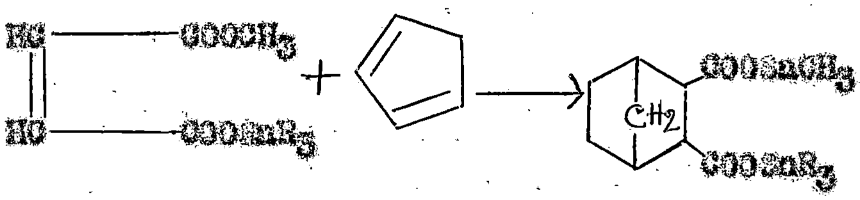
Action of alkoxy derivatives of metals and metalloids on organotin carboxylates produces metallostannoxanes (40, 41) as follows:

$$Ph_3SnOAc + Ph_2Sn(OEt)_2 \longrightarrow Ph_2Sn(OSnPh_3)_2 + 2EtOAc$$

~~2EtOAc~~

$$Bu_3SnOAc + Ti(OBu)_4 \longrightarrow Bu_3SnOTi(OBu)_3 \xrightarrow{(HOCH_2CH_2)_3N} Bu_3SnOTi(OCH_2CH_2)_3N$$

Diels - Alder reactions between organotin carboxylates and dienes are known (20)



($R = n\text{-}C_4H_9$: C_6H_5)

Diorganotin dicarboxylates undergoes redistribution with diorganotin dihalides, di-alkoxides and dihydrides to produce mixed carboxylates of the type $R_2SnX(OCOR')$, where $X = Cl, Br, I, OCH_3, H$ (36).

There are some evidences where carboxylate groups may be exchanged with other, carboxylate groups as follows (9, 42):

$$AcOBu_2SnOSnBu_2OAc + 2Bu^tCOOH \longrightarrow$$

$$(Bu^tCOO)Bu_2SnOSnBu_2(CO\,Bu^t).$$

Oligomeric acetate is usually formed when a dialkyl tin diacetate and a dialkyl tin dialkoxide are heated at 180°C in water for 2 hrs. (43,44).

$$(X+1)Bu_2Sn(OAc)_2 + (X+1)Bu_2Sn(Bu)_2 \longrightarrow$$

$$BuO(Bu_2SnO)_{2x+1}SnBu_2OAc + (2x+1)BuOAc.$$

Oligomeric $\alpha-\omega$ diacetoxy stannoxanes are also obtained by the reaction (45).

$$Bu_2Sn(OAc)_2 + Me_2O \xrightarrow[CH_2Cl_2]{}$$

$$AcO(Bu_2SnO)_x SnBu_2OAc + MeOAc$$

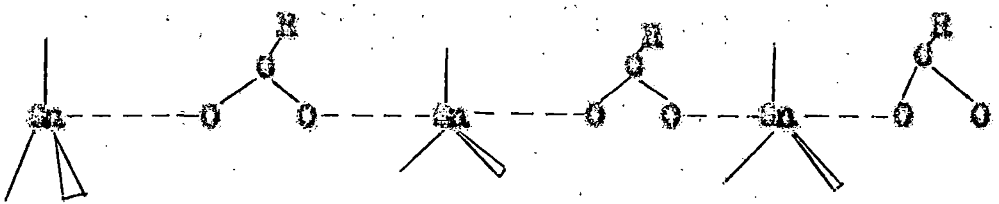
$$(X = 1,3,7,15).$$

Organotin tricarboxylates are easily hydrolysed in benzene solution to give polymeric organotin carboxylates (46).

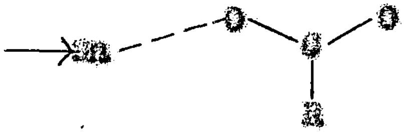
$$RSn(OCOR')_3 + H_2O \longrightarrow [RSn(O)OCOR']_n + 2R'COOH \text{ .}$$

IIB. Structure of Organotin complex

Structural features of organotin carboxylates have been reviewed by Okawara and Wada (38) and by Okawara and Ohara (26). The possibility of chelation or bridging through oxygen atoms of carboxylate group was shown by Beattie and Gilson (49) as an alternative to the previously postulated ionic nature of bonding by Freeman (40) and Okawara and co-workers (49). More recent spectroscopic studies on tin carboxylates in the solid as well as in the solution phase (6,10,50-55) have confirmed that trialkyl tin carboxylates are polymeric in solid state with planar trialkyl tin groups with bridging carboxylate group in between two tin atoms (A) and are expected to be monomeric esters in non-polar solvents (B).



[In solid phase] (A)

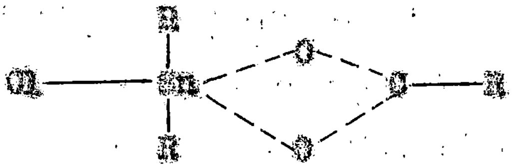


(B) [In solution phase]

IR spectra of trimethyl tin carboxylate in the solid state contain two C – O stretching band at about 1570 cm^{-1} and 1410 cm^{-1} indicating a symmetrical OCO group (54). Appearance of a single Sn – C stretching frequency in $Me_3SnOOCMe$ is consistant with a planar trimethyl tin group. In CCl_4 solution the carboxylate absorption bands are shifted to 1650 cm^{-1} and 1300 cm^{-1} respectively with the appearance of both ν_{as}(Sn – C) and ν_s(Sn – C) bands indicating the breakdown of polymeric structure (A) into monomers with essentially tetrahedral tin atoms having ester like carboxylate groups bonded to it (B). This is supported by the works of Hester (29) and Tagliavines work (55). Similar behaviour of trialkyl tin formates has been demonstrated by Okawara and Ohara (56, 57) from spectroscopic studies and molecular weight in cyclohexane by cryoscopy.

However, tricyclohexyl tin acetate, trineophyl tin formate, trineophyl tin acetate and tribenzyl tin acetate have been suggested to be tetra co-ordinated monomers probably due to steric hindrance arising from the bulky organic groups (58-60). Sams et al (10) have shown that branching at α-carbon atom generally prevent the formation of polymeric structure. Similarly, the trialkyl and aryl tin derivatives of halocarboxylic acids behave more like organic esters and thus possess monomeric structures (8, 61-63).

A monomeric penta co-ordinated structure (C) has been proposed for dialkyl chlorotin formates and acetates by Okawara et al (64)



(C)

Recently Calogero et. al have undertaken systematic studies on organotin carboxylates by means of Mossbauer spectroscopy and X-ray crystal analysis. The compounds studied include:

$[R_2SnO_2CR']_2O$ and $R_2Sn(O_2CR')OSn(OH)R_2$ $[R = n\text{-}Bu, CH_2 = CH, CH_2CH = CH_2]$, $(CH_2 = CH)_3SnO_2CR'$ and $(CH_2 = CH)_2(n\text{-}C_4H_9)SnO_2CR'$ $[R = CH_3, CH_2Cl, CHCl_2, CCl_3CF_3]$ and cyclo $(C_6H_{11})_3SnCl$

It has been pointed out that the crystal data of some tricyclohexyl tin derivatives do not agree well with the structure assigned on the basis of the Mossbauer quadrupole splitting values. The bulky cyclohexyl groups substantially modify the general structural pattern of the compounds of the R_3SnO_2CR' type, which usually have polymeric structure involving five co-ordinated tin atoms. Thus Mossbauer spectroscopic studies have been carried out on the series of tricyclohexyl tin halocarboxylates (Cyclo $C_6H_{11})_3SnO_2CR'$ with R' = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3 and X-ray crystal analysis has been carried out on the trifluoroacetate derivatives so that the results could be compared to those for the corresponding acetate. The crystals belong to orthorombic, space group PCm with unit cell parameters a = 14.590 ± 0.004, b = 8.427 ± 0.004, c = 11.510 ± 0.003 Å.

The structure has been resolved by patterson methods and refined to an R value of 0.147. The co-ordination about the tin atom can be considered distorted trigonal pyramid or distorted tetrahedral. Mossbauer data are explained in terms of distortions of bond angles about the tin atom (63).

Mossbauer data at liquid nitrogen temperature for the (Cyclo $C_6H_{11})_3SnO_2CR'$

Table - 8

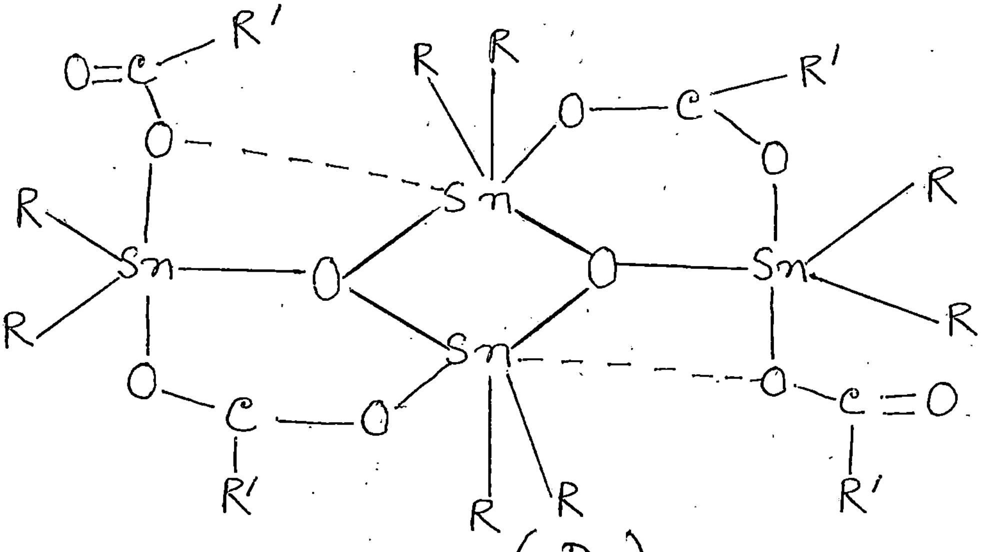
R'	$\delta^{a,b}$ (mms^{-1})	Δ^{a} (mms^{-1})	Δ^{c} (mms^{-1})	C-Sn-C^{d} (o)
CH_3	1.39	3.33	-3.06	106
CH_2Cl	1.42	3.36	-3.12	107
$CHCl_2$	1.53	3.60	-3.26	107
CCl_3	1.50	3.70	-3.30	106
CF_3	1.57	3.73	-3.36	106

a ± 0.03 mms^{-1}. Relative to SnO_2 at R.T.

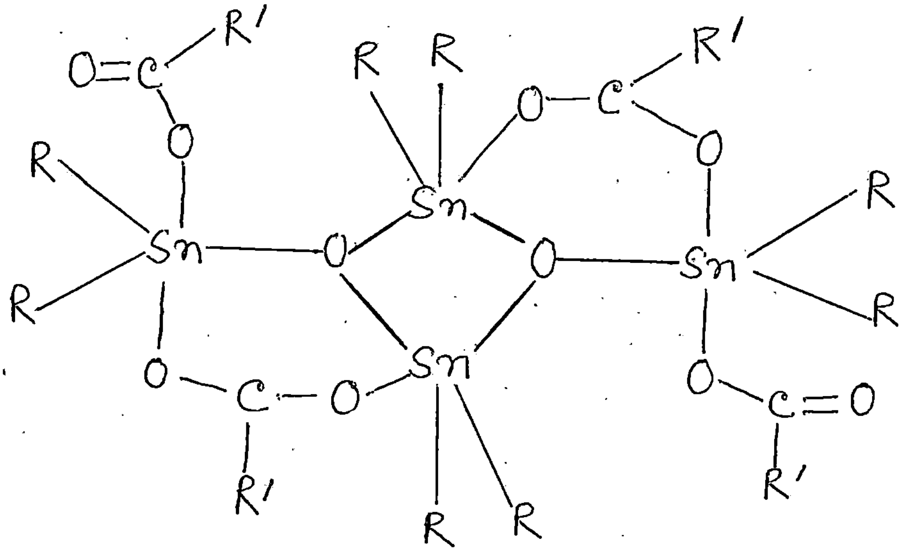
c predicted by simple point charge model. δ = 1.37 and Δ = 3.27

However, Alcock & Timms (69) have studied the structure of tribenzyl and tricyclohexyl tin acetate by X-ray diffraction method. This study confirms that the majority of organotin carboxylates have polymeric structure in the solid state. But with larger organic groups, the structure may become less polymeric and ultimately become monomeric.

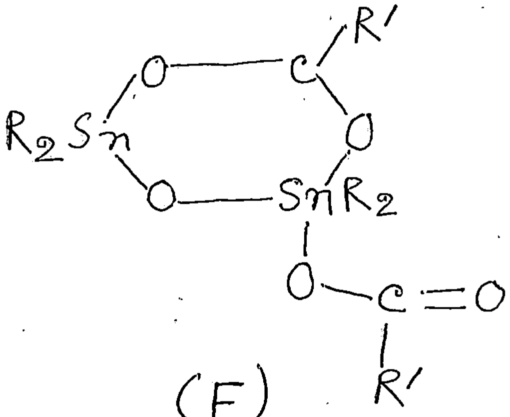
The IR spectrum of a series of compounds $[n\text{-}Bu_2SnX]_2O$ (X = CH_2ClCOO, $CHCl_2COO$, CCl_3COO) in chloroform solution, where these compounds exists in a dimer-monomer equilibrium have shown that in dilute solution, a band at 1715 cm^{-1} arises from a stretching vibration of an ester like carboxylic group. From the behaviour of tetrabutyl-1,3-trichloro acetoxy distannoxane in solution, it appears that it is a dimer in non-polar solvent like carbon tetrachloride. Comparison of the IR spectra suggests that the same molecular structure is maintained in the solid and in CCl_4 solution. In fact, in the COO asymmetric stretching region, only two bands are present (i) one near 1685 cm^{-1} must be attributed to the monodentate chloroacetate groups with the oxygen atom shared between the two tin atoms and (ii) one near 1650 cm^{-1} which arises from the chelate carboxylate group. In CCl_4 the weak Sn-O bond is preferentially broken, whereas the chelate ligands seem to remain unaffected. At varying concentrations, no change is observed in the position of the band centered at 1650 cm^{-1}, whereas that at 1685 cm^{-1} disappears on dilution and a strong band appears at 1715 cm^{-1}. The last band relates to the stretching vibrations of an ester like carboxylate group. It seems only that in CCl_4, a dimeric ladder-type structure such as D is present whereas in chloroform, species like E and F are present (62).



(D)



(E)

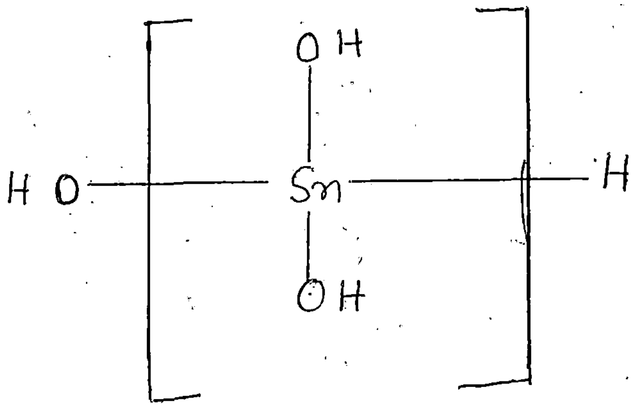


(F)

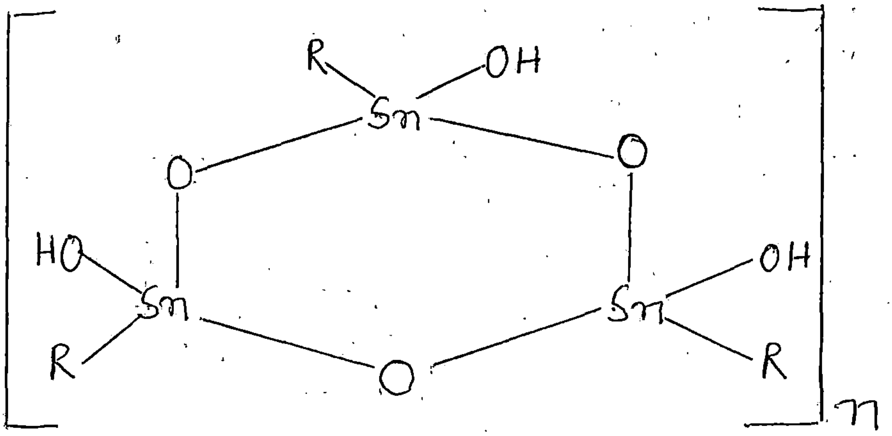
In the dimeric species D, in which two carboxylate groups are acting as bridging bidentate ligands and the other two as bridged monodentate ligands, the tin atoms are in different environments having co-ordination number of 6 and 5 in D, 5 in E and 5 and 4 in F. However, on the basis of IR, molecular wts. of diorganotin dicarboxylates ionic structure with R_2Sn cation, octahedral chelated structure with linear R_2Sn group as well as polymeric structure with bridging carboxylic groups have also been proposed by Okawara et al (49,66-68).

The structure of polymeric mono-organo stannoic acids (69) and their carboxylate derivatives (8, 46, 10) have been studied in details. Herber et al (70) have shown that polymeric tin compounds are most likely to show a Mossbauer effect at ambient temperature.

The stannoic acids are infusible powders for which a polymeric structure (G) have been proposed (71,72). For the partially dehydrated material structure (H) has been proposed by Platt et al (73).



(G)

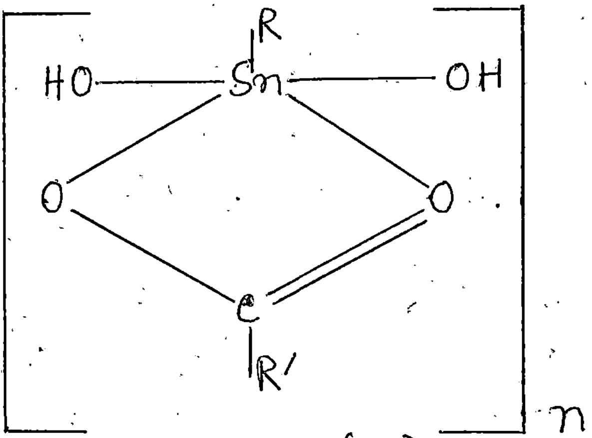


(H)

In both G and H, tin atom is 4 co-ordinated and is enclosed within the tetrahedra formed by the three oxygen atoms and the organic group R.

From the values of quadrupole splitting (E_Q = 1.23 - 1.83 mm/sec) in organo stannoic acids Davies et al (67) have suggested a tetrahedral geometry at tin, though the possibility of association has not been completely excluded. The isomer shift values (δ = 0.40 - 0.78 mm/sec.) are very small because of the very low 'S' electron density at the tin atom resulting from electron attraction by the surrounding oxygens.

On the other hand, carboxylic acid derivatives $[RSn(O)OCOR']$ of the stannoic acids $[RSn(O)OH]_n$ show a larger quadrupole splitting values (E_q = 2.00 - 2.64 mm/sec.) (46,10) indicating a 5 co-ordinated trigonal bipyramidal tin I which would be expected to give a quadrupole splitting of about 2.25 mm/sec. (73).



(I)

Table - 3

Mossbauer parameters for organostannoic acid

Compound	δ mm/sec.	ΔE_q. mm/sec.
$[MeSn(O)OH]_n$	0.40	1.29
$[EtSn(O)OH]_n$	0.76 -0.70	1.61 - 1.70
$[BuSn(O)OH]_n$	0.65 - 0.70	1.52 - 1.71
$[C_8H_{17}Sn(O)OH]_n$	0.66	1.62
$[PhSn(O)OH]_n$	0.73	1.83

(ΔE_q = quadrupole splitting, δ = isomer shift)

Table - 4

Mossbauer parameters for carboxylates of the organostannoic acids

Compound	δ mm/sec.	ΔEq. mm/sec.
$PhSn(O)[OCO(CH_2)_8CH = CH_2]$	0.57	2.31
$PhSn(O)[OCO(CH_2)_{16}Me]$	0.86	2.32
$PhSn(O)[OCO(CH_3)_3]$	0.89	3.00
$PhSn(O)[OCOCCl_3]$	0.72	3.33
$PhSn(O)[OCOCF_3]$	0.66	2.64
$PhSn(O)[OCOMe]$	0.70	2.28
$BuSn(O)OH$	0.63	1.71

On the basis of this discussion the generalisation which could be made regarding the structure of organotin carboxylates are,

(1) These compounds are usually polymeric in the solid state with the carboxy groups acting as the bridges.

(2) Branching at the α -carbon atom of the carboxy group generally resists the formation of polymeric structure probably by steric effect.

(3) Electronegative substituents, e.g., halogens etc. when attached to the carboxy groups as in halocarboxylates diminishes the possibility of polymeric structures, possibly by decreasing the ability of the $>C = O$ group to co-ordinate with the tin atom, possibily due to withdrawal of electron from the oxygen atom via inductive effect.

(4) The polymeric structures are broken down in solution, the extent of splitting being determined by the nature of the solvent and the carboxylate and also on the concentration.

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