INTRODUCTION

Tin has been shown by archaeological discoveries to be one of the earliest metal known to man but the history of organotin chemistry began in 1849 with the preparation of few crystals of diethyl tin iodide by Frankland (1,2) from the reaction of ethyl iodide and metallic tin at 160°. In 1852 Lowig (3) described the action of ethyl iodide on a tin sodium alloy. Though he could not detect the formation of tetraethyl tin, he isolated triethyl tin iodide and hexaethylditin.

The growth of organotin chemistry during next fifty years was rather slow in absence of really efficient and attractive methods for preparing well defined compounds. At the turn of the century, the availability of organo magnesium halides profoundly changed the situation, as organo magnesium halides proved to be general purpose alkylating and arylating agents. The sustained growth of organotin chemistry during the first half of twentieth century resulted in some 330 compounds having four organic groups bound to tin and two thirds of these were R_3SnR'. Factually around 1950, organotin chemistry was quite extensive and at present organotin compounds are more investigated than organic derivatives of any other metal.

The first major review work on organotin compounds was done by Krause and Von Grosse in 1937 (4). Later, Gilman et al (5) published another review of organotin compounds in

1960. In last two decades or so, innumerable reviews and books have been published in the area of organotin compounds. Mention may be made to some of the representative ones (6-28).

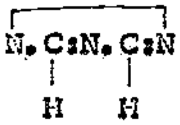
Organotin compounds not only proved to be of theoretical interest but also proved important for diverse commercial applications. The following table indicates diverse applications of organotins (29).

Table 1

Applications	Compounds
R_3SnX	
Antifouling paint biocides	Ph_3SnX (X = OH, OCO.Me, F, Cl, SCS. NMe_2, OCO.CH_2Cl, OCO.C_5H_4N-3) $Ph_3SnOCO.CH_2CBr_2.CO.OSnPh_3$ Bu_3SnX (X = F, Cl) $(Bu_3Sn)_2O$ $Bu_3SnOCO.CH_2CBr_2.CO.OSnBu_3$ $Bu_3SnOCO.(CH_2)_4CO.OSnBu_3$ $-\{CH_2CMe(CO.OSnBu_3)n\}$
Agriculture (Fungicides)	Ph_3SnX (X = OH, OCO.Me)
(Antifeedants)	Ph_3SnX (X = OH, OCO.Me)

Contd..

Table 1 (Contd..)

Applications	Compounds
(Acaricides)	$(cyclo - C_6H_{11})_3SnX$ (X = OH,  $N.C{:}N.C{:}N$ with H on each C, ring closed N–N)
	$[(PhMe_2CCH_2)_3Sn]_2O$
Wood preservative fungicides	$(Bu_3Sn)_2O$
	Bu_3Sn (naphthenate)
	$(Bu_3Sn)_3PO_4$
Stone preservation	$(Bu_3Sn)_2O$
Disinfectants	$Bu_3SnOCO.Ph$
	$(Bu_3Sn)_2O$
Mollusicides (field trials)	Bu_3SnF
	$(Bu_3Sn)_2O$
<u>R_2SnX_2</u>	
Heat and light stabilisers for rigid PVC	$R_2Sn(SCH_2CO.O^1.Oct)_2$
	(R = Me, Bu, Oct, $BuOCO{:}CH_2.CH_2$)
	$(R_2SnOCO.CH{:}CHCO.O)_n$
	(R = Bu, Oct)
	$R_2Sn(OCO.CH{:}CHCO.OR')_2$
	(R = Bu, R' = Oct)

Contd..

Table 1 (Contd..)

Applications	Compounds
	$Bu_2Sn(OCO.C_{11}H_{23})_2$ $Bu_2Sn(SC_{12}H_{25})_2$
Homogeneous catalysts for RTV silicones, polyurethene foams and trans esterification reactions	$Bu_2Sn(OCO.Me)_2$ $Bu_2Sn(OCO.CHEt.Bu)_2$ $Bu_2Sn(OCO.C_{11}H_{23})_2$ $Bu_2Sn(OCO.C_{12}H_{25})_2$ $(Bu_2SnO)_n$
Precursor for forming SnO_2 films on glass	Me_2SnCl_2
Anthelmintics for poultry	$Bu_2Sn(OCO.C_{11}H_{23})_2$
<u>$RSnX_3$</u>	
Heat stabilisers for rigid PVC	$RSn(SCH_2CO.O^iOct)_3$ $(R = Me, Bu, Oct, BuOCO.CH_2.CH_2)$
Homogeneous catalysts for trans esterification reactions	$(BuSnS_{1.5})_4$ $\{BuSn(O)OH\}_n$ $BuSn(OH)_2Cl$
Precursor for producting SnO_2 Films on glass	$BuSnCl_3$ $MeSnCl_3$

In retrospect, the patents granted in 1940 and 1943 to V. Ungve (30) describing the utility of certain dialkyl tin derivatives as heat stabiliser for PVC were landmark, though their full industrial implications did not become apparent until 10 to 15 years later. In fact, the annual industrial production of organotin compounds was less than 50 tons per annum in 1950s. But this figure gradually increased to 2000 tons in 1960 and in 1965 it was 5000 tons, in 1975 it rose to 25000 tons and in 1983 the annual consumption of organotins (Table 2) was about 35000 tons (31). The conservative estimate for the current years will be not less than 40000 tons per annum.

The different outlets of organotin compounds may be indicated as follows:

Table 2

Application	Tons
Heat and light stabilisers for PVC	24,000
Homogeneous catalysts	2,500
Antifouling paint biocides	3,500
Agrochemicals	3,000
Wood preservatives	1,000
Others (disinfectants, glass coatings, etc)	1,000

Since the annual consumption of organotins has reached a significant amount, it may be interesting to discuss briefly the environmental aspects of organotin compounds before going into detailed discussion of organotin coordination compounds.

The principal commercial use of organotins (32) on a tonnage basis is as heat and light stabilizers for PVC and this accounts for some 60% of all organotins produced world wise. Organotin stabilized PVC finds many applications such as potable water piping, drainage piping, food contact grade PVC (mainly beverage bottles and food packing), roofing and glazing materials and more recently window frames. The possible routes by which these stabilizers (which are exclusively the less toxic mono-and di alkyl tin derivatives) may enter the environment are : (a) leaching/weathering (b) land burial and (c) incineration of waste material. Of these atmospheric release of organotins by incineration is probably not significant, as they are likely to undergo thermal decomposition to inorganic tin compounds at the combustion temperatures. This method of disposal is also much less common than land filling.

Leaching of the organotin stabilizers from PVC has been studied in some depth, due to their use in food contact applications for which they have been approved in many countries. The levels of stabilizers employed are typically 0.5-2.0% and studies on the leaching from the potable water piping and food contact packing have shown that these are very low. The actual rates of loss depends upon the nature of the leachent (pH and aqueous or organic character) and the length of the organotin species present. It is interesting to note that although leaching rates are very low, it has been found that organotin stabilized PVC is not suitable for certain medical applications, due to localized adverse tissue reactions towards the organotins.

With regard to the environmental fate of organotin stabilizers in PVC waste disposed of by land fill, little is known about, and no systematic studies have been carried out in this area. It seems reasonable to assume that leaching in aqueous media contiaues to occur, but the relationship between chemical environment, soil adsorption, leaching rates and degradation are unknown. However it can reasonably be inferred that the waste would be distributed evenly in domestic rubbish and the concentrations involved would be very low indeed.

The use of mono and dialkyl tins as homogeneous catalysts (accounting some 2000 tons of organotin compounds annually) in the production of poly urethane foams and silicon elastomers, and for esterification processes, results in their incorporation into the finished product at low levels, especially in terms of the final volume. A typical concentration of organotin catalysts e.g di butyl tin dilaurate in a flexible poly urethane foam formation is of 0.02%. Therefore the method of release of these compounds will be similar to those encountered with the PVC stabilizers.

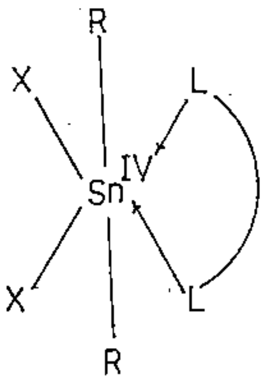
From the foregoing discussion, it can be concluded that although PVC stabilizers and homogeneous catalysts together comprise the largest consumption of organotin compounds, it is unlikely that these would contribute significantly to the undesirable levels in the environment.

Triorganotin compounds particularly tributyl tin oxide (T.B.T.O) are being used as commercial wood preservatives, paint preservatives, antifouling agents etc. A review of T.B.T.O based wood preservatives has been given by Richardson (33).

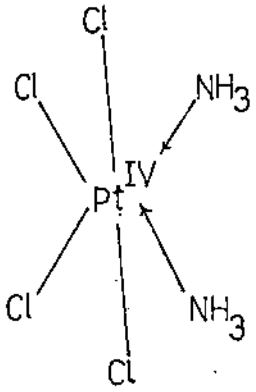
Triphenyl tin compounds have been registered as fungicides in many countries, where as tricyclohexyl and tris neophenyl tin compounds are being used as agricultural miticides. Agricultural applications of organotin pesticides are so far been restricted to a comparatively small, though very important, number of plant diseases and pests. On the basis of 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 in 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, bacteria control, paint preservation etc. are also known (23).

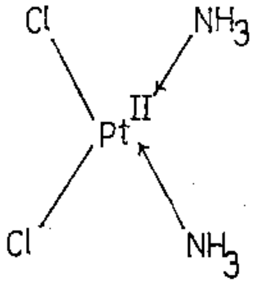
Recently, a series of organotin dihalide complexes, $R_2SnX_2.L_2$ (I), (where R = Me, Et, n-Pr, n-Bu, Ph; X = Cl, Br, I, NCS; L = O- and N donor ligand) have been tested for antitumour activity (34). These compounds were modelled on the active platinum compounds (35). Cis-$Pt(NH_3)_2Cl_4$ (II) and Cis-$Pt(NH_3)_2Cl_2$ (III).



(I)



(II)



(III)

The diorganotin complexes chosen for test contain Cis-halogen groups and certain of the compounds inhibit P388 leukaemia 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 those 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. Hence they do not pose any significant problem for environmental pollution and possibly therefore have been cleared as safe, agricultural pesticides by World Health Organisation (35). In view of the above discussions, it may be said that the preparation of new organotin compounds and their detailed studies will be on increasing interest.

Tin the element having atomic number 50, is a member of group IVA of the periodic table with an electronic configuration $[Kr]4d^{10}5s^{2}5p^{2}$ in the ground state (36). The common four covalent state is derived from the sp^{3} hybridisation. The four covalent state occurs far more frequently than the two covalent state and the great majority of organotin compounds possess a four covalent tin atom in simple compounds.

But when simple compounds reacts with ligands, due to availability of 5d 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 in case of organotin 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 preceeding years a large number of organotin adducts have been reported in the literature. 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-) 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 substituents attached to tin etc. Thus the ability of organotin halides to form adducts increases in the order $R_3SnX < R_2SnX_2 < RSnX_3$ (37-38).

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 (39). 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.

Kumar Das (40) 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 phenanthroline (phen) etc. 1:1 complex of HMPA with Ph_3SnX (X = Cl, Br, I, N_3, CN) have been prepared (41-42) by the general reaction e.g.

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

$Ph_3SnNO_3.L$ (L = HMPA, DMSO and phen) complexes are relatively good electrolytes in absolute alchohol, 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 (40).

Substituted Pyridine N-oxides are known to form a large number of 1:1 adducts with triphenyl tin chloride (43). These compounds are precipitated when the solutions containing equimolecular amounts of the reactants in petroleum ether are mixed together (44). From the stability constant measurements of the compounds, $Me_3SnCl.L$ (L = substituted pyridine N-oxides), it has been known that these ligands give stable adducts with Me_3SnCl.

Cotton et al (45) studied the ^{119}Sn NMR on adduct formation and stereo chemistry of organotin (IV) halides. They recorded ^{119}Sn and ^{31}P NMR spectra for a series of adducts of $RSnX_3$ (R = Me, Ph; X = Cl, Br). The adducts were either 1:1 five coordinate or 1:2 six coordinate complexes. The ^{119}Sn NMR spectra of mixtures of corresponding chloro and bromo complexes revealed in most cases, all possible mixed halide species but much additional structural information was obtained from these spectra, which could not be explained from the spectra of individual compounds themselves. Thus in some cases, the five coordinate species the Berry Pseudo rotation between isomers within a particular stoichiometry could be showed on the NMR time scale which allowed a determination of the molecular structure. An equimolecular mixture of $[PhSnCl_3]^{-2}$ and $[PhSnBr_5]^{-2}$ showed eleven of the twelve the geometries possible for $[PhSnCl_nBr_{5-n}]^{-2}$. In the six coordinate series $[RSnX_4P]^-$ the ^{119}Sn NMR spectra of the mixture of $[RSnCl_4P]^-$

and $[RSnBr_4P]^-$ allowed the geometry to be determined as *trans*.

Smith and Liengme (46) have reported the formation of 1:1 complexes of tri organo tin chlorides and thio-cyanates with tridentate chelating agents 3-[2-(1,10 phenanthrolyl)]-5,6-diphenyl-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.

Biddle, Gray and Crowe (47) synthesised and reported ^{119}Sn Mossbauer spectra of a series of organotin complexes of general formula R_2SnCl_2L ($R = 4\text{-}R'C_6H_4$, R' = Me, CF_3, F, Cl, OMe; L = 2,2' bipyridyl, 1,10 phenanthroline, 2-aminomethyl pyridine). The complexes fall into two isomeric types with either a *trans*-or-*cis*- [RSnR] geometry. For this series, 2-amino methyl pyridine gives exclusively the cis-[RSnR] geometry in its complexes.

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 composition : $Me_2SnCl_2.2Py$, $Me_2SnCl_2.Phen$ (48,49); $Me_2SnX_2.bipy$ (48,50) (X = Cl, Br, I); $2R_2SnX_2$ Terpy (50) (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 petroleum ether or benzene by mixing the reactants. Pyrazine (51) and tripyridyl amine apparently function as bidentate ligands forming 1:1 adducts with organotin dihalides. $R_2SnCl_2.2(P\text{-tolyl})_2SO$ (where R = Me or Ph) and R_2SnX_2L (L = $BipyO_2$, $diphosO_2$ etc., R = Me, Ph) complexes have also been reported (40). With dimethyl formamide (DMF), Ar_2SnX_2 formed complexes of the type $Ar_2SnX_2.2DMF$ (Ar = Ph, O-tolyl, P-tolyl, benzyl and X = Cl, Br, I). These were prepared by mixing the reactant in any molar ratio (53). 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 veryfying the weak donor ability of DMF compared to the ligand examined (53). In this connection mention also may be made of the adducts $Me_2SnCl_2(Ph_3PO)$ (54) and $BuSnX_2.Phen$ (55).

The oxygen donor dimethyl sulfoxide forms 1:2 complexes with dimethyl and diphenyl tin dichloride. In this compounds the diorganotin group is in trans, cis, cis-octahedral arrangements. The structural differences in 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 (56). But the pyridine N-oxide ligand, the 2:1 complex of dimethyl tin dichloride contains in all trans-octahedra arrangement (57).

The 2,2'-bipyridyl complex of diphenyl tin dichloride is in the expected trans diphenyl tin, cis, cis-distorted octahedral arrangement (58).

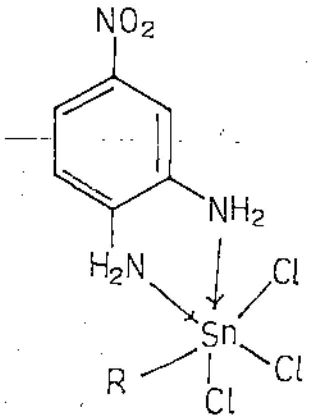
Davies et al have prepared a number of adducts of butyl tin trichloride with different Lewis bases (59).

A number of complexes of this type can be mentioned e.g., $BuSnCl_3 \cdot 2L$ (L = Ph_3PO, Py, DMSO etc.). The 1:1 complexes of $BuSnCl_3$ with bipyridyl (60) and phenanthroline (61) are also known. $MeSnX_3$ (X = Br, I) can also form 1:1 adducts (50) with bipyridyl. But the complexes of $MeSnX_3$ (X = Cl, Br, I) with terpyridyl vary in composition (50) e.g., 3 $BuSnCl_3 \cdot$2 Terpy, $MeSnBr_3 \cdot$Terpy, $MeSnI_3 \cdot$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 (62).

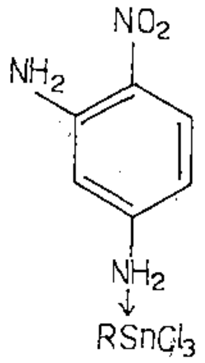
Srivastava et al (63) have isolated organotin adducts of the general formula $Ar_2SnCl_2 \cdot nI$ (where Ar = Ph, tolyl (o.m.p); n = 1 for MEA and DEA and n = 2 for TEA) I = MEA, DEA or TEA. by the direct interaction of diaryl tin dichlorides with mono di- and tri ethanol amine (MEA, DEA, TEA) in acetonitrile 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 (64).

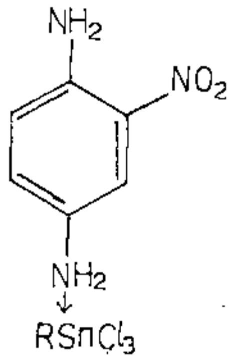
Organotin adducts of 1,2-diamino-4-nitro benzene (A), 1,3-diamino-4 nitro benzene (B) and 1,4 diamino-3-nitrobenzene (C) with $RSnCl_3$ (R = Me, n-Bu, Ph) have been isolated and investigated by U.V. absorption spectroscopy (38). The two compounds have five co-ordination at tin (structure B and C) and the third compound (structure A) is hexa co-ordinated.



(A)



(B)



(C)