CHAPTER 1

A brief review of Organotin Carboxylates

1.1. Introduction:

Organotin compounds are defined as those that contain at least one Sn–C bond, the carbon atom being part of an organic group. The ground state for tin is a ^3P state, derived from S^2P^2 configuration[1]. In this state, there are only two unpaired electrons and a covalence of two would be expected. But the tetracovalent occurs much more frequently than divalent state. The four-covalent state is derived from the SP^3 ^5S state of the atom, which is not the ground state but the first excited state. While tin(II) compounds are mostly bent, pyramidal or otherwise distorted (due to the presence of an electron pair that does not participate in bonding and displays stereochemical activity), tin (IV) compounds adopt regular geometries as tetrahedra, bipyramides or octahedra, depending on the coordination number. The electronegativity of tin change with its oxidation number. Tin (II) compounds are more ionic than the corresponding tin (IV) derivatives[2]. The marked increase in stability of R_4Sn compounds over R_2Sn types demonstrates the effect of increased hybridisation. Thus, the organic chemistry of tin is essentially restricted to the +4 oxidation state[3].

The Tin-Carbon bond should be polar since Tin is electro positive with respect to carbon as represented by $\overset{\delta-}{C} - \overset{\delta+}{Sn}$. But the polarity is so low as in the tetra alkyl and aryl derivatives of tin that these are not actually hydrolysed by water. A rather unusual feature of the organotin compounds is the ionisation of some of the R_3SnX and R_2SnX_2 compounds in water[4].

A bond between M-C, where M is carbon, there is possibility of forming double bond ($p\pi - p\pi$). When M substitutes other element of Group IVA of the Periodic Table, such as silicon, germanium, tin or lead, there is enough evidence that the d orbitals of these elements are used for bonding ($d\pi - p\pi$). A simple example illustrates this phenomenon. With the four acids of the type p-$R_3M.C_6H_4.COOH$, where M represents carbon, silicon, germanium or tin, carbon is the most electronegative and should enhance the acid strength to the greatest extent. Actually the carbon compound shows the lowest acid strength, indicating that $d\pi - p\pi$ bonding is operative in the other three compounds[5,6]. It seems that the tendency to use d orbitals in bonding decreases from Si to Sn, since in $(GeH_3)_2S$ and $(GeH_3)_2O$, the Ge-S-Ge and Ge-O-Ge appear to be highly bent[7] whereas in $(SiH_3)_2O$ the Si-O-Si angle is around 150°[8]. However, the possibility of $d\pi - p\pi$ bonding in tin cannot be completely ignored, at least with elements of higher atomic numbers e.g., Cl, Br, I etc. In fact, $d\pi - p\pi$ bonding is partly responsible for higher values of Sn-Cl stretching frequency in certain tin compounds[9] and Sn-O frequency in $(Ph_3Sn)_2O$[10].

The first chemist to report the existence of "Organic bodies of tin", as they were then known, seems to have been E. Frankland[11,12]. But his work remained unknown to most of his contemporaries as well as to later authors. The work of Carl Lowing[13] in 1852 has usually been considered to represent the beginning of organotin chemistry. The search to isolate a series of dialkyltin (R_2Sn) compounds in the second half of the 19th century was destined to be unsuccessful could only be established by experiment, and in the course of experimental studies of this point, there were a number of erroneous reports[14,15]. The isolation of diethyltin and diphenyltin are now known to be polymers of tin (IV), that is, $(Et_2Sn)_2$ and $(Ph_2Sn)_2$[16].

In 1879, Frankland[17] studied the reaction between stannous chloride and diethyl zinc, hoping by analogy with results obtained by Buckton[18] simply to displace the chlorides with ethyl groups. The product, however was not Et_2Sn, but Et_4Sn. As a route to Et_4Sn, this reaction proved superior to Buckton's original method[18], which used $SnCl_4$. This new reaction remained the method of choice for preparing tetraalkyltins until the early years of the 20th century, when Pope and Peachey[19] first made use of the action of a Grignard reagent on $SnCl_4$. The early history of organotin chemistry has been recently reviewed by N.W. Nicholson[20].

The first review of organotin compounds was achieved in 1937 by Krause and Van Grosse[21]. Ingham, Rosenberg and Gilman[22] extended the literature upto 1959. Weiss[23] compiled an exhaustive list of organotin compounds covering the literature from 1937 to 1964. Afterwords, several monographs by J.J. Zuckerman (Ed)[24], by Newmann[16] and by Poller[25], and a multi-author work edited by A.K. Sawyer[26] were published in 1970-1972 and Davies and Smith in 1980[27] and 1982[28]. Structural aspects of this class of compounds have been reviewed[29] and a comprehensive bibliography of X-ray deffraction studies is available from the International Tin Research Institute[30]. Properties, preparations and applications of the monoalkyltin compounds have been reviewed by Guo, Yushen in 1991[30a].

The basic studies in the field of organotin compounds have been developed due to the success of a large number of modern techniques applied to the organotin compounds. Investigations can be performed by the general techniques such as UV[25], IR[25,31], ^{1}H-NMR[25,32], ^{13}C-NMR[33], Mass Spectroscopy[34] and also by the specialised techniques of ^{119m}Sn Mossbauer Spectroscopy[25,28] and ^{119}Sn NMR[28,35] spectrometry. Because of diverse applications in industry and in basic research, the chemistry of organotin compounds has gained considerable importance[28,36].

1.2. Organotin Carboxylates:

In the even expanding field of Organotin Chemistry, Organotin Carboxylates comprise one of the most important class of compounds. Apart from the theoretical and structural interests, organotin carboxylates are finding tremendous importance in industry and agriculture. New applications are likely to emerge in the near future.

The compounds containing — OCOR' groups bonded to tin are defined as organotin esters which may be either monomeric or polymeric and 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. Many discussions with varying degrees of details are available on these compounds[16,25,26,37] and as such only the more important aspects will be presented here.

1.2.1. Preparative Methods:

Among the preparative methods employed for the synthesis of organotin carboxylates, the oldest and the most general procedure is the reaction of organotin oxides (or hydroxides) and carboxylic acids or their anhydrides[38,39,40].

$$R_3Sn - O - SnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O \qquad \ldots (1)$$

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

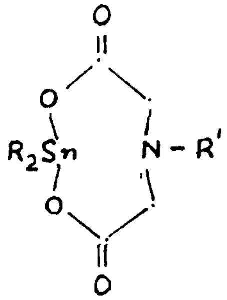
$$R_3Sn{-}O{-}SnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR' \qquad \ldots (3)$$

A Dean-Stark apparatus is used to azeotropically distil out the water formed during the reactions (equations (1) & (2)). Alternatively, the reactants are heated in neat mixture until the evolution of water ceased, e.g.[41].

$$(Bu_3Sn)_2O + 2{-}O{-}HO{-}C_6H_4{-}COOH \xrightarrow[\text{Neat mixture}]{100{-}110^{\circ}C} 2{-}O{-}OH{-}C_6H_4COOSnBu_3 + H_2O \qquad \ldots . (4)$$

Diorganotin (IV) derivatives of bis(Carboxymethyl)amine and its N-Me derivative may be prepared by the condensation of R_2SnO and $R'N(CH_2COOH)_2$, where R = Bu, Octyl, CH_2Ph; R' = H, Me[42,42a].

$$R_2SnO + (HOOCCH_2)_2NR' \longrightarrow$$

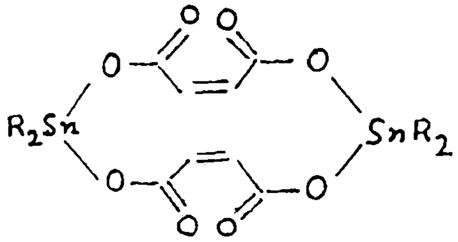


One of the convenient methods is the reaction between metal salts of carboxylic acids and organotin halides[43,44,45], or silver salts of carboxylic acids and organotin sulfides[46].

$$R_{4-n}SnX_n + xM(OCOR')_y \longrightarrow R_{4-n}Sn(OCOR')_n + xMXy$$

$$R_2SnS + 2Ag(OCOR') \longrightarrow R_2Sn(OCOR')_2 + Ag_2S.$$

In a refluxing polar organic solvent R_2SnS (R = Bu, octyl) reacts with Cu, Hg or Pb maleate to give the following dimeric compound[47]:



The reaction of $(Bu_2SnX)_2O$ (X = Cl, Br) with Li and subsequent alkylation with RX' (R = Me, Bu; X' = Br, iodo) and Ac_2O gives RBu_2Sn OAc, an organotin carboxylate with different alkyls[48].

Tagliavini et al[49] have given a novel method of preparation of trialkyltin carboxylates by electrochemical method using the cleavage of organic groups from R_4Sn (R = Me, Et, Pr, Bu) and Hg(I) carboxylates. At room temperature tetramethyltin produces trimethyl tin acetate when treated with Hg(I) acetate in MeOH.

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

Organotin carboxylates are prepared by the cleavage of one or more organic groups of tetraorganotin compounds by carboxylic acids[50,51].

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

The cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on temperature[52,53]. Vinyl groups are cleaned more readily than saturated alkyl radicals, but less readily than phenyl[22] and successive groups are lost with increasing difficulty. Tetralkyltin is more reactive than tetravinyltin[51].

Triorganostannate esters of dicarboxylic acids can be prepared by the reaction of triorganotin hydroxide with dicyclohexylammonium salt of the dicarboxylic acid[54]. Thus Ph_3SnOH reacts with dicyclohexyl ammonium oxalate (M^+ oxalate) to give $M^+ [(C_6H_5)_3SnOC(O)C(O)O]^-$.

Organotin halocarboxylate, $R_2Sn(X)OCOR'$, may conveniently be prepared by heating equimolecular mixture of the diorganotin dihalide and diorganotin dicarboxylates in an inert solvent[55].

$$Bu_2SnBr_2 + Bu_2Sn(COMe)_2 \longrightarrow 2Bu_2Sn(Br)OCOMe.$$

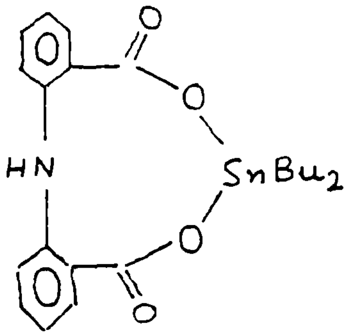
C. Deb and B. Basu have showed that alkyl or aryl esters (carboxyl group attached to primary or tertiary carbon atom) may be transesterified to triorganotin carboxylates[56].

$$R'-COOR'' + (R_3Sn)_2O \longrightarrow R'-COOSnR_3 + R''OSnR_3.$$

Organotin tricarboxylates, $RSn(OCOR')_3$ are usually prepared from the corresponding organotin trichloride by the action of silver salts of carboxylic acids[43].

$$RSnCl_3 + 3R'COOAg \longrightarrow RSn(OCOR')_3 + 3\ AgCl.$$

Willem et al[57] have prepared a number of compounds of the type $Bu_2Sn(O\text{-}X\text{-}Y\text{-}O)$ by the cyclocondensation of Bu_2SnO with the corresponding dihydroxyl organic compound, e.g.,



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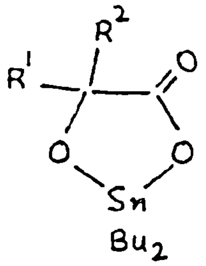


($R' = Me$, $R^2 = Me, H$;
$R' = H$, $R^2 = Ph$).

Reaction between R_2SnO and tri-methyl acetic acid in 1/1 stoichiometry gives $\{[R_2Sn(O_2CCMe_3)]_2\ O\}_2$ (R = Me, Et, Pr, Bu), which adopt the dicarboxylatotetraorganodistannoxane structure[58].

Holmes et al[58a] prepared oxocarbxoylate tin lader clusters, $[BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6 \cdot 3C_6H_6$ and $[MeSn(O)O_2CC_6H_{11}]_2MeSn(O_2CC_6H_{11})_3]_2$ were prepared from the stannoic acid and carboxylic acids.

1.2.2. Physical Properties of Organotin Carboxylates:

Many of the carboxylates have low melting points which indicates that these are covalent compounds. The carboxylates with small organic groups are more soluble in alcohol, ether etc than in water[16] because the Sn-O bond is essentially covalent. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric associated structure.

The melting (or boiling) points of some common organotin carboxylates are listed in Table - 1[16,25,26,43,59,60].

Table - 1

Compound	M.P. (°C)	B.P. (°C/mm Hg)
1. $R_3SnOCOR'$		
$Ph_3SnOCOPh$	84-85.5	
$Ph_3SnOCOH$	202-203	
$Cy_3SnOCOMe$	62-63	
$Bu_3SnOCOMe$	85	
$Bu_3SnOCOPh$		166-168/1
$Me_3SnOCOMe$	196.5-197.5	
$Pr_3SnOCOCF_3$		88-90/1

Contd..

Table - 1 (Contd..)

Compound	M.P. (°C)	B.P. (°C/mm Hg)
2. $R_2Sn(OCOR')_2$		
$Ph_2Sn(OCOMe)_2$	116-117	
$Bu_2Sn(OCOCH = CHMe)_2$	34	
$Bu_2Sn(OCOMe)_2$		144.5-145.5/10
3. $R\ Sn(OCOR')_3$		
$BuSn(OCOCH_3)_3$		117-119/1
$EtSn(OCOPh)_3$		171-173/1
4. $R_2SnX(OCOR')$		
$Et_2SnCl(OCOMe)$	94	
$Bu_2SnBr(OCOMe)$	67-68.5	

1.2.3. Chemical Properties of Organotin Carboxylates:

The Sn-C bond is covalent in nature due to small electromegativity difference between Sn and C. However, Sn-C bond can readily participate in ionic reactions through polarisation, where the carbon atom acts as a nucleophile and the tin atom as an electrophilic centre. On the other hand, the bonds between tin and heteroatoms (Sn-X, where X = O, N, halogen, etc.) are thermodynamically stable but are chemically highly labile and readily participate in substitution reactions. The large size of the tin atom (covalent radius $1.4A^{o}$), the greater polarisability of the Sn-X bond relative to that of C-X bond and the possible participation of the tin 3d orbitals spear to be the major factors responsible for the greater ease of substitution reaction at tin than at carbon[61].

Thermal decarboxylation of triorganotin esters[31] may be utilised in the preparation of unsymmetrical tetraorganotin compounds of the type $R'SnR_3$, where the R-Sn bond formation takes place. However, trialkyltin formate leads to the formation of trialkyl tin hydride[62].

$$R_3SnOCOH \xrightarrow[(R=Bu,\ Pr)]{100\text{-}170^{o}C} R_3SnH + CO_2$$

Trialkyltin carboxylates of unsaturated acids give trialkylalkynyltins on decarboxylation

$$Bu_3SnOCOC \equiv CPh \xrightarrow{60^{o}C} Bu_3SnC \equiv CPh + CO_2$$ [62]

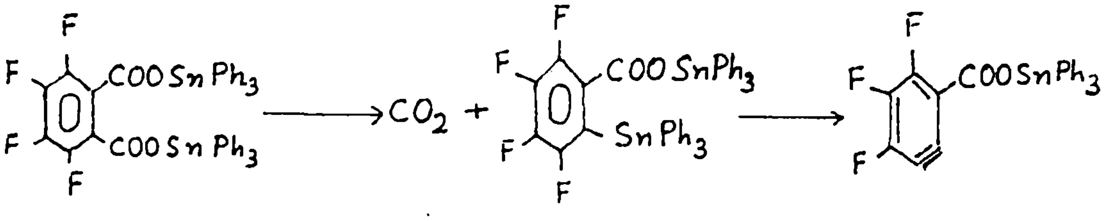
$$R_3SnOCOC \equiv COOSnR_3 \xrightarrow[(R=Bu,Pr,\ Et)]{160^{o}C} R_3SnC \equiv CSnR_3 + 2CO_2$$ [63]

Deacon and Farquharson[64], in 1977 prepared several polyfluoro phenyl stannanes utilising this thermal decarboxylation in boiling pyridine.

$$RCOOSnPh_3 \xrightarrow[\text{(boiling)}]{\text{Pyridine}} R\text{-}SnPh_3 + CO_2$$

$(R=C_6F_5,\ p\text{-}MeO.C_6F_4,\ p\text{-}EtOC_6F_4 \text{ or } o\text{-}HC_6F_4)$

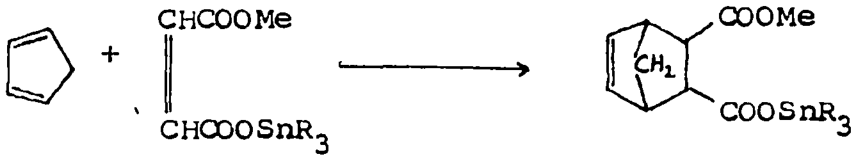
They also reported that thermal decomposition of bis(triphenyltin) tetrafluorophthalate gave a high melting solid, Ph_3SnF, identified by IR spectroscopy[65]. A possible mechanism comprising hemidecarboxylation[66] followed by elimination of the fluorine ortho to the bulky triphenyltin substituent[67], was proposed.



(X)

However the aryne (X) was not isolated or characterised.

Unsaturated organotin carboxylate also undergoes Diels-Alder type reactions with dienes[68,69].



(R = Ph, Bu)

Mixed organotin carboxylates can be formed by redistribution of organotin carboxylates with other organotin compounds[26,70,71].

$$Bu_3SnOCOC_5H_4N\text{-}2 + RSnCl_3 \xrightarrow{MeOH}$$

$$RSn(OCOC_5H_4N\text{-}2)Cl_2 + Bu_3SnCl$$

(R = Ph, Bu)

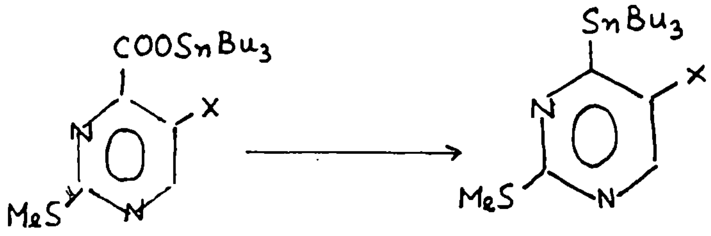
$$R_2Sn(OCOR')_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR')X$$

(X = hal., OR, H, etc.)

Van der Kerk and Luijten[72] prepared triphenyl cyanomethyltin by heating triphenyltin cyanoacetate under vacuum.

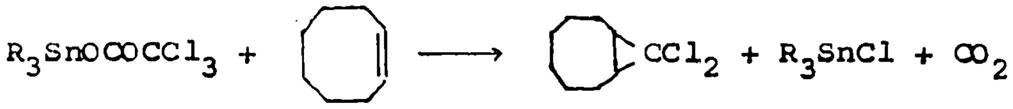
$$Ph_3SnOCOCH_2CN \xrightarrow{140\text{-}15^{o}C} Ph_3SnCH_2CN + CO_2$$

The decarboxylation can be catalysed by Pd(II) complex and then better yields are obtained[73], e.g. thermal decarboxylation of the 2-methyltio derivatives in refluxing anisole gave the 4-stannylated products in only 30-40% yield whereas use of bis(acetonitrile) and bis(triphenyl phosphine) palladium(II) dichloride increased the yield of 4-stannylated product upto 70% after refluxing in anisole.



(X = Cl, Br)

Seyferth and his associates[74] found that by heating, organotin esters of trichloro acetic acid were able to transfer dichloro carbene which reacted with unsaturated substrates

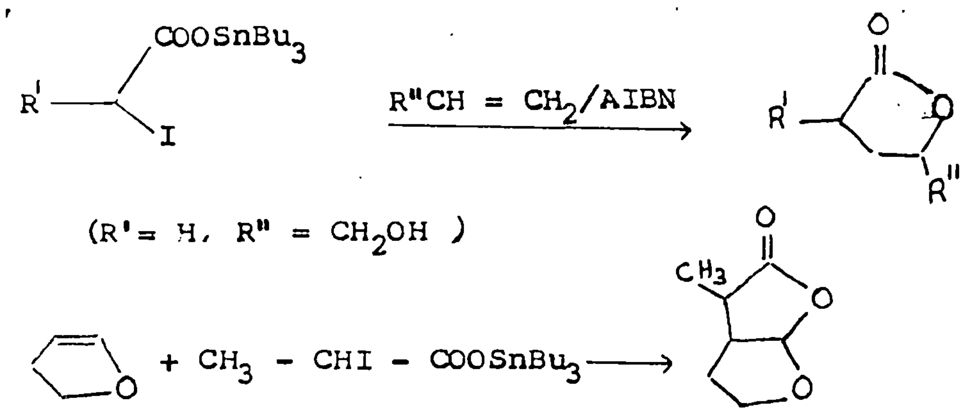


(R = Me, Ph)

A state of equilibrium is established with thiols and the reaction can be carried out in forward direction by removing the organic acid from the mixture[75].

$$R_3SnOCOR' + R^2SH \rightleftharpoons R_3SnSR^2 + R'COOH$$

α-iodo triorganotin carboxylates react with electron-rich alkenes in the presence of radical initiator to produce γ-lactone. AIBN was found to be more effective and convenient than any other initiation procedure[76].



The authors proposed the generation of a radical which then added to the alken before cyclisation, with simultaneous elimination of the tributyl-stannyl radical. This reaction proved to be of high synthetic value.

Recently, the copolymerisation of functional and alkyl methacrylates with tributyl tin methacrylates have been described by Babu et al[77]. They showed that the presence of functional units in the copolymers can be utilised to selectively cross-link the polymers so that the rate of release of tin moiety can be controlled which is believed to have played a role in biocidal properties.

Complex formation by esters is less extensive than by organotin halides due to weaker acidity of organotin esters which may be related to the lower electron-withdrawing power of OCOR group compared to Cl atom[78]. The presence of electron-withdrawing groups attached to the tin and/or carboxylate moiety will favour complex formation, e.g. $Ph_3SnOCOCCl_3.MeOH$[79,79a],

$(CH_2 = CH_2)_2Sn(OCOCF_3)_2$. bipy[80], $Me_3SnOCOC_5H_4N$-2.H_2O[81] and $Sn_4Ph_8(O_2CCCl_3)_6(OH)_2$[79a] which is a novel linear chain connected by hydroxy and acetate bridges.

$Et_2Sn(OAc)Cl$ reacts with $RC \equiv CH$ to give $RC \equiv CSnEt_2OAc$ in 53 to 84% yields ($R = Ph, Bu, Me_3Si$)[84a]

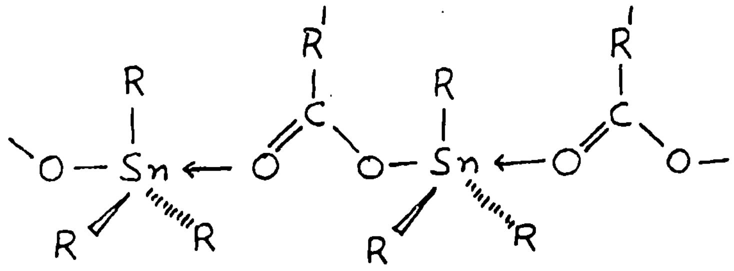
$$PhC \equiv CH + Et_2Sn(OAc)Cl \longrightarrow PhC \equiv CSnEt_2OAc \ .$$

1.2.4. Structure of Organotin Carboxylates:

The structure of organotin esters are studied by IR, NMR and Mössbauer spectroscopy and by X-ray crystallography. Tin possesses, two spin of one half isotopes, ^{117}Sn and ^{119}Sn which become important in NMR studies. Tin has stable isotopes, which allow the easy identification of the tin-bearing fragments in the mass spectrometer. Mössbauer resonance from the ^{119}Sn nucleide can be easily recorded. Further tin-carbon stretching frequencies in the IR and Raman spectra can be assigned in most cases.

A vast literature on the structure of organotin carboxylates were covered in the review written by Davies et al[28] and on ^{119}Sn-NMR spectroscopy by P.J.Smith and A.P. Tupcianskas[35a] and by B. Wrackmeyer[35b]. The subject has also been discussed and reviewed by R.C. Poller[25], R. Okawara and M. Wada[26,37].

In the absence of hindered groups, organotin carboxylates exist in polymeric associated form in the solid phase.

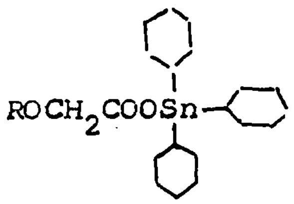


This chain polymer, involving bridging carboxylate groups and planar or near planar R_3Sn moieties, has been demonstrated crystallographically, e.g., for $Me_3SnOCOMe$[82], $MeSnOCOCF_3$[82] $(CH_2 = CH)_3SnOCOCH_3$[83] and $Bz_3SnOCOMe$[84].

V.G. Kumar Das and his coworkers[85] analysed X-ray data for a number of polymeric triorganotin carboxylates which gave a repeat distance of 5.19 ± 0.21 A° for the carboxylate-bridged R_3SnO_2CR' unit that defines the crystal lattice. The repeat distance is sensitive to the organic substituents on either the tin or carboxylate group.

Sterically hindered groups, prevent the association. $Cy_3SnOCOMe$ is present as monomer with the Sn atom occupying a distorted tetrahedral geometry[86].

Q. Xie and J. Zheng[87] in 1991 showed by IR, ^1H-NMR and ^{13}C-NMR studies that compounds of the type:

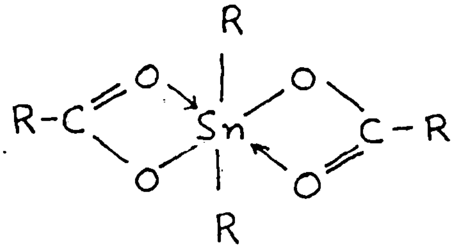


(R = Ph, substituted Ph)

adopt a distorted tetrahedron containing four coordinated Sn atom.

The structural aspects of triorganotin carboxylates in the solid state and in solution phase have been investigated by several workers[88a,88b,88c] by IR and far-IR spectroscopy. Conclusion was that upon dilution of the associated triorganotin esters in organic solvents usually produces oligomeric and finally monomeric species containing tetrahedral tin atom and free ester carbonyl functionality[88a,88b,88c,89].

Dialkyltin dicarboxylates were suggested to be monomeric with hexa coordinate tin[90].



N.W. Alcock and S.M. Roe[79a] established the structure of some phenyltin trichloroacetate complexes by X-ray crystallography. The complex $SnPh_3(O_2CCCl_3)(MeOH)$ is a five-coordinate monomer. Two isomers of $\{[SnPh_2(O_2CCCl_3)]_2O\}_2$ are centrosymmetric dimers with all their carboxylate groups bridging and with half of them unidentate respectively. The complex $Sn_6Ph_6(O_2CCCl_3)_{10}O_4 \cdot 2C_6H_6$ is a linear hexatin compound containing three $(Sn-O)_2$ stannoxane rings. The hexatin compound $[SnPh(O_2CCCl_3)_3]_6 \cdot 3C_6H_6$ has a drum structure. The complex $Sn_4Ph_8(O_2CCCl_3)_6(OH)_2$ is a linear chain connected by hydroxy and acetate bridges.

E.R.T. Tiekink and his coworkers[58] established by X-ray crystallography, that the compounds, $\{[R_2Sn(O_2CCMe_3)]_2O\}_2$ (R = Me, Et, Pr, Bu), adopt the dicarbxoylate tetraorganodistannoxane structure.

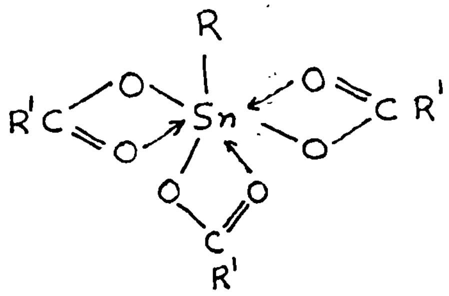
Attempts have been made to correlate tin-proton coupling constants with the structures of organotin esters and it is now generally accepted that the values of $J(^{119}Sn-C-H)$ increase with increasing percent S-character of the Sn-C bond.

^{13}C-NMR spectroscopy has certain advantages over ^{1}H-NMR in the elucidation of structure of organotin carboxylates[92]. For example (i) the differences in the coupling constant $^{1}J(C-Sn)$ are much greater than those in $^{2}J(H-Sn)$; (ii) since the carbon of the alkyl or aryl group is directly bonded to Sn, the variations in $^{1}J(C-Sn)$ more accurately reflect rehybridisation at the tin atom than do those in $^{2}J(H-Sn)$; (iii) for alkyl groups like propyl, butyl etc., it is possible to measure

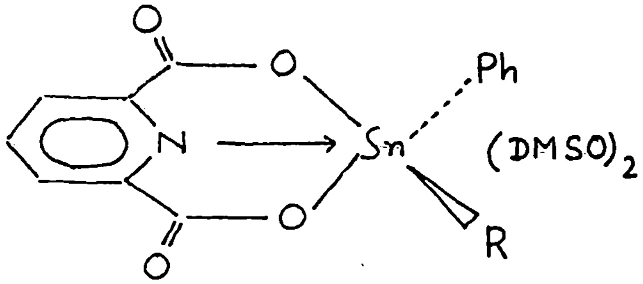
${}^{1}J$(C-Sn) accurately where ${}^{2}J$(H-Sn) can not be measured under normal conditions; (iv) for such long-chain alkyl groups the identity of the compound and within limits, its purity can be established undoubtedly.

K.C. Molloy[93] in his study of solid state ^{119}Sn-NMR of organotin carboxylates found that compounds which undergo auto-association in the solid to yield coordination polymers should be identified by an upfield chemical shift in the solid and a lower field shift in solution. Both Ph_3SnO_2CMe and Ph_3SnO_2C-$C_6H_4N_2$-2 meet these structural criteria.

The IR spectra of a number of monoorganotin tricarboxylates in CCl_4 show coordinated carbonyl stretching band, and additionally, $BuSn(OOCMe)_3$ and $BuSn(OOCEt)_3$ were found to be monomeric in camphor solution[43]. This is indicative of a 7-coordinated tin atom geometry for these compounds.



The ^{1}H-NMR spectra in the pyridine proton region of 2,6-pyridine dicarboxylato(phenyl)(organo)tin compounds of the type:



(R = Me, Pr, $CHMe_2$, Bu, CMe_3, $PhCH_2$)

in DMSO-d_6 solutions exhibit a pattern that, together with ^{13}C coupling data and ^{119}Sn chemical shifts, can be interpreted by a hepta coordinated pentagonal bipyramidal structure in which the Sn atom likely to be surrounded by two DMSO ligands in equatorial positions[94].

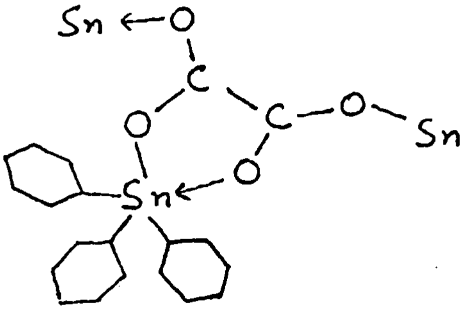
Handlir et al[95] investigated the structure of the compounds $Bu_2Sn[(O_2C)_2X]$ [X = $(CH_2)_n$ (n = 0-8), cis- and trans- CH :CH; O-, p-C_6H_4] by IR and ^{13}C-, ^{17}O-& ^{119}Sn-NMR spectroscopy and camaup to the conclusion that the crystalline compounds are formed as linear or cyclic oligomers composed of the central tin atom substituted by two Bu groups and coordinated with both oxygen atoms of two amiso bidentate carboxylic groups derived from different molecules of a dicarboxylic acid.

Holmes et al[58a] reported a new structural class of organotin compounds, the oxo carboxylate tin ladder clusters, e.g. (I) $[\mathrm{BuSn(O)O_2CC_6H_4NO_2\text{-}2}]_6\cdot 3\mathrm{C_6H_6}$, (II) $[\mathrm{MeSn(O)O_2CC_6H_{11}}]_2\ \mathrm{MeSn(O_2CC_6H_{11})_3}]_2$ and (III) $[\mathrm{BuSn(O)O_2CR}]_2\mathrm{BuSn(O_2CR)_3}]$ (R = Ph, Me). X-ray analysis showed that II and III have unfolded drum or ladder structure and that I has a drum structure. ^{119}Sn-NMR data showed that the drum and ladder structure interconvert reversibly.

In 1990, J. Li and coworkers[96] studied the ^{13}C- and ^{119}Sn-NMR spectra of some tricyclohexyl tin (IV) carboxylates and showed that the chemical shifts ($\delta\,^{119}$Sn) and the coupling constants ^1J (^{13}C, ^{119}Sn) depend markedly on the coordination number of the Sn atom. The chemical shifts and coupling constants ^1J (^{13}C, ^{119}Sn) for aliphatic tricyclohexyltin (IV) carboxylates are in the range 6-11 ppm and 341-345 Hz, and for aromatic tricyclohexyltin (IV) carboxylate, the range is 10 to 40 ppm and 310-340 Hz, which provide evidence that the compounds are monomeric species in solution irrespective of their structure in the solid state.

Recently Thomas C.W. Mak and his coworkers[121] obtained μ-oxalato bis(tricyclohexyltin), μ-$(\mathrm{O_2CCO_2})[(\mathrm{C_6H_{11}})_3\mathrm{Sn}]_2$ in the attempt to prepare $[(\mathrm{CH_3})_4\mathrm{N}]^+[(\mathrm{C_6H_{11}})_3\mathrm{SnO_2CCO_2}]^-$ by the reaction of $[(\mathrm{CH_3})_4\mathrm{N}]\mathrm{Cl}$, $(\mathrm{C_6H_{11}})_3\mathrm{SnCl}$ and $\mathrm{Ag_2O_2CCO_2}$ in methanol. The X-ray diffraction study of the compound revealed the presence of two symmetry-independent molecules, each of which contains a pair of tin atoms in an isomeric cis-, trans- $\mathrm{C_3SnO_2}$

trigonal bipyramidal configuration arising from the quadridentate (chelating and bridging) behavior of the oxalato ligand.



1.2.5. Biological properties of organotin carboxylates:

With the possible exception of organomercurials, organotin compounds have received more attention for their biological effects than organic compounds of any other metal. The inorganic tin compounds hardly have any biological activity whereas organotin compounds exhibit high biocidal activity, probably due to their lipid solubility, which facilitates better transport to the reaction sites than the corresponding inorganic tin compounds.

Due to their high mammalian and phytotoxicities, a number of present applications of organomercurials may be partly taken over by highly effective but relatively non toxic organotin preparations in near future[97].

The systematic studies of biological activities of organotins were initiated in 1950 by the pioneering work of the TNO group[98].

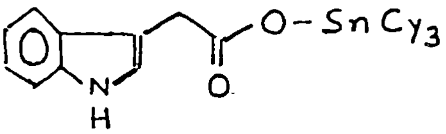
Van der Kerk and Luijten[99] in 1954 published that many organotin derivatives having the general formula of R_3SnX are powerful fungicides. Within any R_3SnX series, the activity is markedly dependent upon the nature of the organic group (R) but relatively independent of the anionic radial X[100]. For a high anti fungal activity the total number of carbon atoms in the alkyl groups of a trialkyltin compound should be about 9-12[100a]. The toxicity of tin compounds were reviewed in 1959[101] and 1964[102].

The following table[119] will show a considerable influence of the length of the alkyl groups.

Anti fungal Activity of some Triorganotin Acetates:

Compounds	Minimal concentration in mg/l causing complete inhibition of growth of the fungi		
$R_3SnOCOCH_3$ R =	Botrytis allii	Penicillium italicum	Aspergillus niger
CH_3	200	500	200
C_2H_5	1	10	2
n-C_3H_7	0.5	0.5	0.5
n-C_4H_9	0.5	0.5	1

K.C. Molloy and his coworkers[109] proposed that in order to obtain possible synergistic activity between an organotin and a ligand of complementary activity, the ligand should be C-bonded to tin, rather than through readily hydrolysable Sn-O, Sn-S or Sn-N (etc) bonds and reported the pesticidal, bactericidal and fungicidal activity of



Four coordinate tin monomers or five-coordinate tin polymers are often more active than chelated five coordinate tin species[116].

The principal advantages of the organotin agro chemicals (which mainly possess prophylactic action) are their relatively low phytotoxicity, their generally low toxicity[103,104] to non-target organism and the lack of resistance by crop pests to these chemicals. Furthermore, triorganotin compounds undergo degradation in the environment, eventually, to form harmless inorganic tin residues[105].

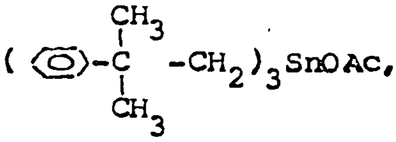
Inorganic tin compounds have no anti tumour activity although a number of organotin compounds with antitumour activity are known[106,107]. A possible mechanism suggested recently for the antitumour activity of the tin compounds is that the tin, whatever its form, is biochemically converted to the anticarcinogenic entities in the thymus and thus distributed around the body as anticarcinogen through lymph fluids[106]. The possibility of generation of some active free radicals causing interaction with DNA can not be ruled out.

In general organotin carboxylates show biocidal activity[117].

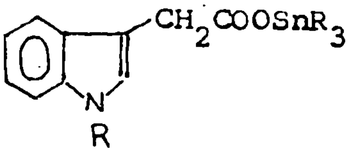
The toxicological and biological properties as manifested in the organotin carboxylates are summarised in Table-2[100,108].

Table - 2

Property	Compounds
1. Fungicidal	
a) Agricultural	$Ph_3SnOOC.CH_3$, $BuSn(OOC.CH_3)_3$
b) Horticultural	Bu_3SnOCO (Naphth)
2. Phytotoxicity	$Ph_3SnOCOCH_3$, $Ph_3SnOOC.C_6H_5$
3. Bacteriostatic	$Bu_3SnOCOCH_3$, $Ph_3SnOCOCH_3$ $Bu_3SnOCOC_6H_5$
4. Insecticidal	$R_3SnOCOCH_3$ (R = Me, Et, Bu, Ph) $Me_3SnOCO.CH_2Cl$ $Et_3SnOOC.C(Me) = CH_2$ $Pr_3SnOOC.C(Me) = CH_2$
5. Mammalian toxicity	$R_3SnOOC.CH_3$ (R=Me,Et,Pr, Bu, Ph)

The first commercial products were introduced during the early 1960's : triphenyltin acetate (fentin acetate : Brestan) by Hoechst and triphenyltin hydroxide (fentin hydroxide : Duter) by Philips Duphar. Both compounds are effective against almost the same range of fungi as the copper fungicides, but about one-tenth the dosage[114]. A promising anti spider compound, trisneophyltin acetate,  $(\bigcirc\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2)_3SnOAc$, is marketed by Shell[118].

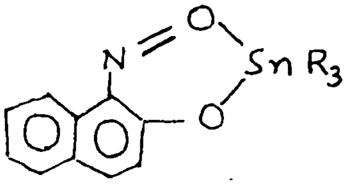
Recently, Molloy et al[109] showed that triorganotin indolylacetates of the type:



(R = Me, H, Cy)

possess fungicidal, bactericidal and insecticidal activity.

The compounds :

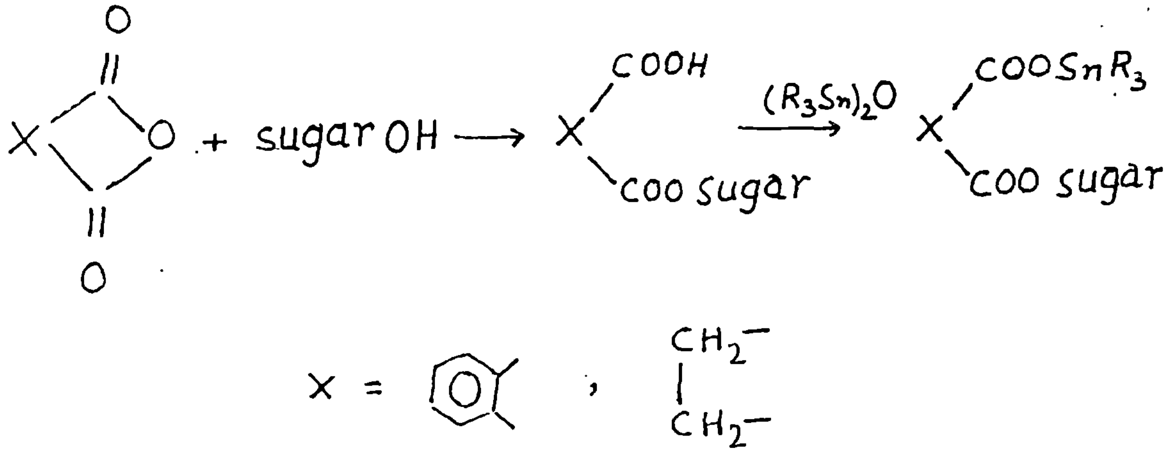


(where R = Bu, Ph, Cl) which contain Sn–O bond and a nitrogen atom in the molecule show an antibacterial activity comparable to or higher than that of streptomycin sulfates[110].

As many as thirty butyltin carboxylates were shown that they may be used as fungicides for fruit by Hu et al[111].

Organotin carboxylates having biological activity are being reported continuously[112,113]. Use of organotin compounds as fungicides have been comprehensively reviewed by Bock[115].

In a recent study, Poller et al[120] reported that direct phthalation and succinylation of sugars gave mono esters which were converted to stannyl sugar esters having enhanced biocidal properties:



The organotin compounds show a unique combination of chemical, physical and biological properties, and our understanding of their fundamental chemistry is now well advanced. The applications of these compounds, however, have still been relatively little explored and even less exploited. This is a field which would repay further study, and novel applications can confidently be expected.

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