CHAPTER - I

Organotin Carboxylates : A Brief Review

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I. A. Introduction:

Organotin carboxylates comprise one of the most important class of compounds in the even expanding field of organotin chemistry. Apart from the theoretical and structural interests, organotin carboxylates are finding tremendous importance in industry and agriculture. Many of these groups of compounds have already found important uses and new applications are likely to emerge in the near future.

The compounds containing -OCOR groups bonded to tin which may be either monomeric or polymeric are of the 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 tetracarboxylates, $Sn(OCOR)_4$, are not organotin compounds in the strict sense of the term, but are nevertheless included in the discussion of organotin carboxylates for the sake of comparison and convenience. Many discussions with varying degrees of details are available on these compounds[1-4] and as such only the more important aspects will be presented here.

I. B. Preparation

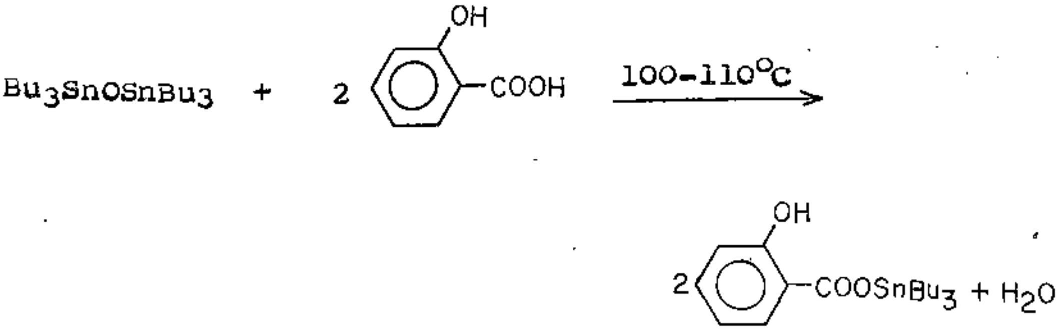
A number of methods are employed for the synthesis of organotin carboxylates, one of the most important being the reaction between organotin oxides (or hydroxides) and carboxylic acids or their anhydrides[5-13].

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

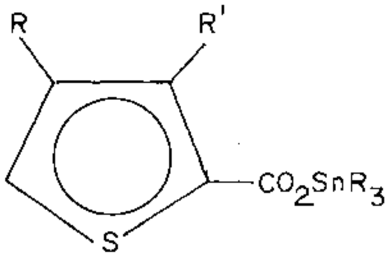
$$R_3SnOSnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR'$$

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

The water produced in these reactions is removed usually by azeotropic distillation or alternatively by refluxing at higher temperature[14] for example :



A number of organotin thiophene carboxylates[15] of the type I and II have been prepared from the thiophene carboxylic acids and R_3SnOH or $(R_3Sn)_2O$



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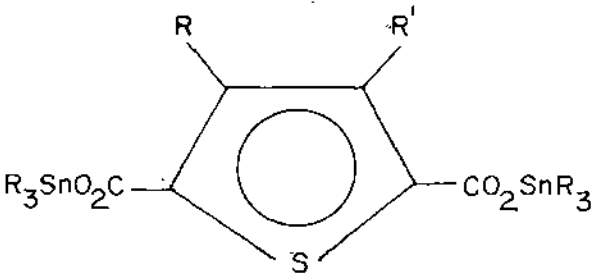


(II)

R = Ph, H; R' = Bu, Me, Cyclo-C_6H_{11}, etc.

The triphenyltin carboxylates, Ph_3SnO_2CR (R = Ph, $p\text{-}MeOC_6F_4$, $p\text{-}EtOC_6F_4$), $p\text{-}(Ph_3SnO_2C)_2C_6F_4 \cdot H_2O$ and $o\text{-}(Ph_3SnO_2C)_2C_6F_4 H_2O$ have been prepared by the reaction of Ph_3SnOH with the appropriate polyfluoro carboxylic acids in MeOH[16].

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 at RT or by refluxing the reactants in a suitable solvent[12,17-19].

$$R_nSnX_{4-n} + (4-n)MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} + (4-n)MX$$

(M = Na, Ag, K or Tl; X = halogen)

Another method for the preparation of organotin esters involves the cleavage of one or more organic groups of tetraorganotin compounds by carboxylic acids[20,21].

$$R_4Sn + nR'CO_2H \longrightarrow R_{4-n}Sn(OCOR')_n + nRH$$

In this acidolysis reaction, the cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on the temperature[22-24]. Vinyl groups are cleaved more readily than saturated alkyl radicals, but less readily than phenyl[25] and successive groups are lost with increasing difficulty. Tetralkyltin is more reactive than tetravinyltin[21].

A novel method of preparation of tri-alkyltin carboxylates by electrochemical method using the cleavage of organic groups from R_4Sn (R = Me, Et, Pr, Bu) and Hg(I) carboxylates have been described by Tagliavini et al[26]. At room temperature tetramethyltin produces trimethyltin acetate when treated with Hg(I) acetate in MeOH.

$$2Me_4Sn + Hg_2(OCOMe)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_6H_6$$

Organotin hydrides react with carboxylic acids to form the corresponding organotin esters[27-28] with the evolution of hydrogen.

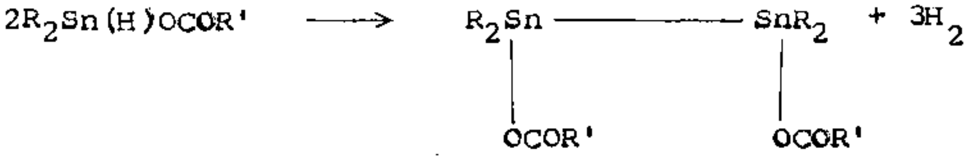
$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2$$

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

The initially formed dicarboxylate equilibrates with unreacted dihydride as follows[29].

$$R_2Sn(OCOR')_2 + R_2SnH_2 \rightleftharpoons \underset{(III)}{2R_2Sn(H)OCOR'}$$

With di-n-butyltin dihydride, the intermediate hydride carboxylate (III, R = n-Bu) decomposes to give distannane dicarboxylates (IV, R = n-Bu) when the acid is deficient.



$$2R_2Sn(H)OCOR' \longrightarrow \underset{OCOR'}{R_2Sn} - \underset{OCOR'}{SnR_2} + 3H_2$$

(IV)

Using similar methods distannane 1,2-di carboxylates have also been prepared[27,30,31]. The nature of the products sometimes depends on the carboxylic acid. Action of benzoyl peroxide on di n-butyltin dihydride produces 1,2-dibenzoate[32].

Halocarboxylate derivatives of organotin compounds are most conveniently synthesised by heating equimolecular mixture of the diorganotin dicarboxylates and the diorganotin dihalides in an inert solvent[33,34].

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

These compounds may also be prepared by the reaction as follows[35,36].

$$Bu_2SnCl_2 + KOCOR' \longrightarrow Bu_2Sn(Cl)OCOR' + KCl$$

At 100°C trimethyltin chloride reacts with carboxylic acids to give diorganochlorotin carboxylates[37] which may also be prepared by the exchange reaction between dimethyltin dichlorides and triorganotin carboxylates in CCl_4 or C_6H_6 at room temperature[33].

$$Me_3SnCl + RCOOH \longrightarrow Me_2Sn(OCOR)Cl + MeH$$

$$R_2SnCl_2 + R'_3SnOCOR'' \longrightarrow R_2Sn(OCOR'')Cl + R'_3SnCl$$

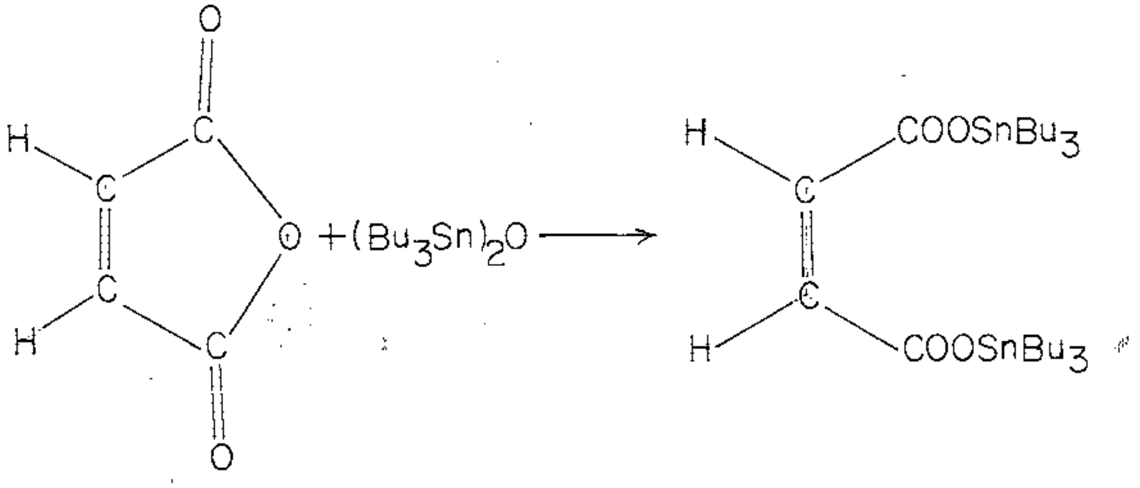
A number of dialkylhalotin acetates have been synthesised according to the reactions[38].

$$(R_2ClSn)_2O + 2CH_3COOH \longrightarrow 2R_2ClSnOCOCH_3 + H_2O$$

$$(R_2ClSn)_2O + (CH_3CO)_2O \longrightarrow 2R_2ClSnOCOCH_3$$

$$R_2SnO + Cl\text{-}\underset{\underset{O}{\|}}{C}\text{-}R \longrightarrow \underset{\underset{Cl}{|}}{R_2SnOCOR}$$

Anhydride of an unsaturated acid (e.g., maleic anhydride) when reacted with hexabutyl distannoxane produces disubstituted organotin esters[39].



Organotin carboxylates may also be prepared from the carboxylic esters by the following reactions[40,41].

$$(R_3Sn)_2O + R'COOEt \longrightarrow R_3SnOCOR' + R_3SnOEt$$

$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH$$

Tricarboxylate derivatives of the type $RSn(OCOR')_3$ are usually prepared from the corresponding organotin trichloride by the action of silver salts of carboxylic acids[42].

$$RSnCl_3 + 3R'COOM \longrightarrow RSn(OCOR')_3 + 3MCl$$

I.C. Physical Properties of Organotin Carboxylates

In organotin carboxylates the Sn - O bond is essentially covalent but undergoes polar reactions depending on the solvents and the attacking groups. This is why the carboxylates with small organic groups are more soluble in alcohol, ether etc. than in water[4]. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric associated structures. Many of the carboxylates have low melting points indicating these to be covalent compounds.

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

The melting points (or boiling points) of some common organotin esters are listed in Table - 1[1,2,4,42-45].

Table - 1

Compounds	B.P. (°C/mm Hg)	M.P. (°C)
I. $R_3SnOCOR'$		
$Me_3SnOCOMe$		196.5 - 197.5
$Ph_3SnOCOH$		202 - 203
$Ph_3SnOCOPh$		84 - 85.5
$Bu_3SnOCOH$	120 - 125/0.7	
$Bu_3SnOCOMe$		85
$Bu_3SnOCOPh$	166 - 168/1	
$(Cy\text{-}Hex)_3SnOCOMe$		62-63
$Pr_3SnOCOCF_3$	88-90/1	
II. $R_2Sn(OCOR')_2$		
$Bu_2Sn(OCOMe)_2$	144.5-145.5/10	
$Ph_2Sn(OCOMe)_2$		116-117
$Bu_2Sn(OCOCH=CHMe)_2$		34
$Bu_2Sn(OCOC_{11}H^{n}_{23})_2$		22-24
III. $R_2SnX(OCOR')$		
$Et_2SnCl(OCOMe)$		94
$Bu_2SnBr(OCOMe)$		67-68.5
IV. $RSn(OCOR')_3$		
$BuSn(OCOCH_3)_3$	117-119/1	
$EtSn(OCOPh)_3$	171-173/1	

I.D. Chemical properties of organotin carboxylates

Generally triorganotin carboxylates are hydrolytically stable, whereas the diorganotin derivatives undergo partial hydrolysis to produce $R_2Sn(OCOR')OSnR_2(OCOR')$ and $R_2Sn(OCOR')OSnR_2OH$[2,46].

The monoorganotin tricarboxylates are easily hydrolysed in EtOH (or benzene) solution to give polymeric monoorganotin oxycarboxylates[13,42]

$$nRSn(OCOR')_3 + nH_2O \xrightarrow{EtOH} \{RSn(O)OCOR'\}_n + 2nR'COOH$$

The most widely studied reactions of organotin carboxylates are decarboxylation and disproportionation. The thermal decarboxylation of triorganotin carboxylates[47] has been used for the preparation of trialkyltin hydrides[48].

$$R_3SnOCOH \xrightarrow{100-170^{\circ}C} R_3SnH + CO_2$$

$$[\ R = n\text{-}Pr,\ n\text{-}Bu\ ]$$

Trialkyltin carboxylates of unsaturated acids give trialkylalkynyltins on decarboxylation[49,50].

$$Bu_3SnOCOC \equiv CPh \xrightarrow{60^{\circ}C} Bu_3SnC \equiv CPh + CO_2$$

$$R_3SnOCOC \equiv CCOOSnR_3 \xrightarrow{160^{\circ}C} R_3SnC \equiv CSnR_3 + 2CO_2$$

$$[\ R = Et,\ n\text{-}Pr,\ \text{or}\ n\text{-}Bu\ ]$$

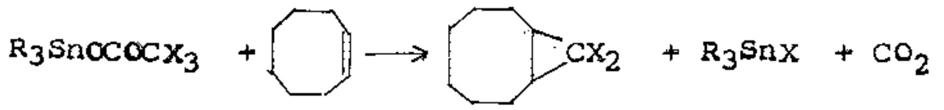
An interesting triphenylcyanomethyltin (yield 50%) is formed when triphenyltin cyanoacetate is heated under vacuum[51].

$$Ph_3SnOCOCH_2CN \xrightarrow{140-150^\circ C} Ph_3SnCH_2CN + CO_2$$

In the aliphatic series this type of conversion is less pronounced, the triorganocyanomethyltins are produced in low yield.

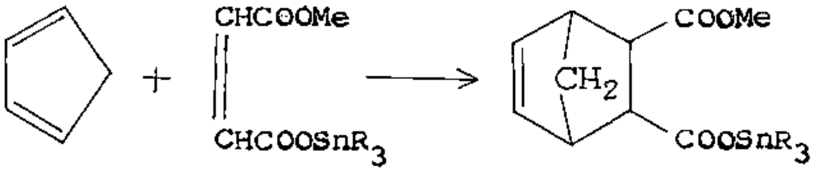
Thermal decomposition of $Ph_3SnOCOR$ (where $R = C_6F_5$, p-$MeOC_6F_4$ or p-$EtOC_6F_4$) in boiling pyridine give the corresponding polyfluorophenyltriphenyltins[16]. This also undergoes disproportionation reaction resulting in the formation of Ph_4Sn and $Ph_2Sn(OCOR)_2$. Para-$(Ph_3SnOCO)_2C_6F_4$ is readily decarboxylated to produce p-$(Ph_3Sn)_2C_6F_4$.

Seyferth et al[52] have used successfully the reaction of triorganotin carboxylates of halogen substituted carboxylic acids with cyclooctene as a carbene transfer reaction, although the reaction mechanism is not yet established.



[R = Me, Ph; X = Cl, Br]

Diels-Alder type reactions have been carried out with organotin carboxylates and dienes[35,39].



(R = Bu^n or Ph)

With thiols the following equilibrium is established and the reaction can be driven from left to right by removing the organic acid from the mixture[53].

$$R3SnOCOR' + R''SH \rightleftharpoons R_3SnSR'' + R'COOH$$

Action of alkoxy derivatives of metals and metalloids on organotin carboxylates produce metallostannoxanes[54,55] as shown below:

$$Ph_3SnOAc + Ph_2Si(OEt)_2 \longrightarrow Ph_2Si(OSnPh_3)_2 + 2\ EtOAc$$

$$\begin{tikzcd} Bu_3SnOAc + Ti(OBu)_4 \arrow[r] & Bu_3SnOTi(OBu)_3 \arrow[d, "(HOCH_2CH_2)_3N"] \\ & Bu_3SnOTi(OCH_2CH_2)_3N \end{tikzcd}$$

Organotin carboxylates readily undergo redistribution with other organotin compounds to form mixed organotin carboxylates[2,56,57].

$$Bu_3SnOCOC_5H_4N\text{-}2 + RSnCl_3 \xrightarrow{MeOH} RSn(OCOC_5H_4N\text{-}2)Cl_2 + Bu_3SnCl$$

[R = n-Bu, Ph]

$$R_2Sn(OCOR')_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR')X$$

[X = hal., OR, H, etc.]

In some cases carboxylate groups may be exchanged with other carboxylate groups as shown below[17,58] :

$$AcOBu_2SnOSnBu_2OAc + 2\ Bu^tCOOH \longrightarrow (Bu^tCOO)Bu_2SnOSnBu_2(OCOBu^t) + 2AcOH$$

Oligomeric acetate is usually formed when a dialkyltin diacetate and a dialkyltin dialkoxide are heated at 180°C in water for 2 hrs[59,60]. Oligomeric α-ω -diacetoxy stannoxanes are also obtained by the reaction[61].

$$Bu_2Sn(OAc)_2 + H_2O \xrightarrow{CH_2N_2} AcO(Bu_2SnO)_nSnBu_2OAc + MeOAc$$

(n = 1, 3, 7, 15)

Generally the organotin esters are weaker Lewis acids than organotin halides, so complex formation by esters is less extensive than by the halides. This weaker acidity appears to be essentially an inductive effect and may be related to the lower electron-withdrawing power of the OCOR' group compared to chlorine atom[62]. The presence of electron-withdrawing organic groups attached to the tin and/or carboxylate moiety will favour complex formation, e.g., $Ph_3SnOCOCCl_3 \cdot MeOH$[63], $Me_3SnOCOC_5H_4N$-2. H_2O[64], and $(CH_2 = CH_2)_2Sn(OCOCF_3)_2 \cdot bipy$[65]. Thermodynamic data (ΔH^o, K) have been reported for the formation in benzene solution of 1/1 adducts of $Ph_2Sn(OCOMe)_2$, $Bu_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$ with N-donor ligands like Pyridine, 4-methylpyridine, N,N,N',N'- tetramethyl-1,2-diamino ethane and 1,10-phenanthroline[62].

I.E. Biological properties of Organotin Carboxylates

In contrast to inorganic tin compounds which are non-toxic, many organotin compounds are toxic to various organisms and have a variety of fungicidal, insecticidal and bacteriostatic activities. These compounds are, therefore, being used to a significant extent biocidal agents in agriculture and industry.

The toxicological and biological properties as manifested in the organotin carboxylates are summarised in Table -2[96,97,99].

Table - 2

Property	Compounds
1. Mammalian toxicity	$R_3SnOOC.CH_3$ (R = Me, Et, Pr, i-Pr, Bu, C_6H_{13}, C_8H_{17}, Ph)
2. Anthelmintic	Dibutyltindilaurate $Bu_2Sn(OOC(CH_2)_{10}CH_3)_2$
3. Fungicidal	
a) Agricultural	$Ph_3SnOOC.CH_3$, $BuSn(OOC.CH_3)_3$
b) Horticultural	$Bu_3SnOCO(Naphth)$
4. Phytotoxicity	$Ph_3SnOOC.CH_3$, $Ph_3SnOOC.C_6H_5$
5. Bacteriostatic	$Bu_3SnOOC.CH_3$, $Ph_3SnOOC.CH_3$, $Bu_3SnOOC.(CH_2)_4.COOSnBu_3$, $Bu_3SnOOC.C_6H_5$
6. Insecticidal	$Bu_3SnOOC.(CH_2)_6CH_3$, $Me_3SnOOC.CH_2Cl$, $Et_3SnOOC.C(Me) = CH_2$, $Pr_3SnOOC.C(Me) = CH_2$, $R_3SnOOC.CH_3$ (R = Me, Et, Bu, Ph)

I.F. Structures of organotin carboxylates

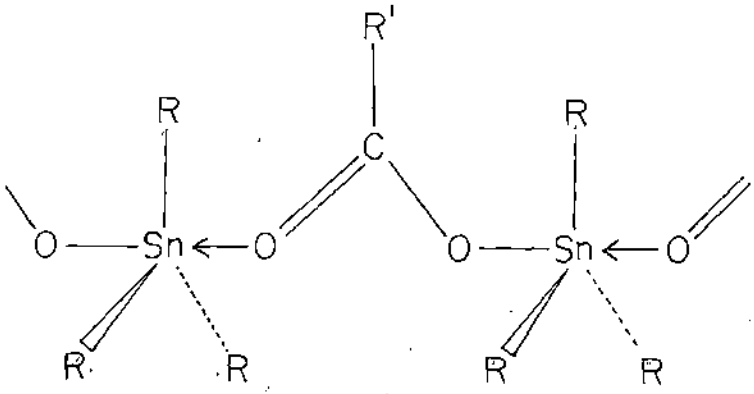
As early as 1961, it was pointed out by Beattie and Gilson[66] that intermolecular bridging through carboxyl oxygen atoms was an alternative to the previously postulated ionic bonding in organotin carboxylates by Freeman[67] and Okawara[68]. Since then, various physical methods like IR, ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopy have been utilised to deduce structures of this class of compounds. The subject has been discussed and reviewed by several authors[1-3]. We present below the important physical methods on the basis of which structures of organotin carboxylates are deduced.

I. Infrared Spectroscopy:

(i) Carbonyl group absorptions:

A comparison of the IR spectra $Me_3SnOOCCH_3$ with that of $Me_3SiOOCCH_3$ points to the essential different of structures between these two class of compounds. The trimethyl silyl derivative possesses normal ester structure as evidenced by the appearance of asymmetric stretching frequency of the carboxyl group (ν_{as}OCO) at 1725 cm^{-1}[18,69]. The trimethyl stannyl acetate, on the other hand, shows ν_{as}(OCO) at 1576 cm^{-1}, the absorption frequency being similar to ν_{as}(OCO) of 1578 cm^{-1} in $NaOOCCH_3$. Presence of a symmetrical carboxyl group of the ionised $RCOO^-$ type [ν_{as}(OCO) 1550-1610 cm^{-1}

and ν_s(OCO) 1300-1400 cm^{-1} _7 is, therefore, indicated[70]. All carboxylates of the type $R_3SnOOCR'$ and $R_2Sn(OOCR')_2$ (R = alkyl/aryl group) show such symmetric and asymmetric carbonyl absorptions in solid state. On dissolving the compounds in non-polar, non-coordinating solvents, the asymmetric stretching frequencies are raised to the region 1650-1700 cm^{-1} while the symmetric frequencies are lowered to a relatively small extent indicating that in solution the molecules possess ester-like structures. Further, the difference between the asymmetric and symmetric stretching frequency $\Delta\nu$ (ν_{as}OCO - ν_sOCO) is generally found to be less than 200 cm^{-1} in solid state and greater than 250 cm^{-1} in solution[69,71]. This has been interpreted in terms of bidentate and an almost symmetrical carboxyl group forming intermolecular bridges in solid state giving rise to polymeric carboxylates (VA) while in solution depolymerisation occurs resulting in ester-like monomeric species (VB)[30,72-74,85,86] having a mono dentate carboxyl group. Molecular weights of the carboxylates in benzene, CCl_4 also supports monomeric structures (VB) in solution with the exception of trimethyltin formate which exists as an equilibrium of associated and unassociated forms in $CHCl_3$[72]. On the other hand, when the group R bonded to the tin atom is too bulky or when there is branching at the carbon atom α- to the tin atom (e.g. triphenyltin 2-ethyl



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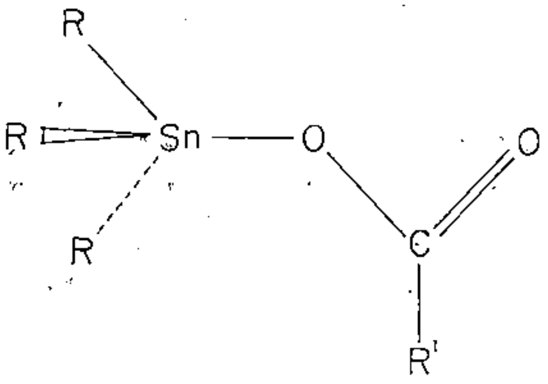
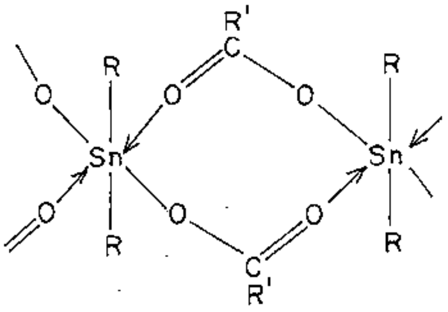


(VB)

hexoate) the compounds assume monomeric ester like structures in solid state as a result of steric hindrance exerted by the bulky organic groups[18,75-79]. Thus, tricyclohexyl, tri-isopropyl-, trineophyl- and tri-α-napthyl tin acetates absorb at 1645 cm^{-1} both in solid state and in solution confirming monomeric structures in both phases. Steric interaction between the alkyl or aryl groups bonded to tin and "tail" of the carboxylate group can also prevent polymerization. For Ph_3Sn derivatives, while $Ph_3SnOOCCHMe_2$ and $Ph_3SnOOCCH = CH_2$ are penta coordinate polymers,

$Ph_3SnOOCCMe_3$, $Ph_3SnOOCCMe = CH_2$ and $Ph_3SnOOCCl_3$ are tetra coordinate monomers in the solid state[12]. Recently it has also been claimed that triphenyltin derivatives of substituted benzoic acids are always monomeric in solid state[85,86]. An analogous situation is also observed in the oxinate-carboxylates, e.g. $RSn(OX)_2OOCR'$ which also have monomeric structures in solid state[80]. Trimethyltin glycinate also has a polymeric chain structure in solid state ($\nu_{as}OCO$ and ν_sOCO are 1630 and 1398 cm^{-1} respectively), but bridging occurs via the NH_2 groups[81].

The structure of dialkyltin dicarboxylates was first suggested for dimethyltin diformate by Okawara[68] which included a linear Me_2Sn cation and a formate anion. Further studies have been carried out on dialkyltin diacetates[82,83] which suggest that in the neat liquid or solid state, those adopt a polymeric structure (VIA) with intermolecularly bridging carboxylate groups and an octahedral trans- R_2SnX_4 tin atom geometry. In solution, these compounds are monomeric as evidenced by raising of ν_{as}(OCO) frequencies. The molecules have been suggested to be octahedral with intra-molecularly chelated carboxyl groups (VIB)[2]. It is, however, equally likely that these compounds assume a non-chelated ester-like structures in solution (VIC). The dialkyl chlorotin carboxylates $R_2Sn(OCOR')Cl$ are also believed to possess inter-and intra-molecularly chelated structures in the solid state (VIIA) and solution (VIIB) respectively with the tin atoms occupying a trigonal bipyramidal cis- R_2SnX_3 geometry[38].



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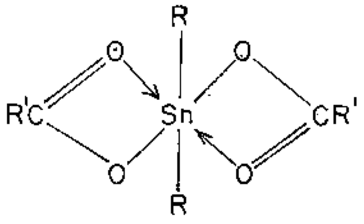

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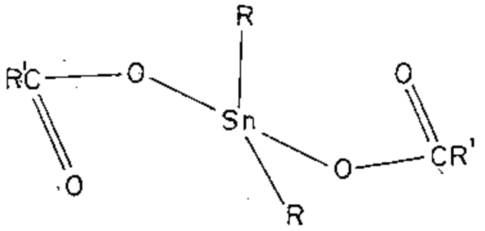
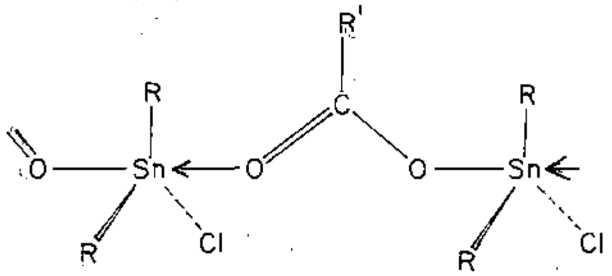
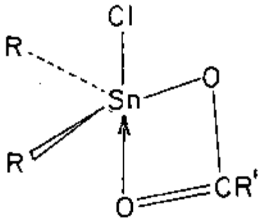


(VIC)



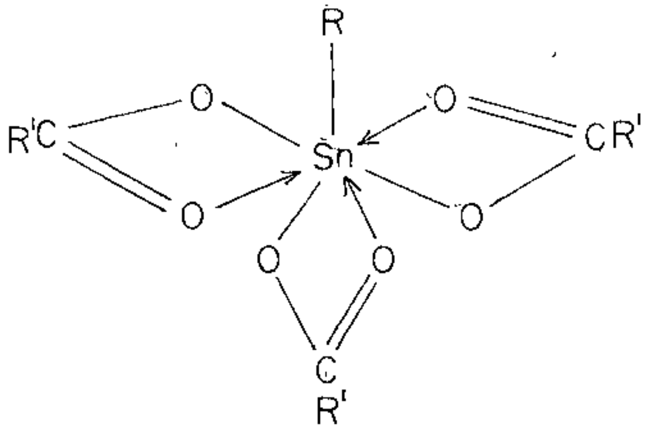
(VIIA)



(VIIB)

The structure of the bis (trimethyl stannyl) ester of a dicarboxylic acid (malonic acid) has recently been determined and shows that in $Me_3SnOOCCH_2COOSnMe_3$, each carbonyl group links planar Me_3Sn moieties intermolecularly to form a three-dimensional polymeric network[84].

The IR spectra of a number of monoorganotin tricarboxylates in CCl_4 show coordinated carbonyl stretching bands, and, additionally, $BuSn(OOCMe)_3$ and $BuSn(OOCEt)_3$ were found to be monomeric in camphor solution[42]. This is indicative of a 7-coordinated tin atom geometry for these compounds (VIII).



(VIII)

Tin tetra carboxylates are also associated in solid state and undergo dissociation in solution to the monomeric species[2].

Infrared data on carboxyl group frequencies of some tri- and di-organotin carboxylates are summarised in Table - 3.

Table - 3

Carbonyl stretching frequencies in some organotin carboxylates (cm^{-1})

Compound	Solid state		Solution	
	ν_{as}(OCO)	ν_s(OCO)	ν_{as}(OCO)	ν_s(OCO)
1. $Me_3SnOOCH$	1575	1357	1585[a] 1648	1352
2. $Me_3SnOOC \cdot CH_3$	1564	1346	1645	1314
3. $Me_3SnOOC \cdot CH_2I$	1581	1383	1659	1320
4. $Me_3SnOOC \cdot CH_2Cl$	1618	1382	1687	1339
5. $Me_3SnOOC \cdot CCl_3$	1647	1348	1701	1295
6. $Me_3SnOOC \cdot CF_3$	1652	1340	1720	1290
7. $Bu_3SnOOC \cdot CH_3$	1572	1410	1647	1300
8. $Et_3SnOOC \cdot CH_3$	1572	1412	1655	1302
9. $(C\text{-}Hex)_3SnOOC \cdot CH_3$	1645	1408	1650	1304
10. $(i\text{-}Pr)_3SnOOC \cdot CH_3$	1645	-	1645	-
11. $Me_3SnOOC \cdot C_{11}H_{23}$	1567	1410	1642	1302
12. $Me_2Sn(OOC \cdot CH_3)_2$	1560 1600	1438	1607	1433
13. $Et_2Sn(OOC \cdot CH_3)_2$	1570 1600	1422	1607	1432
14. $Pr^n_2Sn(OOC \cdot CH_3)_2$	1570 1605	1432	1609	1425
15. $Ph_3SnOOCH$	1559	1390	1644	1358

Contd..

Table - 3 (Contd..)

Compound	Solid state ν_{as}(OCO)	Solid state ν_s(OCO)	Solution ν_{as}(OCO)	Solution ν_s(OCO)
16. $Ph_3SnOOCCH_3$	1548	1420	1640	1370
17. $Ph_3SnOOC.C_2H_5$	1535	1412	1632	1381
18. $Ph_3SnOOC.CMe{=}CH_2$	1593	1346	1610	1360
19. $Ph_3SnOOCCH(Et)Bu$	1630	1336	1625	1340
20. $Ph_3SnOOC.CMe_3$	1622	1330	1624	1332
21. $Ph_3SnOOC.CCl_3$	1700	1305	1700	1292
22. $Ph_3SnOOC.C_6H_4NHCOCH_3$	1625	1338	1640	1352
23. $Ph_3SnOOC.C_6H_4OH$	1611	1345	1612	1347
24. $Ph_3SnOOC.C_6H_4Cl$	1640	1330	1650	1340
25. $Ph_3SnOOC.C_6H_4CH_3$	1620	1342	1626	1342

(a) both polymeric and monomeric forms are presented in equilibrium in $CHCl_3$

(ii) Tin-carbon stretching frequencies:

The di- and tri- alkyl tin compounds generally show two bands, ν_{as}(Sn-C) and ν_s(Sn-C) modes causing absorption essentially in the range 500-600 cm^{-1} and 470-530 cm^{-1} respectively[87]. The intensities of these bands vary considerably and, in some cases, only very weak absorption is observed. The position of the absorption bands depends also on the nature of the alkyl group. For example, in the compounds

$Bu^n_nSnX_{4-n}$ (X = halogen), ν_{as}(Sn-C) and ν_s(Sn-C) have been found to occur at 592-602 cm^{-1} and 503-522 cm^{-1} respectively[90]. In phenyltin derivatives, ν_{as} and ν_s(Sn-C) appear at 261-382 cm^{-1} and 225-249 cm^{-1} respectively[87].

However, the organotin carboxylates in solid state being polymeric with intermolecularly coordinated carboxyl groups, show only the ν_{as}(Sn-C) mode confirmingplanar R_3Sn or linear R_2Sn residues. In solution these compounds are depolymerised to tetrahedral stannyl esters and both asymmetric and symmetric Sn-C stretching vibrations are observed, as expected, for non planar R_3Sn and non-linear R_2Sn moieties. Thus, $Me_3SnOOCH$ in $CHCl_3$ shows both ν_{as} and ν_s(Sn-C) but as pyridine is added to the solution, the ν_s(Sn-C) band slowly disappears as the Me_3Sn group assumes a planar configuration in the penta-coordinated 1:1 pyridine complex[73].

ν(Sn-C) IR spectral data of some organotin carboxylates are shown in Table - 4[2,30,85,87,88].

Table - 4

Tin-Carbon stretching frequencies
of some organotin carboxylates.

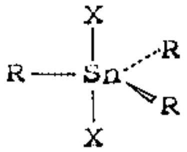
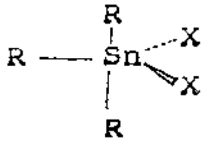
Compound	$\nu_{(Sn-C)}cm^{-1}$	
	Solid	Solution
1. $Me_3SnOOCH$	554	555,516
2. $Me_2SnOOCCH_3$	554	548,517
3. $Me_3SnOOCCH_2I$	551	
4. $Me_3SnOOCCH_2Br$	551	
5. $Me_3SnOOCCH_2Cl$	555	548,515
6. $Me_3SnOOC.C_2H_5$	552	595,516
7. $Me_3SnOOC.C_{11}H_{23}$	548	548,516
8. $Ph_3SnOOCC_6H_4CH_3$[a]	228,267	
9. $Ph_3SnOOC.C_6H_2(CH_3)_3$[a]	232,261	
10. $Ph_3SnOOC.C_6H_4OH$[a]	228,267	
11. $Ph_3SnOOC.C_6H_4NO_2$[a]	235,270	

a) these compounds have been shown to be tetra-coordinate monomers in solid state (ref. 85)

II. Mössbauer Spectroscopy:

Mössbauer spectroscopy offers an excellent tool for investigating structures of organotin compounds in terms of nature of bonding and coordination number of the tin atom. The two Mössbauer parameters of primary interest are the isomer shift, δ (mm/sec) and the quadrupole splitting ΔE_Q (mm/sec). The isomer shift values are dependent upon the S-electron density at the ^{119}Sn nucleus, and, for all tin compounds, fall in the range ± 5 mm/sec, with a positive δ corresponding to an increase in nuclear S-electron density at the tin atom. Since the electron density at the tin nucleus is related to the S-electron density in the valance shell of the tin atom, δ should vary with the polarity of the tin-ligand bonds[89]. For example, for the series of anionic monobutylpentahalogeno stannate salts $M_2^+ [BuSnX_{5-n}Y_n]^{-2}$, an increase in electronegativity of the halogen attached to tin produces a steady reduction in the nuclear S-electron density, with a concomitant drop in δ. Similarly in a series of organotin derivatives which contain no inorganic radicals, e.g. R_4Sn, or in which the anionic group remains constant, such as R_3SnOH, the isomer shift increases with the electron donating power of the alkyl group. The strongly electron withdrawing nature of a phenyl group attached to tin is reflected in the isomer shift values of the phenyltin derivatives which are usually lower than their alkyltin counterparts. A change in coordination number or stereochemistry at the tin atom will also affect the isomer shift parameter. If the coordination number of the tin increases from four to five or six or seven, the increased use of the metal's 5d-orbitals for bonding results in a reduction in the 5s-electron density at the tin nucleus and a drop in δ, e.g., Ph_2SnI_2 : δ= 1.51 mm/sec, Ph_2SnI_2 bipy : δ= 1.41 mm/sec. For a given coordination number, change of stereochemistry affects δ. Cis-complexes have significantly lower δ than the trans-complexes and this is probably due to a higher percentage S-character of the Sn-C bonds in the trans-isomer[89].

The δ values for most organotin (IV) compounds fall within the approximate range of -0.50 mm/sec to + 2.70 mm/sec.

If the tin atom has a perfectly spherical symmetry (Me_4Sn, for example), then only a single line is observed in the ^{119m}Sn Mössbauer spectra. However, any deviation of the ^{119}Sn nuclear charge from spherical symmetry results in a two-line quadrupole-splitting in the spectrum and ΔE_Q is the separation between the two peaks in mm/sec. The principal cause of any asymmetry in the ^{119}Sn nucleur charge is an imbalance in the tin atom's 5p valence electrons, which in turn is affected mainly by the spatial arrangements of the organic groups about the metal atom. For regular tetrahedral R_3SnX and R_2SnX_2 compounds ΔE_Q falls within the range 1.00-2.40 mm/sec. Five coordinate triorganotin compounds R_3SnX_2 may have various ΔE_Q values depending on the stereochemistry. For the trans- structure  , if both axial Sn-X bond lengths are equal, as in Me_3SnOH which consists of chains of planar Me_3Sn groups linked symmetrically by bridging X radicals, ΔE_Q is close to 3.00 mm/sec. However, an increasing difference between the two axial Sn-X bond lengths causes a movement of ΔE_Q towards 4.00 mm/sec[89]. The cis-isomers of R_3SnX_2 give ΔE_Q values in the range 1.70-2.40 mm/sec while the trans-mer form  is expected to have values in the range 3.50-4.10 mm/sec[89]. Octahedral R_3SnX_3 compounds have ΔE_Q values from 0.00 mm/sec to $\sim$ 3.50 mm/sec depending on cis- or trans-stereochemistry. Diorganotin compounds of the type of R_2SnX_4 have ΔE_Q values $\sim$ 4.00 mm/sec and $\sim$ 2.00 mm/sec for trans- and cis-isomers respectively[89]. The ΔE_Q values increase smoothly with increasing C-Sn-C angle for octahedral diorganotin complexes, for example, $Me_2Sn(OX)_2$ 2.02 mm/sec (C-Sn-C = 110.7°) and $Me_2Sn(acac)_2$ 4.02 mm/sec (C-Sn-C = 180°).

Herber et al[90] have argued that so long as the range of bond ionicities in a series of compounds is not too large, the ratio of quadrupole splitting to isomer shift ($\rho = \Delta E_Q/\delta$) can be used to distinguish between compounds in which the tin atom is penta-coordinate and those in which it is tetra- coordinate. They suggest that (with δ relative to SnO_2), a value of $\rho > 2.1$ is evidence of penta- coordination about the tin atom, whereas if $\rho < 1.8$, the tin atom is tetra- coordinate.

It is therefore obvious from the foregoing discussions that ^{119m}Sn Mössbauer spectroscopy provides a very effective tool for elucidating the structural varieties exhibited by organotin carboxylates. The two main types, e.g., the intermolecularly carboxyl bridged polymeric molecules with penta- coordinate tin atom and the normal ester type tetra- coordinate species can be easily distinguished from the δ and ΔE_Q values as shown in Table - 5. The data in Table - 5 have been collected from references[2,12,18,87,88,92]. Effect of electronegative substituents attached to the carboxyl residue on the density of S-electrons at the tin nucleus and on the Sn-C bond ionicities have also been elucidated from the Mössbauer parameters[12,88,95].

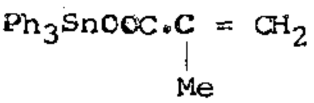
Table - 5

^{119m}Sn Mössbauer parameters of some organotin carboxylates.

Compound	δ mm/sec	ΔE_Q mm/sec	Structure in solid state
1. (Neophyl)$_3$SnOOCMe	1.35	2.45	Monomer
2. Bu$_2$Sn(OOCMe)$_2$	1.40	3.45	Polymer
3. Bu$_2$Sn(OCC.C$_7$H$_{15}$)$_2$	1.45	3.50	"
4. Bu$_2$Sn(OOC.C$_{17}$H$_{35}$)$_2$	1.45	3.30	"
5. Bu$_2$Sn(OOC.CH$_2$Cl)$_2$	1.60	3.65	"
6. Bu$_2$Sn(OOC.CCl$_3$)$_2$	1.65	3.80	"
7. Me$_3$SnOOC.CH$_3$	1.35	3.68	"
8. Me$_3$SnOOC.CCl$_3$	1.44	4.15	"
9. Me$_3$SnOOC.CF$_3$	1.38	4.22	"

Contd..

Table - 5 (Contd..)

Compound	δ mm/sec	ΔE_Q mm/sec	Structure in solid state
10. $Bu_3SnOOC.CH_3$	1.46	3.64	Polymer
11. $Ph_3SnOOCH$	1.37	3.58	"
12. $Ph_3SnOOCMe$	1.27	3.40	"
13. $Ph_3SnOOCEt$	1.33	3.42	"
14.  $Ph_3SnOOC.\underset{\displaystyle Me}{\underset{\vert}{C}} = CH_2$	1.21	2.26	Monomer
15. $Ph_3SnOOCH(Et)Bu$	1.21	2.26	"
16. $Ph_3SnOOCCMe_3$	1.21	2.40	"
17. $Ph_3SnOOC.CCl_3$	1.30	2.97	"

Besides the carboxylates mentioned in Table 5, there are also ^{119m}Sn Mössbauer investigations by Harrison et al[92] on the organotin complexes of arylazobenzoic acids prepared by Majee and co-workers[93,94].

III. X-ray Crystallography:

Single crystal X-ray crystallography has demonstrated chain polymeric involving bridging carboxylate groups and planar or near planar R_3Sn moieties (VA), structures for $Me_3SnOOC.Me$,

$Me_3SnOOC.CF_3$, $Me_3SnOOCH$, $(C_6H_5CH_2)_3SnOOC.Me$ and $(CH_2 = CH)_3SnOOCCCl_3$.[98] Trimethyltin glycinate $Me_3SnOOC.CH_2NH_2$ also has a polymeric chain structure but bridging occurs via the NH_2 groups[98]. Although tricyclohexyltin acetate was earlier shown to contain discreet monomeric molecules, recent more refined XRD analysis has revealed this compound and the tricyclohexyltin trifluoroacetate to be one-**dimensional** chain polymers involving, however, weakly Syn, anti-bridging carboxylato groups[92]. The first example of a truly monomeric carboxylate as demonstrated by X-ray crystallography is the compound triphenyltin ortho-(2-hydroxy-5-methyl-phenylazo) benzoate[92].

No X-ray studies are yet available on any diorganotin dicarboxylates or monoorganotin tri- carboxylates[98].

IV. ^{119}Sn NMR Spectroscopy:

Comparatively recently, ^{119}Sn NMR spectroscopy has emerged as yet another important physical method for characterisation of organotin carboxylates[86,87,88].

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