INTRODUCTION

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During the last few decades organotin compounds have drawn wide attention of the chemists throughout the world and conspicuous achievements relating to their physical, chemical, structural and biocidal properties have already been obtained. The first organotin compound was reported by Frankland (1,2) in 1849, though he could not characterise it properly untill 1853. In 1852 Lowig (3) isolated an organotin compound by the reaction of sodium-tin alloy with ethyl iodide. These works put some new dimension in the field of organometallic chemistry and in later decades significant contributions in the field of organotin compounds were made.

A number of review articles in this area have been published. The first comprehensive review covering the literature upto 1935 was done by Krause and Von Grosse (4), Ingham, Rosenberg and Gilman (5) extended the literature work upto 1959. Weiss (6) compiled an exhaustive list of organotin compounds covering the literature from 1937 to 1964. From 1964, a literature of organotin chemistry is being published in annual surveys (7-16). The tin annual survey covering the year 1974 has been published (17). Another review of organotin derivatives of tin and lead with 464 references has been published by Harrison (18). Harrison published another review of organotin compounds in 1973 (19). Apart from these review articles, several books have recently been published (20-23).

Organotin compounds in recent years have been put into large scale commercial exploitation. In retrospect, the patents granted in 1940 and 1943 to V.Ungve (24) describing the utility of certain dialkyl tin derivatives as heat stabilizers for PVC, were a land mark, although their full industrial significance did not become apparent until 10 to 15 years later. In 1950, the annual industrial world production of organotin compounds was less than 50 tons. In 1960 it was 2000 tons, in 1965, 5000 tons, in 1970, 25,000 tons with a selling value of around 150 million dollars, may be a conservative estimate. The present estimate is about 30,000 tons.

The applications of organotin compounds are diverse in nature (25) and some of which may be indicated as follows:

Stabilization of P.V.C. by dialkyl tin and to a much lesser extent by mono alkyl tin compounds are currently used. In recent years ester tin compounds have shown a great promise in this field. The present trend in P.V.C. products has now been shifted from flexible to rigid products, the latter requiring much higher processing temperatures. There is a consensus that dialkyl tin compounds are the best general purpose stabilisers for rigid P.V.C. especially, if colourlessness and transparency are required.

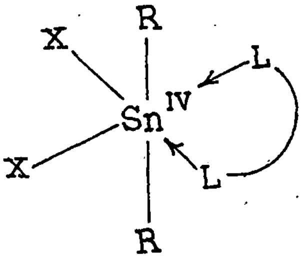
Triorgano tin compounds, particularly tributyl tin oxide (T.B.T.O.) are being used as commercial wood preservatives, paint preservatives, anti fouling agents, etc. A review of T.B.T.O. based wood preservatives has been given by Richardson (20).

Triphenyl tin compounds have been registered as fungicides in many countries, whereas tricyclohexyl and tris neophenyl tin compounds are being used as agricultural miticides. Agricultural applications of organotin pesticides are so far been restricted to a comparatively small, though very important, number of plant diseases and pests. On the basis of the more recent investigations on environmental pollution and also because tin compounds in several cases are fully active against resistant varieties, it may be expected to have a further growth of the uses of organotins in agriculture.

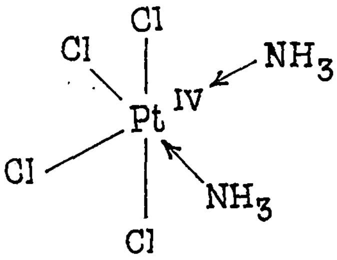
A number of small and quite diverse applications such as slime control in paper mills, water disinfection, molluscicide control, bacterial control, paint preservation etc. are also known (21c).

Tin compounds has been proved to be a successful catalyst in the commercial production of polyurethane. The world wide consumption of tin based catalysts for polyurethanes is about 2500 tons annually (27).

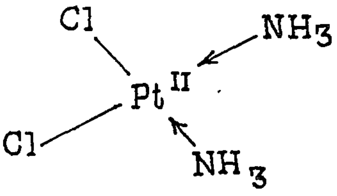
Organotin compounds have not previously been shown to have any significant antitumour properties. Recently, a series of organotin dihalide complexes, $R_2SnX_2.L_2$ (I), where R = Me, Et, n-Pr, n-Bu, Ph; X = Cl, Br, I, NCS; L = O- or N- donor ligand have been tested for antitumour activity (28). These compounds were modelled on the original active platinum compounds (29) Cis- $Pt(NH_3)_2Cl_4$ (II) and Cis- $Pt(NH_3)_2Cl_2$ (III).



I



II



III

The diorganotin complexes chosen for test, contain cis-halogen groups and certain of the compounds inhibit P388 leukemia in mice. The most encouraging results have been observed for diethyl tin complexes. 1,10-phenanthroline and 2,2' bipyridyl adducts exhibit anti-leukaemic activity towards the P388 tumour system.

Organotin pesticides that are in current use do not accumulate in soil with successive applications. They are degraded readily to non-toxic inorganic tin compounds within a short time (3-4 days). Hence they do not pose any significant problem for environmental pollution (29) and possibly therefore have been cleared as safe agricultural pesticides by World Health Organisation (30).

Tin, the element having atomic number 50, is a member of group IVA of the periodic table with an electronic configuration (31) $[Kr]\ 4d^{10}\ 5s^{2}\ 5p^{2}$ in the ground state. The common four co-valent state is derived from the sp^{3} hybridisation. The four co-valent state occurs far more frequently than the two co-valent state and the great majority of organotin compounds possess a four co-valent tin atom in simple compounds.

But when simple compounds react with ligands, due to availability of 4d orbitals, tin can very easily assume penta or hexa or even higher co-ordination. The existence of penta or hexa co-ordinated tin atom has been extensively observed with organo tin adducts and complex compounds.

Organotins can form a large number of complex compounds with suitable donor and chelating ligands. When the complexes are formed only through the donation of lone pair from the ligand to the organotin moieties, the stability of the compounds may vary greatly. On the other hand, the intramolecularly co-ordinated compounds are generally stable in nature.

Organotin Adducts

In recent years a large number of organotin adducts have been reported in the literatures. Organotin compounds which can act as Lewis acids react with certain electron pair donors, i.e., Lewis bases to form addition compounds. All the three types of organo (mono-, di- and tri-) tin compounds are known to form adducts with mono-, di- and polydentate ligands. The acceptor strength of organotin compounds depend upon many factors viz., the nature of the ligands, the organic groups, the substituents attached to tin etc. Thus the ability of organotin halides to form adducts increases in the order $R_3SnX < R_2SnX_2 < RSnX_3$ (32-33). For a series of Me_3SnX compounds, it is found that the acceptor strength is proportional to the electronegativity of the substituents bonded to tin (34). Thus the order of acceptor strength of Me_3SnX moiety is

$$F^- > Cl^- > Br^- > I^-$$

This fact can be easily explained because stronger the electron attracting power of the substituent, the less is the electron density around tin.

But the apparent acceptor strength also depends upon the nature of the donor group e.g., the stability of the donor-acceptor complexes with nitranilines.

Kumar Das (35) has prepared complexes of the type $R_3SnX.L$ (where R = Me, Ph; X = Cl, NO_3 and L = Hexamethyl phosphoric tri amide (HMPA), Dimethyl sulphoxide (DMSO), 1:10 phenthroline (phen) etc. 1:1 complex of HMPA with Ph_3SnX (X = Cl, Br, I, N_3, CN) have been prepared (36-37) by the general reaction.

$$Ph_3SnX + HMPA \xrightarrow[\text{or pet ether}]{\text{Chloroform}} Ph_3SnX.HMPA,$$

$Ph_3Sn\,NO_3.L$ (L = HMPA, DMSO and phen.) complexes are relatively good electrolytes in absolute alcohol, indicating a weak co-ordination of nitrate group to the tin atom. I.R. spectral data substantiate the co-ordination of nitrate group in these complexes and from Mossbauer spectral data these three nitrate complexes have been found to be penta co-ordinated(38).

Substituted pyridine N-oxides are known to form a large number of 1:1 adducts with triphenyl tin chloride (38). These compounds are precipitated when the solutions containing equimolecular amount of the reactants in pet-ether are mixed together (39). From the stability constant measurements of the compounds, $Me_3SnCl.L$ (L = substituted pyridine N-oxide), it has been known that these ligands give stable adducts with Me_3SnCl.

Smith and Liengme (40) have reported the formation of 1:1 complexes of tri organo tin chlorides and thiocyanates with tridentate chelating agents 3- [2-(1, 10-phenanthrolyl)]-5,6-diphenyl-1,2,4-triazine (I) and 3-[2-(1,10 phenanthrolyl)-5,6-dimethyl-1,2,4 triazine (II). The isolated complexes were $(CH_3)_3SnCl.L$; $(C_6H_5)_3SnCl.L$ (L = I and II) and $(C_6H_5)_3Sn(NCS).L$ (L = I). These complexes are stable crystalline solids, which behave as non-electrolytes in nitrobenzene.

Diorgano tin dihalides form adducts with a number of ligands viz., pyridine (Py) bipyridyl (Bipy), phenanthroline (Phen) terpyridyl (Terpy) etc. which vary in composition. Thus the isolated complexes have the compositions; $Me_2SnCl_2.Py$,

Me_2SnCl_2.Phen (41,42); Me_2SnX_2.bipy (41,43) (X = Cl, Br, I); $2R_2SnX_2$.Terpy (45) (R = Me, Ph; X = Cl, Br, I). Although with diorganotin dihalide and di-isothiocyanates, 1:1 adducts are formed but by treating diphenyl tin di-isocyanate with 2,2'-bipyridyl, the 2:1 adduct $[Ph_2Sn(NCO)_2]_2$. bipy was obtained. These complexes were precipitated quantitatively from pet-ether or benzene by mixing the required reactants. Pyrazine (44) and tripyridyl amine apparently function as bidentate ligands forming stable 1:1 adducts with organotin dihalides. R_2SnCl_2.2(p-tolyl)$_2$SO (where R = Me or Ph) and R_2SnX_2.L (L = BipyO$_2$ diphosO$_2$ etc; R = Me, Ph) complexes have also been reported (35). With dimethyl formamide (DMF), Ar_2SnX_2 formed complexes of the type Ar_2SnX_2.2DMF (Ar = Ph, o-, p-toly, benzyl and X = Cl, Br, I). These were prepared by mixing the reactant in any molar ratio (46). The interaction of Ar_2SnCl_2.2DMF with other Lewis bases stronger than DMF such as 1,10-phenanthroline, 2,2'-bipyridyl, Dimethyl sulphoxide and N, N-dimethyl acetamide (DMA) resulted in complete substitution of the ligand verifying the weak donor ability of DMF compared to the ligands examined (46). In this connection mention also be made of the adducts $Me_2SnCl_2(Ph_3PO)_2$ (47) and $BuSnX_2$.Phen (48).

The oxygen donor dimethyl tin sulfoxide forms 1:2 complexes with dimethyl and diphenyl tin dichloride. In these compounds the diorganotin group is in trans, cis, cis-octahedral arrangement. The structural differences in the two polymorphs of the latter involve mainly the orientation and disorder of the DMSO ligands. The propensity for Cis co-ordination at octahedral tin complexes and its realisation for pointed ligands like DMSO has been recognised from spectroscopic studies (49). But the pyridine N-oxide ligand, the 2:1 complex of dimethyl tin dichloride contains an all trans- octahedral arrangement (50).

The 2,2'-bipyridyl complex of diphenyl tin dichloride is in the expected trans diphenyl tin, Cis, Cis-distorted octahedral arrangement (51).

Davies et al (43) have prepared a number of adducts of butyl tin tri chloride with different Lewis bases (52).

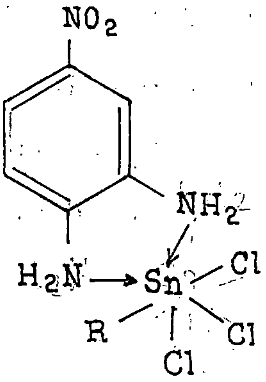
A number of complexes of this type can be mentioned e.g., $BuSnCl_3.2L$ ($L = Ph_3PO$, Py, DMSO etc.). The 1:1 complexes of $BuSnCl_3$ with bipyridyl (53) and phenanthroline (54) are also known. $MeSnX_3$ ($X = Br, I$) can also form 1:1 adducts (45) with bipyridyl. But the complexes of $MeSnX_3$ ($X = Cl, Br, I$) with terpyridyl vary in composition (43) e.g., $3\ BuSnCl_3.2$ Terpy, $MeSnBr_3$.Terpy, $MeSnI_3$ Terpy. 1:1

adduct of $RSnX_3$ (R = Me, Et, Bu and X = Br, I) with phenanthroline and bipyridyl have been reported by Clark et al (55).

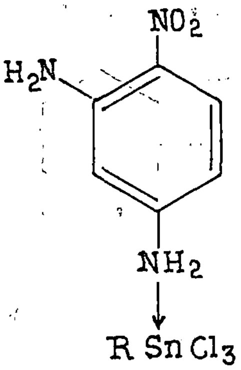
Srivastava et al (56) have isolated organotin adducts of the general formula $Ar_2SnCl_2{\cdot}nL$ (where Ar = Ph, o-, m-, p-tolyl; n = 1 for MEA and DEA and n = 2 for TEA) by the direct interaction of diaryl tin dichlorides with mono-, di- and tri- ethanol amine (MEA, DEA and TEA) in acetonitrile solvent.

Organotin adducts of the type $RPhSnCl_2{\cdot}$ L (where R = Me, Et, n-Bu, benzyl and L = bipyridyl and phenanthroline) have been prepared by Jaura et al (57).

Organotin adducts of 1,2 - di amino-4-nitro benzene, 1,3-diamino-4-nitro benzene and 1,4-diamino-3-nitro benzene with $RSnCl_3$ (R = Me, n-Bu, Ph) have been isolated and investigated by U.V. absorption spectroscopy (35). The two compounds have five co-ordination at tin (structure B and C) and the third compound (structure A) is hexa co-ordinated.



(A)



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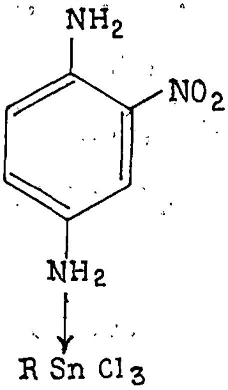


(C)

Organotin Derivatives of Oximes And Schiff Bases:

Mehrotra and his co-workers (59) have reviewed the oxime derivatives of organotin compounds. Organotin oximates are prepared either by the action of sodium or lithium salts with organotin halides (59-61).

$$R_{4-n}SnCl_n + nNa(Li)ON = CR'R'' \longrightarrow R_{4-n}Sn(ON = CR'R'') + nNaCl(LiCl)$$

or by azeotropic distillation of water from a mixture of organotin oxide of hydroxide with oxime in benzene or toluene (48, 59-61):

$$(R_3Sn)_2O + 2HON = CR'R'' \longrightarrow R_3SnON = CR'R'' + H_2O$$

$$R_3SnOH + HON = CR'R'' \longrightarrow R_3SnON = CR'R'' + H_2O$$

Reactions of alkyl tin alkoxides with oximes (48, 53-59, 62, 63) takes place as

$$R_{4-n}Sn(OR')_n + nHON = CR''R''' \longrightarrow nR'OH + R_{4-n}Sn(ON = CR''R''')_n$$

Koheler et al have prepared diorganotin derivatives of a dicyanoformaldehyde oxime by reacting diorganotin dichloride with the silver salt of oxime. A number of various types of butyl tin derivatives of alkanolamines have been obtained by Mehrotra et al (65).

Organotin derivatives of oxime can react with acyl or benzoyl halides and o-acyl or o-benzoyl oxime (53):

$$R_{4-n}Sn(CH = CR'R'')_n + nR''' CO X$$

$$\longrightarrow R_{4-n}SnX_n + nR'R''C = HCOR'''$$

Organotin halides or oxides can react with bidentate, tridentate and tetradentate Schiff bases.

$RSnCl_3$ reacts with $HOC_6H_4CH:NR'$ (where R = Et, n-Bu and Ph; R' = Me, Et and Ph) in cyclohexane and forms 1:2 adducts (66). That these adducts are non electrolytes have been proved by molar conductance measurements in nitrobenzene. Infra-red and Mossbauer spectral studies suggest an octahedral structure for these adducts.

$(CH_3)_2SnCl_2$ reacts with tridentate Schiff bases N-(2-hydroxy phenyl) salicylal dimine $OH.\ C_6H_4CH = NC_6H_4.\ OH$ or its derivatives to form penta co-ordinated structure (67). Tri phenyl tin hydroxide reacts with N-(2-hydroxy phenyl) salicylal dimine to form hexa co-ordinated complex. The structure of N-(2-hydroxy phenyl) salicylal dimine has been determined (68). The structure of the compound is heavily distorted and the organic groups occupy equitorial positions.

Diorganotin oxides react with tetradentate Schiff bases to yield R_2Sn(Salen), R_2Sn(aceto-salen) and R_2Sn (benzo salen) where R = n-Bu, n-octyl and benzyl; [Salen =

bis-(2-hydroxy-5-methyl acetophenone) ethylene diimine; benzo salen = bis-(2-hydroxy-5-methyl benzo phenone) ethylene diimine].

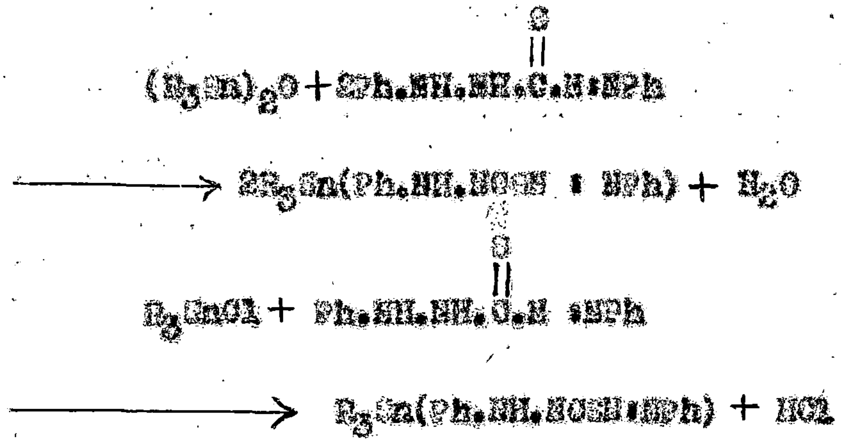
The compound R_2Sn (aceto salen) and R_2Sn (benzo salen) exist in trans form in solid as well as in solution where as R_2Sn(salen) exist both in Cis and trans form (69).

Organotin Dithizonates:

The first observation on organotin dithizonates in solution was made by Alridge and Cremer (70) and they reported that, on extraction with dithizone from a borate buffer, Et_3Sn salt gave a pale yellow complex and those of Et_2Sn^{2+} an orange complex. The complex formed have ϵ_{max} = 23300 at 435 and ϵ_{max} = 70500 at 510 nm respectively (70, 71). Irving and Cox have suggested a 1:1 complex for the former and 1:2 complex for the latter compound.

A number of solid organotin dithizonates of mono, di and tri organotin moieties have been prepared by Ghosh & Ghosh (72a, 72b) and characterised by U.V., I.R., elemental analysis and N.M.R. spectra.

Triorganotin dithizonates were prepared either by the reaction of tri organotin oxide and dithizone in 1:2 molar ratio or by the reaction of one mole of triorgano tin chloride with one mole of dithizone. Liberated hydrochloric acid was neutralised with concentrated ammonia solution.

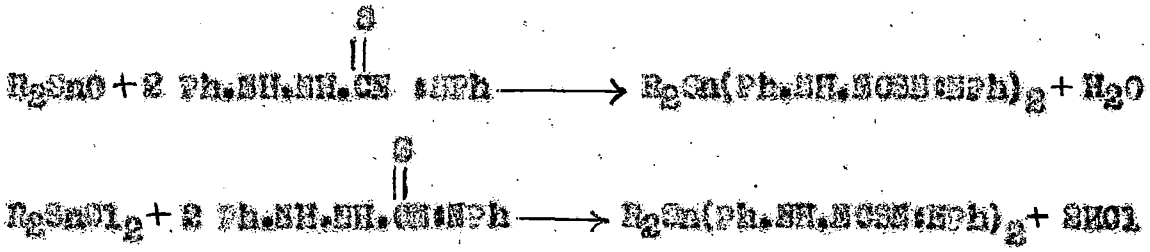


$$(R_3Sn)_2O + 2Ph.NH.NH.\overset{S}{\overset{\|}{C}}.N{:}NPh \longrightarrow 2R_3Sn(Ph.NH.NCS{:}NPh) + H_2O$$

$$R_3SnCl + Ph.NH.NH.\overset{S}{\overset{\|}{C}}.N{:}NPh \longrightarrow R_3Sn(Ph.NH.NCSN{:}NPh) + HCl$$

R = Ph, Bu, Pr,
Bz, p-tolyl

Di organotin dithizonates were prepared by the similar manner with organotin oxide or chloride and dithizone in 1:2 molar ratio in chloroform



$$R_2SnO + 2\,Ph.NH.NH.\overset{S}{\overset{\|}{C}}N{:}NPh \longrightarrow R_2Sn(Ph.NH.NCSN{:}NPh)_2 + H_2O$$

$$R_2SnCl_2 + 2\,Ph.NH.NH.\overset{S}{\overset{\|}{C}}N{:}NPh \longrightarrow R_2Sn(Ph.NH.NCSN{:}NPh)_2 + 2HCl$$

R = Ph, Bu, Me, p-tolyl.

Diorganotin halo dithizonates were prepared either by disproportionation reaction or by metathesis reaction:

$$R_2SnX_2 + R_2SnL_2 \longrightarrow 2R_2SnXL$$

$$(X = Cl^-, Br^-, I^-, SCN^-)$$

$$R_2SnClL + X^- \longrightarrow R_2SnXL + Cl^-$$

$$(X = Br^-, I^-, SCN^-)$$

R = Ph, n-Bu, Me

LH = dithizone.

The presence of hydrogen bonded NH-stretching band in all these dithizonates reveals the fact that the second hydrogen atom of dithizone is not replaced by any organotin moieties.

Organotin Oxinates:

Organotin oxinates (oxine = 8-hydroxy quinoline) are stable, well defined compounds and have been studied quite extensively. These organotin oxinates are generally of the following types:

$R_3Sn(Ox)$, $R_2Sn(Ox)_2$, $RSn(Ox)_3$, $R_2Sn(Ox)X$ and $RSn(Ox)_2X$, where R = organic group, OxH = 8-hydroxy quinoline, X = halogen, isothiocyanate and carboxylates.

The simple organotin oxinates of the type $R_{4-n}SnOx_n$ (R = organic group, OxH = 8-hydroxy quinoline, n = 1,2,3) are prepared either from the organotin halides and sodium oxinate (73).

$$R_2SnCl_2 + 2\ NaOx \longrightarrow R_2Sn(Ox)_2 + 2NaCl$$

$$n\text{-}BuSnCl_3 + 3NaOx \longrightarrow n\text{-}BuSn(Ox)_3 + 3NaCl$$

or from organotin halide and oxine, the hydrogen halide formed is removed by a base such as ammonia (74) and

$$R_2SnCl_2 + 2\ OxH + 2\ NH_3 \longrightarrow R_2Sn(Ox)_2 + 2\ NH_4Cl$$

Organotin oxide with oxine (75, 76)

$$(Ph_3Sn)_2O + 2OxH \longrightarrow 2Ph_3SnOx + H_2O$$

Tri organotin oxinates have also been prepared by reacting triorganotin chloride with a mixture of oxine and sodium methoxide (73).

(Bis-pentafluorophenyl)tin bis oxinates have been prepared from a mixture of tetrakis-(penta fluorophenyl) tin or tris-(penta fluoro phenyl) tin chloride and an excess of oxine in ethanol under reflux (77). The crystal structure of dimethyl tin bis-(8-hydroxy quinolinate) has been determined (78). The compound assumes a structure with cis-dimethyl tin groups (110.7°) in which the oxygen atoms appear trans (the O - Sn - O angle seems not to be listed) and the nitrogen atoms are cis (the N-Sn-N angle = 75.3°). The nearly tetrahedral dimethyltin groupings has tin-carbon internuclear distances that are the same as those observed for the tetrahedral tin compounds, $(CH_3)_nSnX_{4-n}$ and CH_3SnH_3 . In the bonding of the oxinate ligand to tin, it seems that the tin oxygen distances are shorter by 0.23Å than the tin nitrogen distances.

When diphenyl tin dichloride and oxine are allowed to react in benzene in the absence of a base in 1:1 molar ratio, halo oxinate is formed (79,73).

$$R_2SnCl_2 + OxH \longrightarrow R_2SnCl(Ox) + HCl.$$

Halo oxinate compounds can also be obtained through disproportionation of a dihalide and a dioxinate in refluxing benzene or ethanol (80,73).

$$R_2SnCl_2 + R_2Sn(Ox)_2 \longrightarrow 2R_2SnCl(Ox)$$

or, by the reaction of dioxinate and silver halide (79).

$$R_2Sn(Ox)_2 + AgX \longrightarrow R_2SnX(Ox) + Ag(Ox)$$

McGrady et al (81) have prepared dimethyl chloro tin oxinate through the disproportionation of dimethyl tin dichloride and dimethyl tin dioxinate in refluxing benzene. Dialkyl tin isothiocyanate oxinate and acetate oxinate have similarly been prepared (79). Dialkyl tin nitrate oxinate and sulfate oxinate are prepared by the following methods (79).

$$R_2Sn(Ox)_2 + AgNO_3 \xrightarrow{\text{in } CH_3OH} R_2Sn(NO_3)(Ox) + Ag(Ox)$$

$$2R_2SnCl(Ox) + Ag_2SO_4 \longrightarrow [R_2Sn(Ox)_2]SO_4 + 2AgCl.$$

In other halogen substitution reaction the product disproportionates (82) as,

$$R_2SnCl(Ox) + I^- \longrightarrow [R_2SnI(Ox)] + Cl^-$$

$$2[R_2SnI(Ox)] \longrightarrow R_2SnI_2 + R_2Sn(Ox)_2$$

The halogen atom of penta co-ordinated tin halo oxinate undergo ready exchange with groups such as butyl, alkoxy or even with chelating ligands e.g. acetyl acetonates (73,82) which may disproportionate into diorgano tin di oxinates, e.g.,

$$R_2SnCl(Ox) + Tl - OC_2H_5 \longrightarrow R_2Sn(OC_2H_5)(Ox) + TlCl$$

$$\begin{tikzcd}
R_2SnCl(Ox) + n-BuLi \arrow[r] & R_2Sn(n\text{-}Bu)(Ox) + LiCl \arrow[d] \\
 & R_2Sn(Ox)_2 + R_2Sn(n\text{-}Bu)_2
\end{tikzcd}$$

$$\begin{tikzcd}
R_2SnCl(Ox) + Tl-acac \arrow[r] & R_2Sn(acac)(Ox) \arrow[d] \\
 & R_2Sn(Ox)_2 + R_2Sn(acac)_2
\end{tikzcd}$$

Datta (83) have prepared phenyl tin halo oxinates by reacting diphenyl tin dioxinate with mercuric halides in ether at room temperature.

$$Ph_2Sn(Ox)_2 + HgCl_2 \longrightarrow PhSnCl(Ox)_2 + PhHgCl$$

phenyl tin acetate dioxinate has been prepared by Roy (84) by the displacement of chlorine atom from phenyl tin chlorooxinate with sodium acetate. He has also prepared $PhSn(OOCC_2H_5)(Ox)_2$, $PhSn(OOCCH_2Cl(Ox)_2$ and $PhSn(OOCCF_3)(Ox)_2$ complexes by similar method. A novel compound, $[n\text{-}C_4H_9Sn(Ox)_2]_2S$ has been prepared from the reaction of n-butyl tin sesquisulfide and oxine in boiling toluene (85).

Butyl tin isopropoxy oxinates $[BuSn(OPr^{i})_{3-n}(Ox)_{n}]$ have been prepared by Mehrotra et al (86). They have synthesised this compound by the reaction of butyl tin tris-isopropoxide and oxine and isopropanol was removed by azeotropic fractionation with refluxing benzene; the products depend upon the mole ratio of the reactants used. Thus $EtSn(Ox)_3$ has been obtained by the reaction of $EtSn(OPr^{i})_3$ with oxine in 1:3 molar ration.

Ghosh and co-workers (87) have examined the action of mercuric halides on organotin oxinates and probable mechanisms of these reactions have been given. Triphenyl tin oxinate has been shown to react readily with HgX_2 (X = Cl, Br, I) at room temperatures, the hexa co-ordinated diphenyl tin dioxinate is attacked by HgX_2 only when refluxed in benzene or ether. In both the cases, $PhSn(Ox)_2X$ have been found. They have also shown that in $Ph_2SnCl(Ox)$ can react with mercuric chloride with the complete cleavage of the tin-phenyl bond, producing $Sn(Ox)_2Cl_2$, PhHgCl and Ph_2SnCl_2. Srivastava et al (88) have reported organotin derivatives of substituted oxines. They have prepared some diaryl tin bis oxinates/2-methyl oxinates and diaryl tin chloride oxinate/2-methyl oxinates. Sen et al (89,90) have prepared and characterised several diorgano tin bis-(mono- and disubstituted oxinates) by the reaction of diorgano tin dichloride with ligand in 1:2 molar ratio in DMF or ethanol.

Oxine compounds of ester tin has been prepared very recently by V.G.Kumar Das et al (91), Deb & Ghosh (92). Kumar Das et al have reported compounds of the type $R_2Sn(Ox)_2$ and $R_2SnCl(Ox)$ (where R = $MeOCOCH_2CH_2$). The former compounds has been synthesised by the method of Westlake and Martin (93) and the latter compound by the reaction of an equivalent amount of diorganotin bis(oxinate) with R_2SnCl_2 in benzene. The compounds were studied by U.V., I.R., P.M.R. and Mossbauer spectroscopy. It has been proved by P.M.R. data that relative to bis oxinate, the chloro oxinate appears to involve a greater extent of chelation.

Deb and Ghosh (92) have synthesised and characterised co-ordination compounds with β-substituted mono and dialkyl ester tin compounds with ligands like 8-hydroxy quinoline, substituted 8-hydroxy quinoline etc.

Organotin Tropolonates, Kojates, Dithiocarbamates And Acetyl acetonates:

A number of organotin tropolonate complexes of the types Ph_3SnT, Me_2SnXT, R_2SnT_2, $RSnXT_2$ (R = alkyl or Ph; X = Cl, Br, I; TH = Tropolone) have been prepared where the tropolone acts as bidentate chelating agent bonding through both oxygen atoms. Diorganotin bis tropolonates have been prepared (94,95) by the following reactions:

$$R_2SnCl_2 + 2NaT \longrightarrow R_2SnT_2 + 2\ NaCl$$

$$R_2SnCl_2 + 2\ TlT \longrightarrow R_2SnT_2 + 2\ TlCl$$

phenyl tin tris tropolonate and phenyl tin chloride bis tropolonate have been prepared by reacting phenyl tin tri chloride in benzene with a solution of tropolone in ether (96).

Kojic acid can form complexes with organotin compounds. Dimethyl tin bis Kojate was prepared by the reaction of $(CH_3)_2SnCl_2$ and Kojic acid (1:2 mole) (97). Methyl tin chloride and methyl tin bromide bis kojates have been prepared by Otera et al (97).

Organotin dithiocarbamates are prepared by reacting sodium dithiocarbamate and an organotin chloride (98-99).

Organotin compounds can form a number of complexes with bidentate oxygen donor β-diketones. Organotin acetyl acetonates are principally of the types $R_3Sn(acac)$, $R_2Sn(acac)_2$, $RSn(acac)_3$, $RSnX(acac)_2$, $RSnX(OR')(acac)$ and $RSn(acac)_n(OR')_{3-n}$.

R_3SnL [R = Me, Ph; LH = acetyl acetone (acac), benzoyl acetone (bzac)] compounds have been prepared and characterised by I.R., N.M.R. and Mossbauer spectroscopy (100). These compounds have been prepared by Tl(I) salt method (101, 102, 103) e.g.,

$$R_3SnCl + Tl(acac) \longrightarrow R_3Sn(acac) + TlCl.$$

Diorganotin bis acetyl acetonates, $R_2Sn(acac)_2$ have been obtained by adding acetyl acetone to a mixture of diorganotin dichloride and sodium methoxide in methanol(104). These diorganotin bis (β-diketonates) can also be obtained by direct reaction of the reactants in the presence of a base (101).

Srivastava and Saxena have synthesised some diorganotin bis (acetyl acetonates), $R_2Sn(acac)_2$ (R = Ph, o-, m-, p-tolyl) by the method reported by Allred and Thompson (105).

Bachlas and Jain (106) have synthesised tri and diorganotin complexes of 2-Thenoyl trifluoro acetone of the types $R_3Sn(TTA)$ (where R = CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5) and $R_2Sn(TTA)_2$ (where R = CH_3, C_2H_5, C_4H_9 and HTTA = 2-Thenoyl trifluoroacetone). These compounds have ben prepared by the following reactions:

$$CH_3ONa + HTTA \longrightarrow \overset{+}{Na}(TTA)^- + CH_3OH$$

$$R_3SnCl + Na^+(TTA)^- \longrightarrow R_3Sn(TTA) + NaCl$$

$$(R_2SnO)_x + 2x\ HTTA \longrightarrow xR_2Sn(TTA)_2 + xH_2O$$

Organotin Derivatives of Pyridine Carboxylic Acids And Other Ligands:

A series of diorganotin bis (pyridine carboxylates), $R_2Sn(O.CO.C_5H_4N\text{-}n)_2$ (R = Me, n = 2-4; R = Ph, n = 2 or 3), diorgano chloro tin pyridine carboxylates, $R_2ClSn(O.CO.C_5H_4N\text{-}n)$ (R = Me or Ph, n = 2; R = Me, n = 4) and mono organo chlorotin pyridine carboxylates, $RCl_2Sn(O.CO.C_5H_4N\text{-}2)$ (R = Bu or Ph) have been synthesised and their structures investigated by ^{119m}Sn Mossbauer and infra red spectroscopy (107).

The spectra indicate that, in the solid state, the three dimethyl tin bis-(pyridine carboxylates) along with diphenyl tin bis-(3-pyridine carboxylate) and dimethyl chloro and diphenyl chloro tin 2-pyridine carboxylate adopt a trans octahedral R_2SnX_4 geometry. Dimethyl chlorotin 4-pyridine carboxylate, however, possess a five co-ordinated trigonal bipyramidal cis- R_2SnX_3 stereochemistry, while diphenyl tin bis-(2-pyridine carboxylate) adopts an octahedral cis- R_2SnX_4 structure, with two bidentate N-chelating pyridine carboxylate groups.

The structure of dimethyl tin bis-(2-pyridine carboxylate) is likely to involve both bridging and terminal carboxylate groups and co-ordination from pyridine nitrogen atom to tin (Fig. 1).

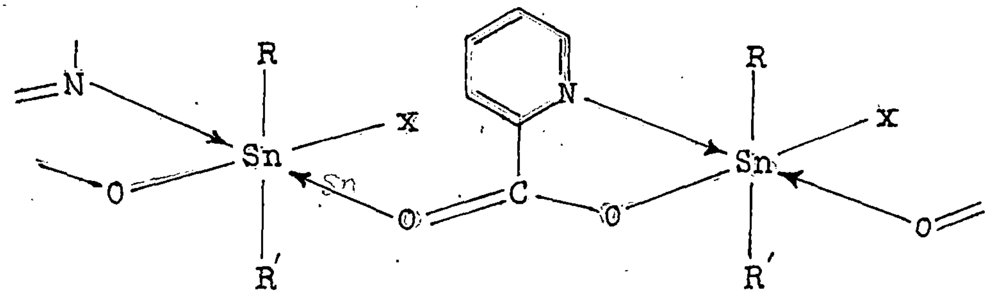


Fig. 1. Stucture of dimethyl tin bis-(2-pyridine carboxylate)

($R = R^1 = Me$; $X = O.CO.C_5H_4N$-2)

Nelson (100) has indicated that the di ethyl-, di n-octyl- and dicyclohexyl- tin derivatives of 2- pyridine carboxylic acid adopt a similar structure in solid phase.

Some novel mixed chelate compounds of diorgano tin (IV) of formula $[SnR_2L'L'')$ involving the chelate ligands N, N-dialkyl dithio carbamate ($S_2CNR'_2$), 8-quinolinate (oxine), 2-methyl-8-quinolinate (quin) and the anion of bis (p- fluoro-benzoyl methane) (fbm) has been synthesised together with the symmetrical bis chelates $[SnR_2(quin)_2]$ (R = Me, Ph) and the cationic complex, $[SnMe_2(PPh_3O)_2(AsPh_3O)_2][BPh_4]_2$, containing mixed monodentate ligands has been prepared (109).

The mixed chelate complexes were prepared according to the reaction scheme,

$$TlL' + [SnR_2ClL''] \longrightarrow [SnR_2L'L''] + TlCl$$

where $R_2 = Me_2$, Bu_2, Ph_2, BuPh and L', L" are the chelating ligands such as $S_2CNR'_2$, 8-quinolinolate (oxine), 2-methyl-8-quinolinolate (quin) and the anion of bis (p-fluoro benzoyl methane) (fbm).

The symmetrical bis chelates, $[SnR_2(quin)_2]$ (R = Me, Ph), were prepared by the method described by Westlake and Martin (93) for the corresponding bis oxinates. The complex, $[SnMe_2(PPh_3O)_2(AsPh_3O)_2][BPh_4]$ was obtained immediately upon adding an ethanolic solution containing the two oxygen donor ligands to an ethanolic solution containing dimethyl tin dichloride and sodium tetraphenyl borate. The reactants were kept in stoichiometric ratio indicated below in the parenthesis:

$[SnMe_2Cl_2]$ (1), $[AsPh_3O]$ (1), $[PPh_3O]$ (2),
$[NaBPh_4]$ (2).

Configurational assignments of the Sn-O bonds in the octahedral structures of these complexes have been made (109) by Mossbauer spectroscopy.

A series of air stable S-triorgano stannyl derivatives of L-cystine and DL-homo cystine have been prepared (110) by reacting the appropriate triorganotin hydroxide or bis (triorganotin) oxide with the sulphydril-containing amino acids in methanol/water at room temperature. Some tributyl stannyl derivatives of types A, B, C formed with glycene, cysteine and histedine are shown in figure (Figure 2)

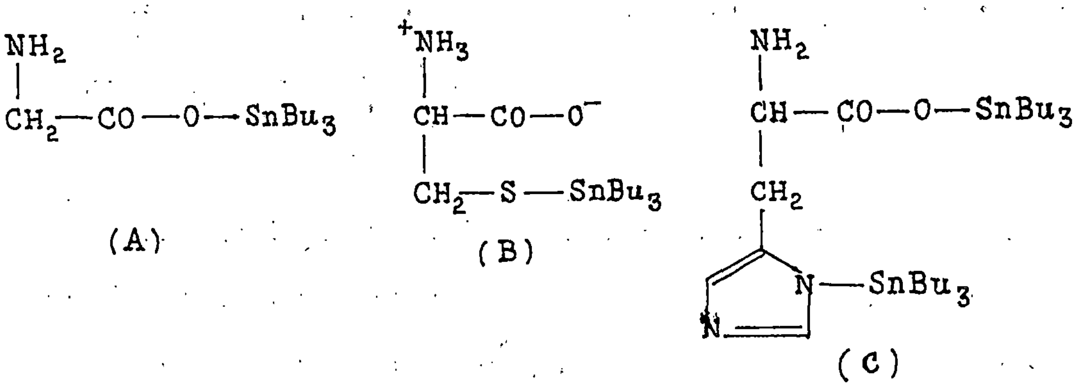


Fig. 2. Types of tributylstannyl derivatives formed from amino acids.

$(R_3Sn)_2O + 2\ HS(CH_2)_nCHNH_2COOH$

$\longrightarrow 2\ R_3SnS(CH_2)_nCHNH_2COOH + H_2O$

(n = 1, R = Np; n = 2, R = Bu or Np)

$R_3SnOH + HS(CH_2)_nCHNH_2COOH$

$\longrightarrow R_3SnS(CH_2)_nCHNH_2COOH + H_2O$

(n = 1, or 2; R = Ph or Cy)

Very recently, ^{119}Sn - N.M.R spectra are reported for toluene solutions of tributyl stannyl ethers of 2,3,4,6-tetra-o-methyl-D-glucose, 1,2:3,4-di-o-isopropylidene-α-D-galacto pyranose, methyl 2, 3-di-o-methyl- α -D-glucopyranoside and methyl 4,6-o-benzylidene- α-D-glucopyranoside and the dibutyl stannyl ether of the last mentioned sugar (111). The structure of dibutyl stannylene derivative of methyl 4,6-o-benzylidene- α-D-glucopyranoside, which in solid state as well as in solution exists as a dimer is shown (Fig. 3).

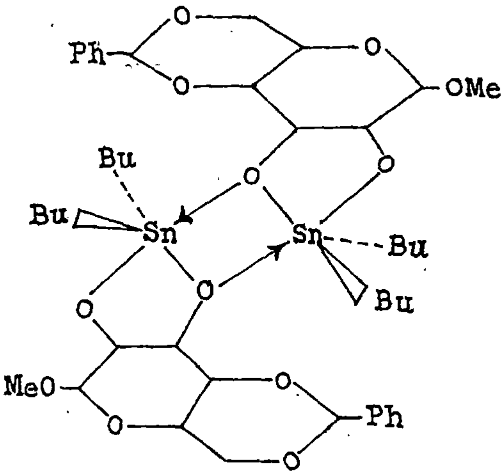


Fig. 3. Structure of dibutyl stannylene derivative of methyl 4,6-O-benzy-lidene α-D-glucopyranoside.

Hydroxamic Acids:

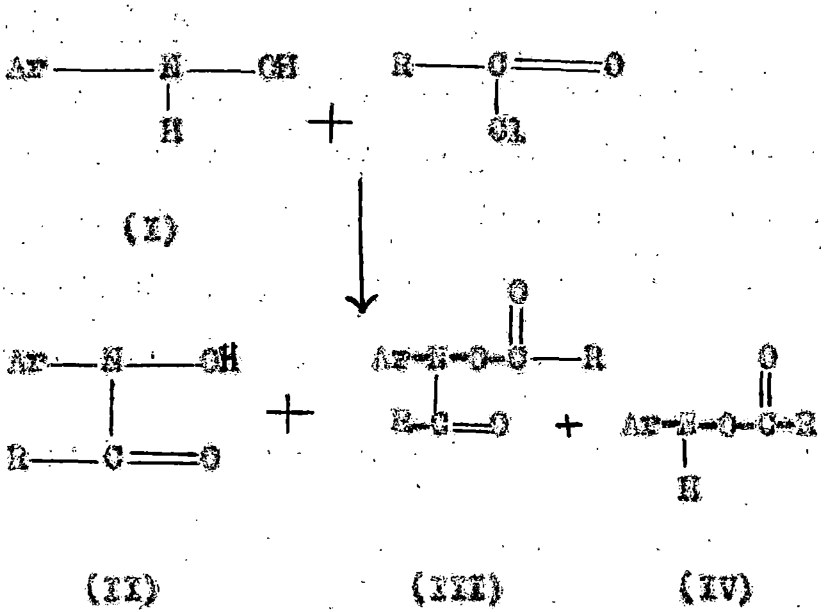
Hydroxamic acids in general are synthesised by reacting an alkyl or aryl ester (RCO_2Et) with hydroxylamine in the presence of alkali and the free acid is obtained by the addition of acid (HX) in the appropriate quantity in cold solution (112).

$$RCO_2.Et + NH_2OH + KOH \longrightarrow RCONHOK + EtOH + H_2O$$

$$RCONHOK + HX \longrightarrow RCONHOH + KX$$

The general methods employed in the synthesis of N-aryl hydroxamic acids are outlined by Yale (113) in a well documented review article.

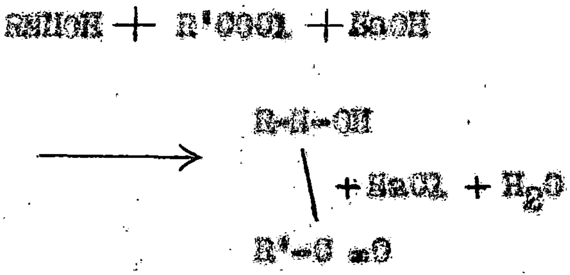
One of the widely used procedure for the preparation of hydroxamic acids is based on Schotten-Baumann reaction (114). This involves the partial acylation of the N-aryl hydroxylamine, I, with acid chloride in aqueous (115) or benzene (116, 117) or diethyl ether medium (118, 119).



The course of acylation is very sensitive to the proper choice of experimental conditions, because, otherwise the concomitant formation of disubstituted hydroxamic acid (and possibly the o-acylated aryl hydroxylamine, IV) takes place.

Most of the workers isolated the desired mono derivative, II, from the crude product by tedious and repeated extraction with concentrated ammonium hydroxide, in which the di derivative (and IV, if present) is insoluble and subsequent acidification with hydrochloric acid (120).

On the basis of Schotten-Baumann reaction, Tandon and co-workers (121, 122) have also prepared several N-aryl hydroxamic acids by reacting N-phenyl hydroxylamine (RNHOH) with acyl chlorides or its derivatives (R'COCl) in the presence of dilute alkali.



$$RNHOH + R'COCl + NaOH \longrightarrow \begin{array}{l} R{-}N{-}OH \\ \quad\big| \\ R'{-}C{=}O \end{array} + NaCl + H_2O$$

Ghosh and Sarkar have synthesised succinyl bis-N-phenyl hydroxamic acid (123) and adipyl bis-N-phenyl hydroxamic acid (124) with phenyl hydroxylamine and corresponding acid chlorides in ice cold di ethyl ether using a base (pyridine).

Many workers have prepared a good number of metal complexes with hydroxamic acids and these hydroxamic acids have been proved to be a very good analytical reagent (125).

<u>Organotin Hydroxamates:</u>

The hydroxylamine derivatives of organotin has been synthesised by Harrison (126, 127) by the azeotropic removal of water from the mixture of appropriate hydroxylamine and the organotin oxides or hydroxides:

$$\begin{array}{l} \frac{1}{2}(R_3Sn)_2O + HONR'R'' \\ \quad\text{or} \\ R_3SnOH \end{array} \longrightarrow R_3SnONR'R'' + H_2O$$

(where R = Me, R' = R'' = Et; R = Me, R' = Ph, R'' = COPh; R = n-pr, R' = Ph, R'' = COPh; R = Ph, R' = Ph, R'' = COPh; R = Me, R' = H, R'' = COPh; R = n-pr, R' = H, R'' = COPh). However, attempts to prepare $Ph_3SnONHCOPh$ by the same method only resulted in the formation of tetraphenyl tin in high yield, presumably by a disproportionation reaction, although no pure diphenyl tin derivative could be isolated.

$$Ph_3SnOH + HONHCOPh \xrightarrow{-H_2O} [Ph_3SnONHCOPh] \longrightarrow Ph_4Sn + [Ph_2Sn(ONHCOPh)_2]$$

The organotin derivatives of N-benzoyl hydroxylamines are extremely stable in moisture. The $Ph_3SnONPhCOPh$ is monomeric in both the crystal and solution phases, whereas the trimethyl tin derivatives are associated in the solid (126, 127).

Di organotin derivatives of N-substituted benzohydroxamic acids have been prepared (128, 129, 129a, 130) according to the following reaction schemes:

$$R_2SnO + 2\ HONR'R''$$

$$\longrightarrow R_2Sn(ONR'R'')_2 + H_2O$$

$$R_2SnCl_2 + 2\ HONR'R'' \longrightarrow R_2Sn(ONR'R'')_2 + 2HCl$$

The liberated hydrochloric acid was neutralised by 25% aqueous ammonia and removed as precipitated ammonium chloride.

Phenyl tin halide bis-(N-phenyl benzo hydroxamates) have been prepared by the reaction of tri phenyl tin N-phenyl benzohydroxamate with mercuric chloride, mercuric bromide and mercuric iodide (130).

Phenyl tin thiocyanate bis- (N-phenyl benzo hydroxamate) has been prepared (130) from the corresponding chloride by the displacement of chloride by thiocyanate.

$$PhSnCl(PBHA)_2 + KCNS$$

$$\longrightarrow PhSn(CNS)(PBHA)_2 + KCl$$

(NPBHA = N-phenyl-N-benzohydroxamic acid)

Compounds of the type R_2SnX (PBHA) have also been prepared by Pradhan and Ghosh (130, 130a) where R = Ph, X = Cl, I, SCN; R = Bu, X = SCN) through disproportionation reaction.

$$R_2SnX_2 + R_2Sn(PBHA)_2 \longrightarrow 2\ R_2SnX(PBHA).$$

But $Ph_2Sn(SCN)(PBHA)$ has been prepared by the reaction of corresponding chloride complex with KCNS (131).

$$Ph_2SnCl(PBHA) + KCNS \longrightarrow Ph_2Sn(SCN)(PBHA) + KCl$$

Pradhan and Ghosh (130) have shown that penta co-ordinated diorgano tin halide N-phenyl-N-benzo hydroxamates disproportionate to the more stable hexa co-ordinated tin compounds when refluxed in non polar solvent like benzene for a long time.

$$Ph_2SnX(PBHA) \longrightarrow PhSnX(PBHA)_2 + Ph_3SnX$$

(where X = Cl, SCN)

However, in polar solvents like methanol, $Ph_2SnX(PBHA)$ was found not to give any triphenyl tin halide and $PhSnX(PBHA)_2$, instead another hexa co-ordinated compound phenyl tin halide methoxy N-phenyl N-benzohydroxamato was formed along with the liberation of one equivalent of benzene (130).

This methoxy compound was also obtained when phenyl tin halide bis-N-phenyl-N-benzohydroxamate was refluxed in methanol with the liberation of one mole of ligand (130).

$$Ph_2SnX(PBHA) \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + C_6H_6$$

$$PhSnX(PBHA)_2 \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + HPBHA$$

Some mono organo tin derivatives of hydroxamic acids were prepared by Narula and V.D.Gupta (131). They have synthesised five, six and seven co-ordinated mono organotin derivatives of hydroxamic acids. They isolated the compounds of the general formulae $R_2Sn_2O_2L_2$, $(RSnL_2)_2O$ (LH = hydroxamic acid derivatives).

Very recently P.G.Harrison et al (120) have prepared a number of new organotin hydroxamates following the usual procedures (126, 127). These compounds are of the types: R_2SnL_2 (where R = Me, n-Bu*, n-octyl, Ph and LH = N-benzoyl N-phenyl hydroxylamine), R_2SnXL (where R = Me; X = Cl, Br, I) and $RSnL_3$ (where R = n-Bu).

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*Reported earlier by Pradhan & Ghosh (130).