A SHORT REVIEW ON ORGANOTIN COORDINATION COMPOUNDS

INTRODUCTION

The unique properties of tin and its compounds have led to their use in a great many different fields. Organotin chemicals are at present widely used in industry and represent a significant and growing outlet for tin. Historically, organotin compounds were among the first organometallic species to be investigated. Extensive research at different Institutes are currently aimed to have a better understanding of the mode of action of these compounds in existing applications and also for finding newer uses, apart from their preparative, structural and other aspects.

The success of a large number of modern techniques applied to organotin compounds has given a great impetus in the basic studies in organotin compounds. Tin possesses, for example, two spin of one-half isotopes, tin-117 and tin-119 which become important in nuclear magnetic resonance, ten stable isotopes (the largest of any element) which allow the easy identification of the tin-bearing fragments in the mass spectrometer, one of the easiest to record Mossbauer resonances from the tin-119m nuclide, and easily assignable tin-carbon stretching frequencies in the infrared and Raman. The availability of two stable oxidation states, tin (II)

and tin (IV), with contrasting chemistries and a wide variety of structural types have afforded a large scope for diverse studies in organotin compounds. Tin (IV) derivatives alone encompass four-, five-, six-, seven- and eight-coordination at tin in neutral, cationic and anionic species, with intra- and intermolecular association to give dimers and higher oligomers with one-, two- and three- dimentional lattices in the solid state, which have provided much interest in extensive studies in these areas.

Apart from these basic interest the studies of organotin compounds have gained further importance due to well developed commercial applications in recent years. Organotins have become a leading commercial organometallic through their use as poly (vinyl chloride) stabilizers and more recently as biocides, where their success is based on their favourable performance/unit weight ratio and by their degradation by chemical action into non-toxic inorganic tin compounds. Today organotins are in wide use as agricultural fungicides and miticides, industrial biocides, wood preservatives, surface disinfactants, anthelmintics and marine antifouling agents etc. Industrial production of organotinsexceeded 25000 tons per year in the free world with a selling price of over $ 150 million during 1975-76.

The first organotin compound was prepared by Frankland (1,2) in 1849 when studying the reaction between tin and ethyl iodide and obtained a product which in 1853, he characterized as diethyl tin di-iodide. In 1852 Lowig (3) described the action of ethyl iodide on a tin-sodium alloy. From that start organotin chemistry developed as a regular though not very exciting, research subject for about a century. The development of organotin chemistry during the first fifty years was rather slow because of the lack of really efficient and attractive methods for making well-defined compounds at will. This situation was changed profoundly when, around the turn of the century, the organomagnesium halides became available as general purpose alkylating and arylating agents. Through Grignard reagents, a wide variety of compounds became readily available for the first time. The development of organotin chemistry was further extended by the discovery of Kocheskov in 1929 of the redistribution reaction between compounds R_4Sn and $SnCl_4$ (or $SnBr_4$). As a consequence of these landmarks, an upsurge of organotin chemistry, both scientifically and technically, has occurred since 1920 and in particular since the thirties.

Krause and Von Grosse (4) published the first comprehensive review covering the literature upto 1935.

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. Since 1964, a number of literature of organotin chemistry is being published in annual surveys (7-21). The "Tin" annual survey covering the year 1978 has been published by Harrison (22). Apart from these review articles, several books have been published (23-27).

In retrospect, the patents granted in 1940 and 1943 to Ungve (28) describing the utility of certain dialkyltin derivatives as heat stabilizers for PVC, were a landmark, 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, and in 1969 it had risen to about 14000 tons and in 1975 a production of 25000 tons was achieved. Current production may be over 30,000 tons as a safe guess. Characteristically, in majority of applications of organotin compounds, only small amounts of tin are needed to see its effect.

The major application of organotin compounds primarily centers around their applications in the area of PVC stabilization, though uses in catalytic activity for polyurethane formation, epoxy resin curing, olefin polymerisation may become highly significant in near future.

Poly (vinyl chloride) [PVC] is an organic polymer of high commercial importance. The growth of PVC manufacture has been phenomental in last two decades. In 1962, the annual world production was 0.5 million ton, which increased to 7.5 million tons in 1972. The rate of growth is still increasing. A major possible drawback of PVC is its tendency to decompose at elevated temperatures and also on exposure to short wave length. Since PVC is processed at temperatures around 200°C, it is necessary to incorporate stabilizer into the mix to avoid decomposition and the resultant discolouring and embrittlement of the polymer. It has been found that the most effective heat stabilizers are certain organotin compounds of the type R_2SnX_2 where R is common methyl, n-butyl, or n-octyl and X is a carboxylic acid ester (usually maleic acid) or a mercapto carboxylic acid ester (usually iso-octyl ester of mercapto acetic acid). The several benefits of using organotin stabilizers are - (a) their unsurpassed effectiveness in conferring heat stability to PVC (the thiotins in particular), (b) high degree of clarity is obtained in the transparent polymer, (c) excellent light stability without which transparent PVC becomes yellowed and embrittled by the action of ultraviolet light, (d) excellent compatibility with the other components and thus minimising possible manufacturing

problems such as "plate out" or chalking, (e) effective in all grades of PVC, including emulsion -, suspension-, and masspolymerised types and also in its copolymers, polyblends or polymer mixtures and (f) low toxicity and good leach-resistance.

In 1957 Luijten and Pezarro (33) proposed di -n-octyl compounds as PVC stabilizers with anticipated mammalian non-toxicity and this was established by Barns in Great Britain and by Kilmer in Germany. An important recent development is that the addition of small amounts (5-10%) of monoalkyltin derivatives to the usual dialkyltin formulations has a synergistic effect on stabilising effectiveness which allow the manufacture of PVC article of perfect colourlessness and clarity. A particular effect of the monoalkyl tins, seemed to be the prevention of so-called early yellowing. The newest promising group of compounds in the field of stabilizers are the "Estertins", which will be discussed later in a greater detail.

Though the industrial application of organotin compounds were confined to diorgano and triorgano tins (34-37), several attempts have been made in recent years to find applications for monoorgano (38) and tetra-organotins (39). Now, monoorganotins have been found to be effective as water repellants for fabrics and building

materials and mineral flotation agents depending on their hydrophobicity, as PVC stabilizer synergistic and as industrial esterification catalysts, whereas tetraorganotins are used to assess as anti-wear additives, anti-oxidents for lubricating oils and delayed action biocides. The generally low mammalian toxicity of the monoorganotins makes them important. The compound, $(BuSnS_{3/2})_4$ (40) or mixture of $RSn(I.O.T.G)_3$ / $R_2Sn(I.O.T.G)_2$ (where R is Me, Oct or $BuOCOCH_2CH_2$ and I.O.T.G is $SCH_2COOioct$) has been approved for use in food contact PVC in a number of countries. The synergistic effect of mono-/dialkyltin stabilizer mixtures was first described by Klimsch and Kuhnert (41). Recent studies at International Tin Research Institute, London and at Akzo Chemie (U.K.) Ltd (42) have shown that the monoalkyltin synergist undergoes a facile exchange of its marcaptide groups (for thioglycolates) with chlorine atoms of the corresponding alkyltin chlorides. At present an interesting approach by Brecker (43) is to combine both functions within same molecule, forming $R_2Sn(SR')S\ SnR(SR')_2$. Mixtures of mono- and di- alkyltin compounds are also used in the production of thin transparent surface films of SnO_2 or glass (44). Recently monoalkyltins, are used to provide scratch resistant stannic oxide film (45); as homogeneous catalyst they show no

problem of corrosion of the stainless steel vessel (46) and are used as active hydrophobic agents (47,48) for building materials and cellulosic substrates. $(Et_4N)_2\{BuSnBr_5\}$ have been demonstrated to improve the flame resistance of wool (49). In series of stannatranes, $RSn(OCH_2CH_2)_3N$, the monophenyl tin derivative was found to show fungicidal activity (50).

Apart from the above properties, organotin compounds, particularly the triorganotin compounds exhibit a varied number of biological properties like antifungal activity, antibacterial activity, anthelmintic activity, molluscicidal activity, insecticidal activity etc. On the basis of investigations of the biological properties, triorganotin compounds can be used for the following areas (29-32).

(a) Control of fungi, bacteria, insects etc. in agriculture

(b) Wood preservation

(c) Control of molluscs.

(d) Antifouling for ships etc.

(e) Slime control in paper mills.

(f) Paint preservation

(g) Water treatment

(h) Textile preservation

(i) Hospital disinfectants

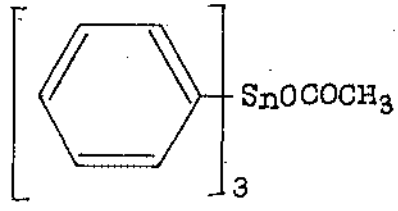
(j) Textile sanitization etc.

From environmental point of view, the organotins have an advantage over many other compounds because they degrade to totally non-toxic tin species. Recent development in understanding the mode of toxic action of di- and tri- organotin compounds have been reviewed by Smith (51). A generalised degradation scheme of trialkyl tin derivatives was also suggested by Seldon (52).

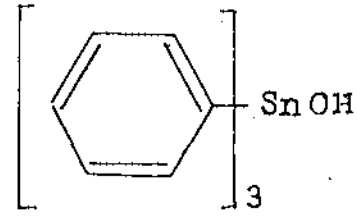
The first proposed wood preservatives were trialkyl tin compounds by van der Kerk and Luijten (53) in 1954. The use of tributyl tins in wood preservation upto 1970 has been the subject of an excellent review by Richardson (54) and a number of developments since that date have also been done (55).

The use of organotin compounds in control of pests is relatively new compared to others. Organotin pesticides do not accumulate in the soil with successive application. They are metabolised readily in animals and soils to inorganic tin compounds which are not taken up by the plants. Hence, they do not pose any significant problem for environmental pollution and possibly therefore have been cleared

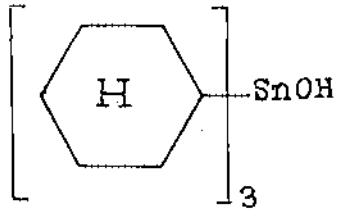
as safe agricultural pesticides by World Health Organisation (56). Few recently used pesticides and miticides are as follows



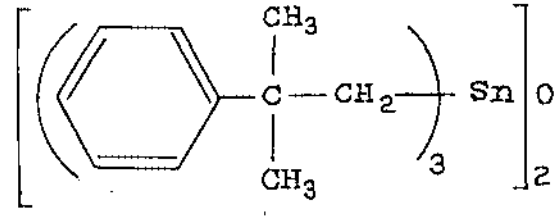
Fentin acetate (Brestan)
(Hoechst)
m.p. 118-120°C
LD_{50} (rats) 125 mg/kg



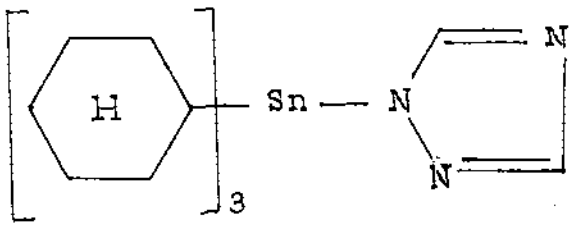
Fentin hydroxide (Du-Ter)
(Philips Duphar)
m.p. 116-120°C
LD_{50} (rats) 108 mg/kg



Cyhexatin(Plictran)
(Dow)
m.p. 195-198°C
LD_{50}(rats) 540 mg/kg
LD_{50}(bees) 32 μg/bee



Fenbutatin Oxide (Vendex)
(Shell)
138-139°C
LD_{50} (rats) 2,630 mg/kg
LD_{50} (bees) 100 mg/bee



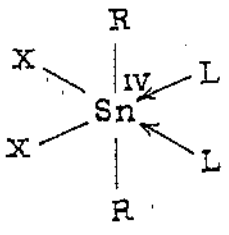
Azocyclotin (Peropal)

(Bayer)

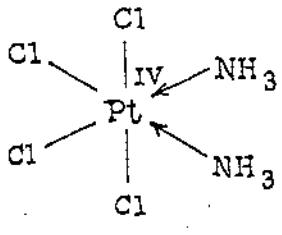
m.p. 218.8°C

LD_{50} (rats) 631 mg/kg

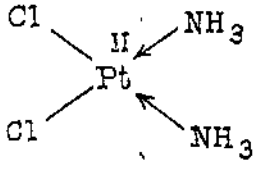
Organotin compounds have not previously been shown to have any antitumour properties. Recently, a series of diorganotin dihalide and di- psuedohalide complexes, $R_2SnX_2 \cdot L_2$ (I) where R = Me, Et, n-Pr, n-Bu or Ph; X = Cl, Br, I, NCS; L = O- or N- donor ligand, ~~which~~ were modelled on the original active platinum compounds (57) Cis - Pt $(NH_3)_2Cl_4$ (II) and cis - Pt $(NH_3)_2Cl_2$ (III).



I



II



III

The organotin complexes chosen for testing, contain Cis-halogen groups (an essential requirement for activity in the Pt - analogues) and certain of these inhibit P_{388} leukaemia in mice (58). Most encouraging results observed for diethyltin complexes are that the 1,10-phenanthroline and 2,2' -bipyridyl adducts exhibit quite significant anti-leukaemic activity towards the P_{388} tumour system, which indicates a potential use in this area in near future.

So far, we have tried to give an outline about the different types of activity of organotin compounds and some of their current and potential uses. The chemistry and structural aspects of organotin compounds are no less interesting than the properties we have discussed so long. In understanding the diverse characters of organotin compounds the studies on Lewis acidity of these compounds have provided a significant contribution.

Lewis acidity of organotin compounds

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 (59). The common four covalent state is derived from sp^{3} hybridisation. The four covalent state occurs for more frequently than the two covalent state and most of the organotin compounds possess a four covalent tin atom in

simple compounds.

Tin differs from the lighter Group IVB element in that its d-orbitals are of sufficiently low energy for them to be frequently used in bonding so that tin can readily expand its coordination number above four. As a consequence of this, many organotin compounds exhibit great Lewis acid character and can form stable adducts with number of Lewis bases. Moreover reactions involving nucleophilic attack at tin are fascilitated by the formation of coordinated intermediates which, however, unstable, lower the energy of transition state. The coordination chemistry of organotin compounds, was discussed by Poller (60) in 1965 and by Gielen and Sprecher in 1966 (61). In recent years a number of review articles on organotin complexes have been published.

Organotins can form a large number of complex compounds with suitable donor and chelating ligands. The presence of an organic group in a molecule usually diminishes the tendency of organometallics to form complexes and hence the observed stability of the complexes should decrease as follows: $MX_4 > RMX_3 > R_2MX_2 > R_3MX > R_4M$. The configuration of the complexes readily follows from the type of metal hybridisation involved. In R_4M complexes Sp^3 - hybrid

orbital exist and tetrahedral configurations are attained. In MX_6^{-2}, the other limitting case, the six Sp^3d^2 - hybrid orbitals of the metal are directed towards the ligands so that the resulting complex will be octahedral. When only one ligand adds to an organometallic molecule, a trigonal-bipyramidal complex (co-ordination number five) may be formed through the participation of the Sp^3d hybrid orbitals of the metal. A number of compounds have been described by Beletskaya, Butin, Ryabtsev and Rentov (62) which show agreement with these simple rules, although in many cases, the structures mentioned are often distorted, due to the different nature of the ligands in an organometallic complex.

Though the present investigation is on the preparation and other studies of Estertin (β-carboalkoxy alkyl tin) coordination complexes of different types of ligands, it will be appropriate to have a prior brief discussion of the methods of preparation, properties and structural aspects of organotin coordination compounds in general, before presenting our findings.

Organotin adducts

The readiness with which the stannic halides form thermodynamically stable adducts of the type $SnX_4.2L$

(L = ligand) with Lewis bases is well known (63). Organotin compounds act as a Lewis acids to react with electron pair donors i.e., Lewis bases to form addition compounds. All the three types of organotin compounds viz, mono-, di- and triorganotin, can form adducts with mono-, di- and polydentate ligands. The acceptor strength of organotin compounds is dependent on many factors, viz, the nature of the ligands, the organic groups, the substituents attached to tin etc. As pointed out earlier, the stability of organotin halides to form adducts increases in the order $R_3SnX < R_2SnX_2 < RSnX_3$ (64,65). The acceptor strength of a series of Me_3SnX compounds is found to be proportional to the electronegativity of the substituent bonded on tin (66a). The stronger the electron attracting power of the substituent, the less the electron density around tin and the acceptor strength increases accordingly. Thus the order of acceptor strength of the Me_3SnX moiety is $F^- > Cl^- > Br^- > I^-$. The apparent acceptor strength depends also on the nature of the donor (65).

It is widely accepted that tin (IV) is a class A acceptor (66b) and using the "Hard and Soft Acids and Bases" (HSAB) concept (67), it is a hard acid. The presence of organic groups on tin may confer some softness (68) and

organotins sometimes show characteristics of class B acceptors towards certain ligands (61) but generally it is believed that in organotin complexes tin retains its class A (hard acid) character. Thus, trimethyl tin chloride forms more stable adducts with oxygen or nitrogen donors than it does with corresponding sulphur or phosphorous compounds (69). However, recent studies (211) in our laboratory on some ligand exchange reactions of the following type

$$R_3SnL + L' \longrightarrow R_3SnL' + L$$

(where L and L' = Dithizone, Diphenyl carbazone, oxine, substituted hydroxamic acids) have shown that dithizone can replace all other ligands from their organotin complexes and the substituted hydroxamic acids form the weakest complexes as they can not replace other ligands mentioned above. These observations indicate the soft character of organotin compounds. Organotins may be considered better as a border line case between hard and soft acid.

1:1 adduct of HMPA (hexamethyl phosphoric triamide), DMSO (Dimethyl sulphoxide), 1,10 phenanthroline (Phen) with R_3SnX (R = Me, Ph; X = Cl, Br, I, N_3, CN, NO_3) have been prepared by several workers (70-72). Of these, the

Ph_3SnNO_3L (L = HMPA, DMSO and Phen adducts appeared to be relatively good electrolytes in absolute alcohol. Evidence for coordinated nitrate group in these complexes comes from IR data and these compounds have been suggested to be penta coordinated from the Mossbauer Spectra (72). A large number of 1:1 adducts of Ph_3SnCl with substituted pyridine - N - oxide are known (73) and the stability constants of $Me_3SnCl.L$ adducts have also been measured (74). Triphenyl phosphine oxide and triphenylarsine oxide ligands can also form adducts with R_3SnX (R = Me, Ph; X = Cl, Br, I) (75,76,77).

The complexation of Me_3SnX (X = halide) in donor solvents e.g. acetone, dioxan, dimethyl ether, pyridine, DMF, DMSO, HMPT and tetramethyl ethylene diamine have been studied by means of ^1H NMR spectroscopy and equilibrium constants were evaluated (78). Adducts derived from the bidentate ligands 2,2'-bipyridyl or 1,10-phenanthroline are readily made by mixing solvents containing equimolar amounts of the two reactants in an inert solvent, such as benzene, when the complexes precipitate (79-81). The $Me_3SnX.$ bipy complexes are very unstable, losing the tin halide quantitatively on exposure to air. These are easily soluble in organic solvents (81). Rechie et al (82)

reinvestigated the structure of Me_3SnCl. bipy using IR, PMR and Mossbauer spectroscopy which indicated that in solid state the complex is trigonal bipyramidal with co-planar methyl groups and the structure altered upon dissolution in CCl_4. Smith (83) also reported the Ph_3SnCl complexes with 2,2'-bipyridyl and 1,10-phenanthroline. Srivastava et al reported $Ph_3SnNCS.L$ (L = $H_2NCH_2CH_2NH_2$, 1-methyl-2-pyrrolidinone, 2-aminothiazole etc) (84) and $Ph_3SnNCO.L$ (85) (L = phenanthroline, DMF, Ph_3PS etc) adducts. They also prepared $R_4SnX_{4-n} \cdot mL$ (R = Me, Ph; X = Cl, Br; n = 1-3, m = 1-2; L = urea, tetramethyl urea) compounds (86). Narula et al (87) reported the 1:1 adduct when an equimolar ratio of liquid SO_3 in CCl_4 is treated with $(R_3Sn)_2O$ (R = Ph, Pr, Bu) in CH_2Cl_2 at -20^oC. The adduct changes to $(Ph_3Sn)_2SO_4$ on reflux in CCl_4.

Smith and Liengme (88) reported the formation of 1:1 adducts of triorganotin 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 complexes isolated were, $(CH_3)_3SnCl.L$; $(C_6H_5)_3SnCl.L$ (L = I and II) and $(C_6H_5)_3Sn(NCS).L$ (L = I). These compounds are stable crystalline solids which behave as non-electrolytes in nitrobenzene.

Diorganotin dihalide also form adducts with a number of ligands viz, pyridine (Py), bipyridyl (bipy), phenanthroline (Phen), terpyridyl (terpy) etc. (81,89,90) which vary in composition. Although with diorganotin dihalides and diisothiocyanates, 1:1 adducts are formed with 2,2'-bipyridyl, diphenyltin diisothiocyanate forms 2:1 adduct, $[Ph_2Sn(NCO)_2]_2$. bipy (91). By contrast to the ion-pair product from dimethyl tin dichloride (92,93), dimethyl tin diisothiocyanate forms a seven coordinated adduct with terpyridyl (94).

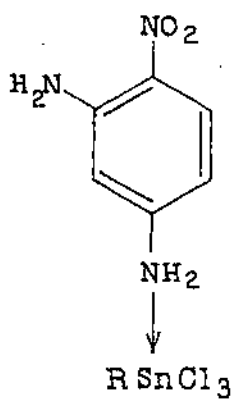
The adducts of diorganotin compounds with a number of donor ligands like pyrazine (95), terpyridyl amine (96), bipy.O_2 and diphos.O_2 (72), dimethyl formamide (97), Ph_3PO (76), phenanthroline (98) etc. have been reported.

The oxygen donor ligand, DMSO forms 1:2 adducts with dimethyl (99) and diphenyl tin dichloride (100,101) in which the diorganotin group is in a trans, cis, cis-octahedral arrangement. Srivastava et al (102) have reported adducts Ar_2SnCl_2 . nI [Ar = Ph, o-, m- & p-tolyl; I = mono- di- and tri-ethanol amine (MEA, DEA and TEA); n = 1 for MEA and DEA and n = 2 for TEA) Adducts of the type $RPhSnCl_2.L$ (R = Me, Et, n-Bu, Benzyl and L = bipyridyl and phenanthroline) was reported by Jaura et al (103). Smith et al reported compounds of R_2SnX_2 with 1,10-phenanthroline, 2-2'-bipyridyl and triazine (104) which were shown to be octahedral structure

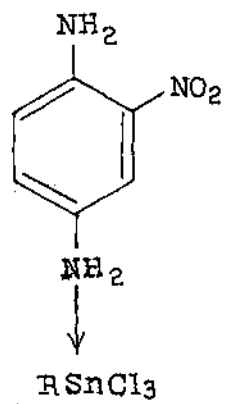
with trans hydrocarbon groups.

The adduct of $RSnX_3$ with a number of ligands like Ph_3PO, Py and DMSO (105) and bipy, phen and terpyridyl (79, 81, 106, 107) have been reported by several workers. The terpyridyl complexes are of variable compositions (81).

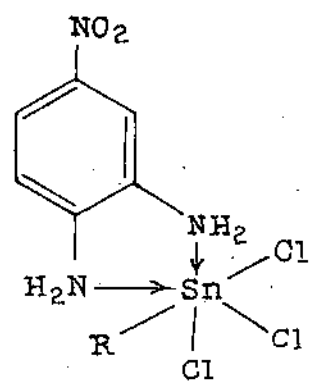
Organotin adducts of $RSnCl_3$ (R = Me, n-Bu, Ph) with aromatic bases such as 1,3-diamino-4-nitrobenzene and 1, 4-diamino-3-nitrobenzene were investigated by UV absorption spectroscopy (65). The two compounds have five coordination at tin (structure A and B) and the third compound (structure C) is hexa coordinated.



(A)



(B)



(C)

Narula et al (108) have reported adducts of the type $EtSnCl_3.L'$, $EtSnCl_3.2L'$, $SnCl_4.L''$ and $SnCl_5.L''$ (where $L' = (Ph_3Sn)_2O$, $L' = (Bu_3Sn)_2O$ and $L'' = Bu_2SnO$). The configuration of $SnBuCl_3.L$ [L = $C_5H_4N(CH{:}NR)$; R = Me, Et, CH, Ph, CMe_3, Ph, C_6H_4Me-p, C_6H_4OMe-p] using ^1H NMR spectroscopy and structure of $SnBu_3Cl$ [$C_6H_4N(CH{:}NPh)$] by single crystal X-ray analysis was determined and repeated by Tanaka et al (109). Adducts $Et_4N(RSnCl_4.L)$ (R = Bu, Ph; L = Py, Me_3N, Bu_3P, Ph_3PO, Ph_3AsO, Me_2SO, DMF) and their Mossbauer spectra studies have been reported by Cunningham et al (110).

Organotin Co-ordination compounds of bi- and polydentate ligands of innermetallic type:

In last few decades inner complexes of organotin compounds have been extensively investigated resulting in well over one hundred publications. Vigorous activities in this area are still continuing in a profilic manner. It is rather difficult to discuss all these publications in detail within the scope of the present discussion. Therefore, an attempt will be made here to discuss certain types of such complexes briefly to give an idea about the extent and nature of such compounds.

One of the most important class of bidentate oxygen donors are the β-diketones. The ability of organotin

moieties to react with β-diketones to form stable organotin complexes of high coordination is well established. The organotin acetylacetonate are principally of the types $R_3Sn(acac)$, $R_2Sn(acac)_2$, $RSn(acac)_3$, $RSnX(acac)_2$, $RSnX(OR')(acac)$ and $RSn(acac)_n(OR')_{3-n}$. Other β-diketonates can be classified similarly. Triorganotin acetylacetonates $R_3Sn(acac)$ [acac = $CH_3COCH_2OC\ H_3$] are obtained by the reaction of triorganotin chloride and thallium acetylacetone (111-113). Other triorgamotin β-diketonates R_3SnL [where L = benzoylacetone (bzac) and dibenzyl methane (bzbz) have also been prepared in a similar way. Many of these compounds have been characterised by IR, NMR and Mossbauer spectroscopy (114). Bachlas et al (115) reported $R_3Sn(p\text{-}BrC_6H_4CO\text{-}CHCOCH_3)$ (where R = Me, Et, Pr, Bu, Ph).

Diorganotin-bis-acetylacetonates (116) have been prepared by reacting diorganotin dichloride and sodium methoxide in methanol followed by addition of acetylacetonate or by direct reaction with β-diketones in presence of a base (111). Dimethyl tin bis-acetylacetone is also prepared by refluxing dimethyl tin oxide in acetylacetonate for several hours (117). Oxidative-addition reactions of tin (II) bis (β-diketonate) with organic halides have been applied to obtain organo halogenotin bis (β-diketonates) (118-120).

Kawasaki et al (121) have synthesized alkyltin halide methoxy acetylacetonates and suggested to be dimeric in nature. Mehrotra et al (122) have reported compounds of the type $RSn(R'COCHCOR'')_n(OPr)_{3-n}$ (where R = Et, R' = CH_3, R'' = C_6H_5 and n = 2; R = Bu, R' = R'' = CH_3, R' = CH_3, R'' = C_6H_5, R' = R'' = C_6H_5 and n = 1 and n = 2). A number of organotin β-diketonates have also been reported by several workers (123-128). Organotin derivatives of thio- β-ketoamines and monothio β-diketones have also been investigated by Mehrotra et al (129, 130).

A number of organotin tropolonate complexes are known such as R_3SnT, R_2SnT_2, R_2SnXT and $RSnXT_2$ (R = alkyl or phenyl; X = Cl, Br, I; TH = Tropolone) where tropolone acts as a bidentate chelating agent bonding through both oxygen atoms. Diorganotin bis-tropolonate have been synthesised by reaction of diorganotin dihalide with sodium or lithium tropolonate (131, 132). Phenyl tin tris-tropolonate and phenyltin chloride bis tropolonate have been prepared by reacting phenyltin trichloride with a solution of tropolone in benzene or ether (133). Komura et al synthesised a mixed chelate dimethyl oxinate tropolonate (134). The existence of the mixed chelate in solution was supported by the NMR studies.

Kojic acid can form complexes with organotin compounds ... Tanaka et al (135) reported the synthesis of dimethyl tin bis-kojate, methyl tin chloride bis-kojate and methyl tin bromide bis-kojate. Dimethyl tin kojate tropolonate (24b) is prepared by the reaction of methanol solutions of dimethyltin dichloride and dimethyl tin bis-kojate with sodium tropolonate in methanol.

Organotin dithiocarbamatesare prepared by reaction of organotin chloride with sodium dithiocarbamate (136, 137) and also by reaction of organotin dithiocarbamates with different alkyl and aryl groups have been prepared by Srivastava et al (139, 141-143, 146) and others (138, 140, 144, 145, 147). Some of these compounds showed considerable biological activities. Alkyl and aryl tin (IV) monothiocarbamates have also been reported by Magee et al (148).

Organotin xanthates are prepared by the treatment of organotin halides and potassium xanthates or by the reaction of organotin halides or oxides with carbon disulphide (149-153).

Organotin halides or oxides react with large numbers of bidentate, tridentate and tetradentate Schiff bases to form complexes e.g., $RSnCl_3$ reacts with HOC_6H_4CH : NR'

(where R = Et, n-Bu and Ph; R' = Me, Et and Ph) to form complexes (154) which have been shown to be non-electrolytes and were assigned an octahedral structure by spectral evidenses. Organotin compounds with tridentate Schiff bases like N-(2-hydroxy phenyl) salicylaldiimines have been reported (155, 156). Diorganotin oxides forms complexes with quadridentate Schiff's bases like salen (bis-salicylaldehydeethylenediimine), aceto-salen, benzoates etc (157). A number of organotin derivatives with a variety of Schiff bases have also been reported by a large number of workers (158-164).

Organotin oximates have been reviewed by Mehrotra et al and his co-workers (165). These compounds are generally prepared by the action of sodium or lithium salts with organotin halides (166-168) or by azeotropic distillation of water from a mixture of organotin oxide or hydroxide with oximes in benzene or toluene (165-167, 169-174). Reaction of alkyl tin alkoxide with oxime also produce organotin oximates (165, 166, 169, 170, 175). Köhler et al (176) have prepared diorganotin derivatives of dicyanoformaldehyde oxime by reacting diorganotin dichloride with silver salt of oxime. Mehrotra et al reported a number of butyl tin derivatives of alkanolamines (177) and oximates $R_2Sn\ (ON \doteq CR'R^2)_2$ and $R_2Sn(OR^3)\ (ON \doteq CR'R^2)$ (179).

Stannylamidoximes have been prepared by Gupta and Goel (178).

Organotin hydroxamates have been synthesised by Harrison (180, 181, 186) mostly by azeotropic distillation of water and he also determined the crystal structure of moisture stable, monomeric (in benzene) triphenyl tin N-phenyl benzo hydroxamate (189).

Extensive work on the organotin complex compounds of N-substituted benzohydroxamic acids have been carried out by Ghosh and others (182-185). They prepared organotin N-substituted benzohydroxamate derivatives of the types R_3SnL, R_2SnL_2, R_2SnLX, $RSnLX_2$ and $RSnX(OCH_3)L$ (where R = Ph, Bu; LH = N-phenyl benzohydroxamic acid, N-phenyl para chloro benzo hydroxamic acid, N-phenyl para nitro-benzohydroxamic acid, N-ortho tolyl benzohydroxamic acid, N-para-chloro phenyl benzohydroxamic acid, N-paratolyl benzohydroxamic acid, N-ethyl parachloro benzohydraxamic acid, oxalyl bis-N-phenyl benzohydroxamic acid, Oxalyl bis-N-paratolyl hydroxamic acid; X = Cl, Br, I, SCN). Some diorganotin derivatives of N-substituted benzohydraxamic acids have also been reported by Das and Nath (187) and monoorganotin derivatives of hydroxamic acids were also prepared by Narula and Gupta (188).

Smith and his co-workers (190) have synthesised a series of diorganotin bis(pyridine carboxylate), diorganochlorotin pyridine carboxylates and monoorgano dichlorotin pyridine carboxylates and investigated their structures by ^{119}Sn Mossbauer and IR spectroscopy. Nelson and Howard (191) also discussed the structures of organotin derivatives of 2-pyridine carboxylic acid.

The complex formation between organotin chlorides and the potentially bidentate ligands like 2-amino methyl Pyridine (AMP) and 2-(2'-aminoethyl) pyridine (AEP) have been investigated by Kumar Das et al (192). The solid state configuration of these compounds have been studied by ^{119m} Sn Mossbauer and IR spectroscopy. Crystal structure and spectroscopic studies of Bis(2-thio-5-nitropyridine)-5-di-n-butyl stannane (IV) compounds have been done by Magee et al (193). Diorganotin derivatives of furoic acid and pyrrole-2-carboxylic acid of the type $(R_2SnS_2CR')_2O$ and $R_2Sn(O_2CR')_2$ (R = Me, Bu, n-octyl, PhCH; R' = 2-furyl, 2-pyrrolyl) have been reported by Sandhu et al (194).

Kumar Das et al (195) have reported the preparation and Mossbauer parameters of several compounds of the type $SnBuPhX_2L_2$, $SnBuPhX_2L$, $SnBuPhL_2$, $SnBu_2PhXL$, $SnBu_2PhL_2$, $SnBu_2PhLL'$, $SnBuPh_2XL$, $SnBuPh_2LL'$ etc where L = DMSO, PPh_3O, $AsPh_3O$, Py, hexamethyl phosphoramide (hmpa), diphenyl

cyclopropane(dpcp), $Ph_2P(O)$, $CH_2P(O)Ph_2$, $Ph_2P(O)CH_2CH_2P(O)Ph_2$ and 2,2'-bipyridyl, N-N'-dioxide, BPh_4 etc. 7.

Organotin derivatives of amino acids habe been the subject of recent interest. A series of air stable s-triorganotin stannyl derivatives of L-cystine and DL-homocystine have been prepared by reacting the appropriate triorganotin hydroxide or bis (triorganotin) oxide with the sulphydril-containing amino acids in methanol/water at room temperature (196). Smith et al (197, 198) reported the structures of sulphur containing amino acids and their esters on the basis of Mossbauer and IR spectra.

Very recently, ^{119}Sn NMR spectra have been reported for toluene solutions of tributyl stannyl ethers of 2,3, 4,6-tetra-o-methyl-D-glucose, 1,2:3, 4-di-o-isopropyliden--D-galacto pyranose, methyl 2,3-di-o-methyl-α-D-gluco pyranoside and methyl 4,6-o-benzilideno-α-D-gluco pyranoside and the dibutyl stannyl ether of the last mentioned sugar (199).

Roy (200) observed that when triphenyl tin hydroxide was refluxed for six hours with alizarin in methanol, a diphenyltin alizarin complex in which two hydrogen atoms of two hydroxyl groups of alizarin were removed, are obtained along with some tetraphenyltin and another unidentified product. Under similar condition triphenyl tin hydroxide reacts with

quinalizarin to produce a polymeric monophenyl tin derivative along with benzene.

A number of organotin (arylazo) benzoates (201, 202) and hepta coordinated organotin aryloxy acetates (203) have been studied by Majee and his co-workers.

Okawara et al (204) first found that dimethyltin and diethyl tin chloride react with 1-nitroso-2-naphthol in methanol in presence of ammonia to form tertaalkyl 1, 3-bis (1-nitroso-2-napthoxy) distannoxanes. Mehrotra and Bachlas (205) described the preparation of a few monotin derivatives of 1-nitroso-2-naphthoxide. Biswas (206) also discussed reaction of organotin compounds with 1-nitroso-2-naphthol or 2-nitroso-1-naphthol. He found these reactions are very complex in nature and a number of products like distannoxanes, polystannoxanes or stannoic acid derivatives could be formed.

1,5-diphenyl thiocarbazone (Dithizone) has been used as a colorimetric reagent for organometallic compounds (207, 208) for a number of years and the isolation of several solid organotin dithizonates with mono-, di- and tri organotin moiety have been reported (209, 210). The organotin dithizonates, $R_3Sn(HDz)$, $R_2Sn(HDz)_2$, $R_2Sn(HDz)X$ and $RSn(HDz)XY$ (R = Me, Ph, Bu, Pr, P-tolyl, Bz; X = Cl, Br, I, NCS; Y = substituted benzohydroxamic

acids; H_2Dz = Dithizone) have been isolated and characterised by analytical and spectral evidences. Test of triphenyl and tributyl tin dithizonates as fungicides showed excellent activity against a number of plant pathogenic fungi (212). Similar to dithizone complexes, organotin complexes of 1,5-diphenyl-carbazone (oxygen analogue of dithizone) have been isolated very recently (211). The well characterised organotin complexes of diphenyl carbazone are of the type R_3SnL, R_2SnL_2, $RSnL_3$, R_2SnLX (R = Me, Bu, Ph, p-tolyl, cyclohexyl, Pr; X = Cl, Br, SCN and LH = Diphenyl carbazone). Some of these organotin diphenyl carbazonates showed excellent fungitoxicity against a number of plant pathogenic fungi (212).

The organotin derivatives of 8-hydroxyquinoline (oxine) and substituted 8-hydroxy quinolines have given a great impetus in the studies of organotin complex compounds. These are stable, well defined compounds and have been studied very extensively.

Organotin oxinates of the type $R_{4-n}SnOx_n$ (R = organic group, OxH = 8-hydroxyquinoline, n = 1,2,3) (111, 213-216) are prepared either from the organotin halides and sodium/thallium (I) oxinate (111, 213) or from organotin halides and oxine itself, the hydrogen halide formed is removed by a base such as ammonia (217) and also by

reacting organotin oxide with oxine (169, 218). Triorganotin oxinates have also been prepared by reacting triorganotin chloride with a mixture of oxine and sodium methoxide (213). Bis-(penta-fluorophenyl) tin bis-oxinates have been prepared from a mixture of tetra-kis (penta fluorophenyl) tin or tris (penta-fluoro phenyl) tin chloride and an excess of oxine in ethanol under reflux (219).

In the crystal structure of dimethyl bis (8-hydroxy-quinolinate) which assumes a cis-dimethyl tin groups (110.7°), 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 = 75.8°) (220).

When a diorganotin dihalide and oxine are allowed to react in a 1:1 molar ratio in the absence of a base the halooxinate is formed (244, 235). These compounds can also be prepared through disproportionation of a halide and a dioxinate, refluxing in benzene or ethanol (213, 216, 221-224) or by the reaction between a dioxinate and a silver halide (221). The halogen in halooxinate can be substituted by other groups (221, 223, 224) like NCS^- or SO_4^{-2} or NO_3^- or I^- etc. The halogen atom of penta coordinated tin halo oxinate undergo ready exchange with groups such as butyl, alkoxy or even with chelates e.g. acetyl-acetonates (213, 224) which may disproportionate into the

diorganotin dioxinates.

Organotin halide bis oxinate, $RSnX(Ox)_2$ (R = CH_3, n-Bu, Ph; X = Cl, Br) have been prepared by reacting organotin trihalides with oxine (1:2 mole) in ethanol followed by neutralisation with aqueous ammonia or sodium acetate (213, 225). Datta (226) has prepared phenyl tin halo oxinate by reacting diphenyl tin dioxinate with mercuric halides in ether at room temperature.

Synthesis of carboxylate derivatives of tin oxinates in which the carboxylate groups are not ionic, chelated or bridging (227) have been reported. The synthesis involve primarily the conventional halogen-carboxylate exchange as well as tin-carbon bond cleavage.

Roy (200) prepared compounds of the type $PhSn(OCOR')Ox_2$ (R = CH_3, CH_2CH_3, CH_2Cl, CF_3) and R_2SnOx_2 (R = CH_3OCO, CH_3CH_2OCO, $ClCH_2OCO$ etc.).

A novel compound, $[n\text{-}C_4H_9Sn(Ox)_2]_2S$ was prepared from n-butyl tin sesquisulphide and oxine in boiling toluene (229).

A few organotin trioxinates have been prepared (216, 218) in good yields by using either of the following reactions:

$$R_2Sn_2O_3 + 6OxH \xrightarrow[\text{benzene}]{\text{boiling}} 2RSnOx_3 + 3H_2O$$

$$RSnCl_3 + 3NaOx \longrightarrow RSn(Ox)_3 + 3NaCl$$

(R = Et, Bu, Ph)

Butyltin isopropoxide oxinate of formula $BuSn(Opr^i)_{3-n}(Ox)_n$ have been prepared by Mehrotra et al (122) by reacting butyltin tris isopropoxide with oxine and removing isopropanol by azeotropic fractionation with refluxing benzene, the products depend upon the mole ratio of the reactants used.

A detailed analysis of spectrophotometric data on triphenyl tin oxinate in 95% ethanol (230) and in methanol and benzene/methanol mixture has been reported (231). The reactions of mercuric halides with some organotin oxinates have also been examined (232).

Organotin derivatives of substituted oxines have also been reported. Srivastava et al (233) have prepared some diaryl tin bis oxinates/2-methyl oxinates and diaryl tin chloride oxinate/2-methyl-oxinates. Sen et al (234, 235) have synthesised and characterised several diorganotin bis (mono- and di-substituted oxinate) of the types R_2SnL_2 where R = CH_3, C_2H_5, C_4H_9 and LH = 5-Nitrooxine; 5, 7-

dichloro oxine, 5,7-dibromo oxine, 5-nitro-7-bromo oxine, 5,7-diiodo oxine, 5,7-dinitro oxine etc.). Sen et al (236) have also reported the synthesis and spectral studies on mono- and triethyl tin (IV) and triphenyl tin (IV) chelates with substituted-8-quinolinols. The compounds are of the types $RSnL_3$, $RSnL_2X$, R_3SnL (where R = C_2H_5, Ph; LH = 5-nitro oxine, 5,7-dinitro oxine, 5,7-dichloro oxine, 5,7-dibromo oxine, 8-mercapto oxine etc.; X = Cl) (8-quinolinato)-(1,3-diphenyl-propanedionato) diethyl tin (IV) and (8-quinolinato) (1-phenyl-1,3-butanedionato) diethyltin (IV) have also been reported.

Smith et al (237) have studied the synthesis and Mossbauer spectra of some mixed chelates of diorganotin (IV) complexes of the types RR'SnLL' (R = R' = Me, Ph, Bu; R = Bu, R' = Ph; L, L' = 8-quinolinate, 2-methyl-8-quinolinate etc.).

Majee et al (238) have synthesised some polynuclear organotin complexes of the types $R'_2Sn(LSnR_3)_2$ ⌈R = Ph, Bu; R' = Ph, Bu; LHH' = 5-(2'-carboxy phenyl) azo-8-quinolinol (H and H' represent respectively, the carboxyl and hydroxyl hydrogen), R_3SnLH and $R'_2Sn(LH)_2$. They have also prepared organotin-copper mixed complex of the type $Cu(LSnPh_3)_2$ where LHH' = 5-(2'-carboxy phenyl)-azo oxine (239). Metal and organometal complexes of ortho-carbazoxines

have been reported (240). The complexes are of three types, viz, the carboxylates, the quinolinates and the carboxylate-quinolinates.

From the preceding discussions, it is apparent that alkyl or aryl tin compounds can form large varieties of inner complexes or adducts with ligands. In all these complexes, it was found that the organotin moieties can form stable complexes with both hard and soft bases, though enough work has not been done so far to find their relative stabilities. Very little work has been done so far about the Lewis acid character of estertin compounds. Estertins have very recently been proved to be highly interesting type of compounds which may be termed as a new generation of PVC stabilizers with unlimited promise. Before discussing the current investigation we would like to discuss briefly about the estertin type of compounds and their properties as PVC stabilizers.

Estertin compounds and their PVC stabilizing properties

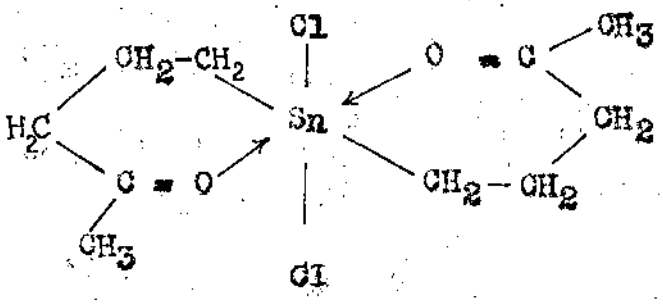
The importance of a stabilizer for PVC polymers, suitable for commercial uses can not be over emphasized. It is generally accepted that the organotin compounds are the best type of stabilizers for PVC, when the question of clarity and high temperature processing are considered.

Organotin compounds were first introduced as stabilizers for PVC since 1939. Initially, dibutyltin dilaurate and dibutyltin maleate followed by other dibutyl tin compounds and dioctyltin and dimethyltin derivatives have gained rapid acceptance in the market over other types of stabilizers inspite of their relatively high cost. In recent years some mono organotin compounds are also used along with diorganotin compounds as PVC stabilizers.

Much has been learnt of the chemistry of PVC stabilization since this topic was reviewed in 1974 (241). The mode of action of the R groups and X groups of R_2SnX_2 as PVC stabilizers have been studied by several workers (242-257). Poller et al (228) after consideration of relevant facts suggested that reduction of the Lewis acidity of the resulting organotin chloride will improve the efficiency of the stabilizer. They prepared (258, 259) di-(4-ketophenyl) tin di (isooctyl thioglycolate) in which it was expected that the keto groups would be free in the stabilizer but coordinated to tin in the corresponding dichloride.

$(CH_3COCH_2CH_2CH_2)_2\ Sn\ (SCH_2COOC_8H_{17}\text{-}i)_2$

$\downarrow HCl$

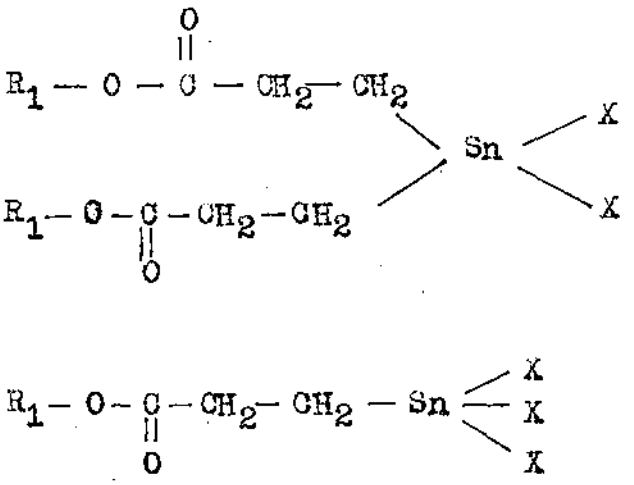


The IR spectra showed that the C = O band in the dichloride at 1680 cm^{-1} (i.e. a position characteristic of co-ordinated carbonyl) was displaced to the "free" position of 1705 cm^{-1} when the more powerful donor 2,2'-bipyridyl was present. NMR spectra showed clearly that coordination of the keto groups is absent in the stabilizer but present in the dichloride. Subsequent tests (259) showed that the ketopentyl tin compounds are more than twice as effective in stabilization than the corresponding butyltin derivatives.

Though the organotin compounds are best type of stabilizers for PVC, these are relatively more expensive and the preparation of intermediate organotin compounds

involve hazardous routes. The major break through in tin chemistry for organotin stabilizers occurred when an entirely new process for organotin intermediate was discovered (26, 260, 261). The process is simple, relatively inexpensive, does not involve the complicated or hazardous routes used for making alkyltin intermediates. This has lead to the development of a completely new class of organotin stabilizers collectively known as "Estertins". Their potentiality as PVC stabilizer has been competently reviewed recently (303).

The estertin stabilizers have the general structure



(R_1 = alkyl or aryl groups; X = halogen)

The unique structure of estertins, compared with alkyltins give low volatility and low extractibility while retaining all the virtues of conventional alkyltins e.g. excellent heat stability and clarity.

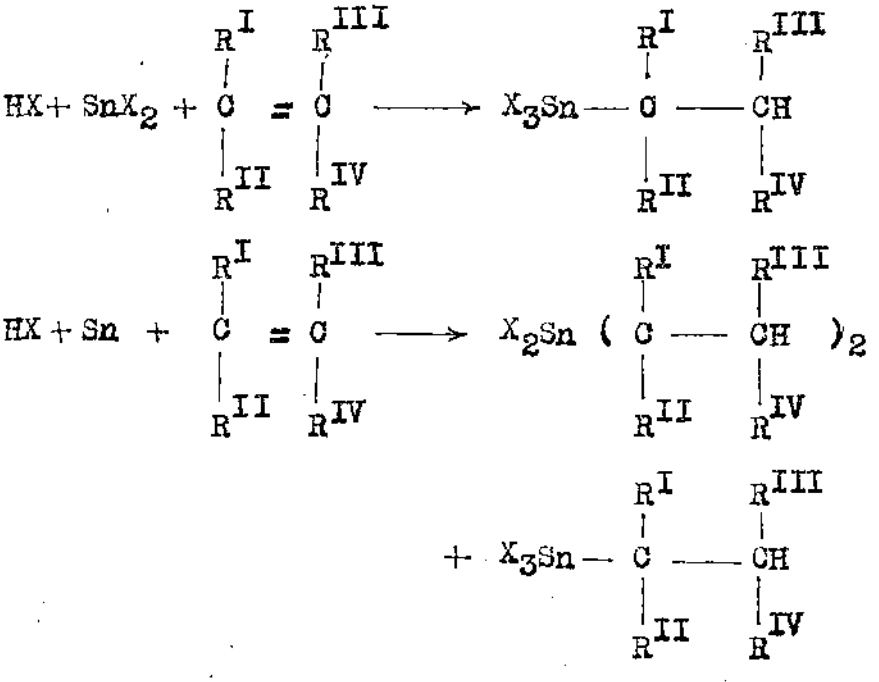
The above types of β-substituted alkyltin halides were known for quite sometime and their synthesis has been described in a review by Omae et al (262). The major reaction was the direct reaction between metallic tin and the corresponding β-substituted alkyl halide.

$$2XCH_2CH_2R + Sn \longrightarrow X_2Sn(CH_2CH_2R)_2$$

[where X = Br, I; R = CO_2H, CO_2R', COR' (R' = alkyl)]

Monoalkyl tin trihalide was prepared either by disproportionation of R_4Sn with SnX_4 (263) or by reaction of RX with SnX_2 (264). By the disproportionation of tetracyanoethyltin with stannic halides a range of cyanoethyltin halides were prepared by Reinfenberg and Conisidine (265). The other widely employed route to functionally substituted organotin compounds is hydrostannation and a review by Leusink (266) demonstrated the importance of this approach. The hydrostannation route was previously limited to the synthesis of tetra alkyltin compounds and trialkyl tin halides.

The novel synthetic route to prepare functionally mono- and disubstituted organotin halides through the hydrostannation route has been recently discovered by the unique work of Hutton et al (267, 263, 260, 261). They have shown that the reactions between hydrogen halides, stannous halides and α,β-unsaturated carbonyl compounds yield β-substituted alkyltin trihalides and the reactions between hydrogen halides, tin and the same α,β-unsaturated carbonyl compounds to give largely bis (β-substituted alkyl) tin dihalides in substantial amount. The following equations represent the overall reactions.



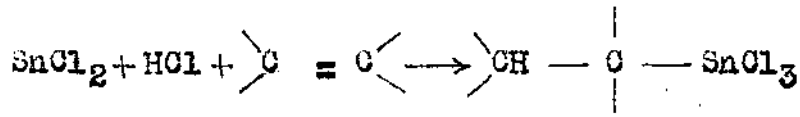
(X = Cl, Br, I; R^{I}, R^{II} and R^{III} are H or Me; R^{IV} contains $-\overset{O}{\overset{\|}{C}}-$)

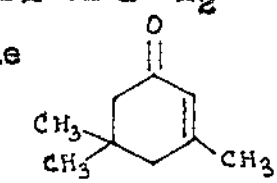
The reaction are non hazardous, highly specific and proceed in high yield at ambient temperatures and atmospheric pressure. A wide variety of activated olefins are used and largely these are α,β-unsaturated esters, α,β-unsaturated ketones, acids and amides etc. Notable exceptions to these rules are maleic acid esters and isophorone. Their lack of reactivity is highly significant. Like hydrochloric acid, hydrobromic and hydroiodic acids will also undergo the reactions. Temperatures between approximately -10 and 120°C can be employed. During the preparation of disubstituted alkyltin dichlorides the formation of monosubstituted alkyltin trihalide can be minimised by slow passage of hydrogen halide which prevents formation of tin(II) chloride. The more sterically hindered monomers tend to have a reduced rate of reaction but still give high yields. In every case only the β-adduct is isolated as shown by NMR spectroscopy. Any solvent which does not interact with HCl may be used. With certain monomers, for example, butyl acrylate, the monomer acts as its own solvent and complexing agent and no other solvent is necessary. The yield of organotin is lowered, because of hydrolysis and hydrochlorination of the monomer. If the trichlorostannane

is performed an oxygenated solvent must be used. Monomers such as styrene which add HCl or polymerise can not be used. Intramolecular carbonyl coordination to tin occurs in these β-substituted organotin compounds.

Hutton et al (loc. cit) suggested that the scope of the above reactions is quite significant and may be indicated by the following Tables I & II.

TABLE - I



Reactive Monomers	Unreactive Monomers
Acrylates $CH_2 = CHCOOR$	Acrolein $CH_2 = CHCHO$
Methacrylates $CH_2 = CMeCOOR$	Alpha Olefins $CH_2 = CH\text{-}R$
Crotonates $CH_3CH = CHCOOR$	Allyl chloride $CH_2 = CHCH_2Cl$
Acrylic Acid $CH_2 = CHCOOH$	Allyl Alcohol $CH_2 = CHCH_2OH$
Methacrylic Acid $CH_2 = CMeCOOH$	Styrene $Ph\text{-}CH = CH_2$
Acryloyl Chloride $CH_2 = CHCOCl$	Isophorone 

Contd..

TABLE - I (Contd..)

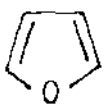
Reactive Monomers	Unreactive Monomers
Vinyl Ketones $CH_2 = CHCOR$	Vinyl Acetate $CH_3COOCH = CH_2$
Phorone $Me_2C = CHCOCH = CMe_2$	Acetylene $CH \equiv CH$
Propiolic Acid $CH \equiv CCOOH$	Furan 
Acrylamide $CH_2 = CHCONH_2$	Maleic Acid Esters $ROOCCH = CHCOOR$
Diethyl Ethylidene Malonate $MeCH = C(COOEt)_2$	Phenyl Acetylene $Ph-C \equiv CH$

TABLE - II

$$Sn + 2HCl + 2 \rangle C = C\langle \longrightarrow \left(\rangle CH - \overset{|}{\underset{|}{C}} - \right)_2 SnCl_2$$

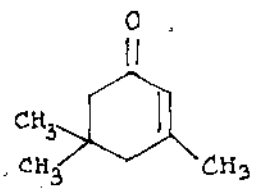
Reactive Monomers	Unreactive Monomers
Acrylates $CH_2 = CH.COOR$	Alpha olefins $CH_2 = CH-R$
Methacrylates $CH_2 = CH.MeCOOR$	Styrene $PhCH = CH_2$
Crotonates $CH_3CH = CH.COOR$	
Acrylic Acid $CH_2 = CH.COOH$	Isophorone 

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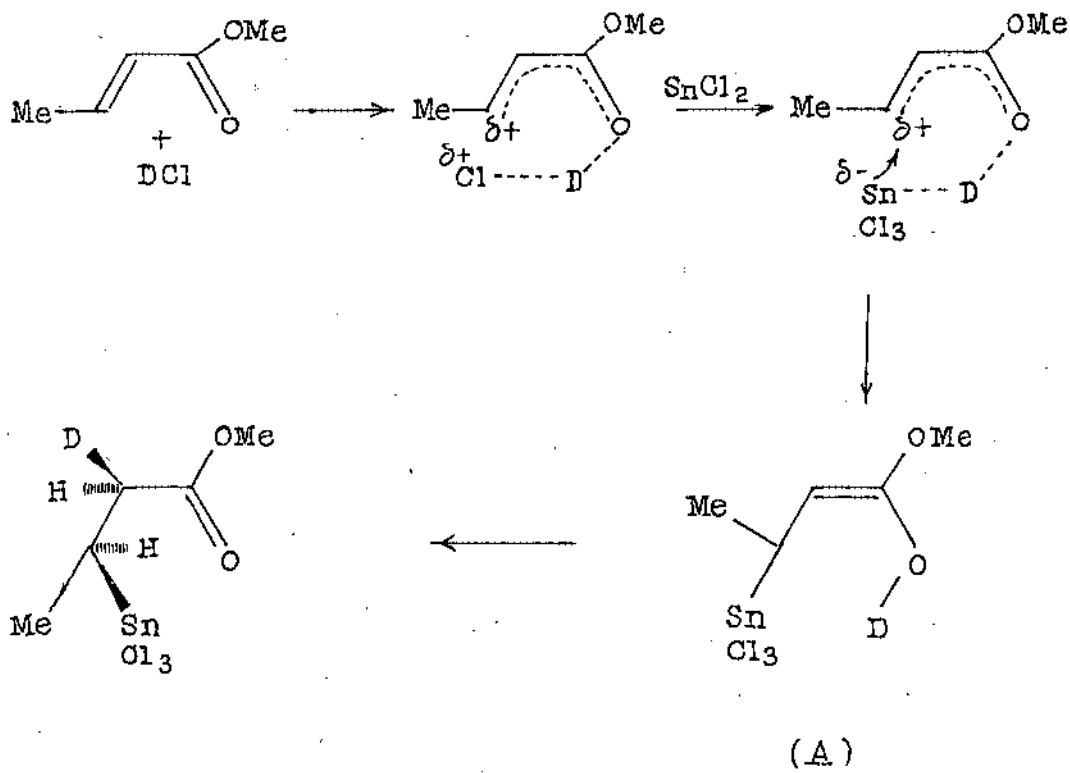
TABLE - II (Contd..)

Reactive Monomers	Unreactive Monomers
Acryloyl chloride $CH_2 = CH.COCl$	Maleic Acid
Methyl Vinyl Ketone $CH_2 = CHCOCH_3$	ROOCCH = CHCOOH
Phorone $Me_2C = CH.COCH = CMe_2$	Maleic Acid
Propiolic Acid $CH \equiv C.COOH$	Esters ROOCCH = CHCOOR
Acrylamide $CH_2 = CH.CoNH_2$	
Diethyl Ethylidene Malonate $MeCH = C(COOEt)_2$	

Hutton et al (loc. cit) explained the experimental observations by proposing the following mechanism. The primary step in the in-situ reaction condition (in non-polar and possibly in all solvents) must be monomer solvation of HCl. This solvated HCl then interacts with $SnCl_2$ to give monomer:$\longrightarrow HSnCl_3$ aggregate which then collapses by attack of $Cl_3Sn^{\delta-}$ at the carbon atom β to the ester group. The complete reaction sequence may be shown as follows for $DSnCl_3$ and MeCl.

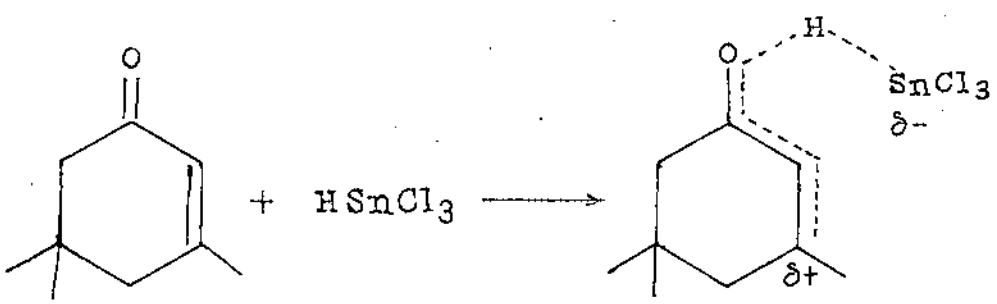


(A)

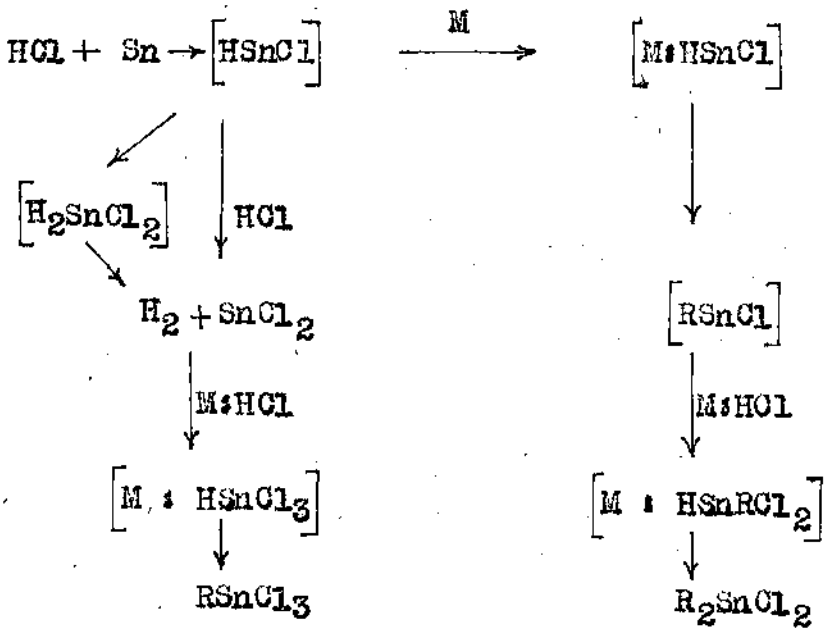
The above mechanism represents a tin hydride addition to a C = C double bond with the $Sn^{\delta-}---H^{\delta+}$ polarisation of the tin-hydrogen bond. The $HSnCl_3$ provides a unique example of a tin-hydride species reacting in this fashion unlike all the previous tin-hydride additions have been either by free radical or with the $Sn^{\delta+}---H^{\delta-}$ polarisation of tin hydrogen bond.

In order to achieve "Cis" addition to the double bond, ketonisation of the enole intermediate [Structure (A) in the above reaction] must occur by an intra-, rather than an intermolecular process. The latter process would almost certainly result in "trans" addition, by analogy with the addition of DCl to α,β-unsaturated esters, in which the final ketonisation step is catalysed by other DCl molecule (269). In the present case, the deuterium transfer may be assisted by a chlorine atom of the $SnCl_3$ group.

The inactivity of the isophorone results from the unfavourable geometry of the complex, since the $SnCl_3^-$ entity will be located too far from the active site as shown below



Formation of Bis(β-substituted alkyl) tin dihalide is, somewhat more difficult to explain. Initially, Hutton et al (268) proposed a tentative mechanism of the following type,



(where, M = $\begin{matrix} R^{I} & R^{III} \\ | & | \\ C & = C \\ | & | \\ R^{II} & R^{IV} \end{matrix}$; R = $\begin{matrix} R^{I} & R^{III} \\ | & | \\ C & -- CH \\ | & | \\ R^{II} & R^{IV} \end{matrix}$;

R^{I}, R^{II} and R^{III} are H or Me; R^{IV} contains $-\overset{O}{\overset{\|}{C}}-$)

The discovery that ester substituted monoalkyltin trihalides can react with metallic tin to give the corresponding β-substituted dialkyltin dichlorides, suggested a simpler mechanism for the formation of the dialkyltin compounds in the reaction between hydrogen chloride, tin and α,β-unsaturated carbonyl compounds.

$$2RSnCl_3 + Sn \longrightarrow R_2SnCl_2 + 2SnCl_2$$

(where, R = $-\overset{R^{I}}{\underset{R^{II}}{C}}-\overset{R^{III}}{\underset{R^{IV}}{C}}-$; R^{I}, R^{II}, R^{III} = H or Me; R^{IV} contains $-\overset{O}{\overset{\|}{C}}-$)

In view of several experimental observations, it appeared that the most feasible mechanism for the formation of Bis (β-substituted alkyl) tin dihalides from the interaction of hydrogen halide, tin and α,β-unsaturated carbonyl compounds is as follows

$$HCl + Sn \longrightarrow [HSnCl] \xrightarrow{HCl} H_2 + SnCl_2$$

$$CH_2 = CHCO_2Me + HCl + SnCl_2 \longrightarrow [CH_2 = CHCO_2Me + HSnCl_3]$$

$$\downarrow$$

$$RSnCl_3$$

$$RSnCl_3 + [HSnCl] \longrightarrow [RHSnCl_2] + SnCl_2$$

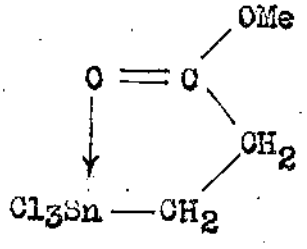
$$[RHSnCl_2] + CH_2 = CHCO_2Me \longrightarrow R_2SnCl_2$$

$$(R = -CH_2CH_2CO_2Me)$$

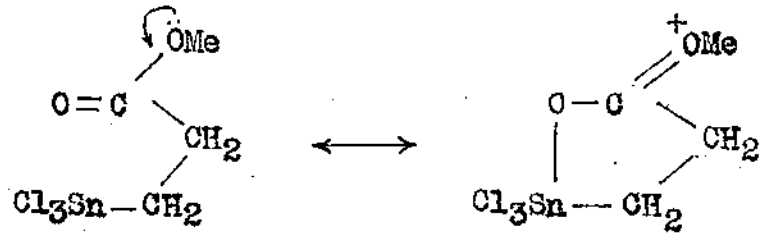
Initially the monoalkyl tin trichloride ($Cl_3SnCH_2CH_2CO_2Me$) is formed and is then largely converted to the dialkyltin compound via the halogenostannane intermediate ($Cl_2SnHCH_2CH_2CO_2Me$). It appears possible that this step involves the intermediate formation of $[HSnCl]$ which is effective in the reduction.

With a very few exceptions the carbonyl stretching frequencies in most of the monosubstituted alkyl tin trichlorides lie between 1655 and 1665 cm^{-1} roughly 80 cm^{-1} in most cases to lower the frequency than the saturated analogues of the parent α,β-unsaturated carbonyl compound. The ester methyl signal in $Cl_3SnCH_2CH_2CO_2Me$ is situated down field from the corresponding signal in $CH_3CH_2CO_2Me$ and a similar effect is observed for the methyl signals in $Cl_3\overset{Sn}{\wedge}CH_2CH_2COMe$ and CH_3CH_2COMe. These spectroscopic effects are consistent with carbonyl coordination to Sn, since this phenomenon reduces the C = O bond order (270) (and hence the carbonyl stretching

frequency) and also the perturbation of the electron distribution causes a deshielding effect on the relevant protons. Since the carbonyl stretching frequency for any compound is unaffected by dilution in toluene or ethereal solvents, the carbonyl coordination to Sn is almost certainly intramolecular in origin. For example, the structure of β-carbomethoxy ethyl tin trichloride can be represented as



The IR spectra of $Cl_3SnCH_2CH_2CO_2Me$ and $CH_3CH_2CO_2Me$ shows that ν(C - O) for the ester group in $Cl_3SnCH_2CH_2CO_2Me$ lies some 63 cm^{-1} to higher frequency than the same vibration in $CH_3CH_2CO_2Me$ (1270 cm^{-1} vs 1207 cm^{-1}). Possibly the methoxy oxygen lone-pair electrons are also involved in the delocalisation of the ester carbonyl electron density to Sn. The intramolecular coordination may, therefore, be represented as follows



Intramolecular carbonyl coordination of the type described above is significantly stronger in the esters and ketones than that in the corresponding dialkyltin compounds described in the review of Omae (262).

In all applications tested the preference of estertins was found to be equivalent to or better than available commercial alkyltin stabilizers. Furthermore primary tests to assess the health and safty aspects of the estertins showed them to be only mild skin irritants and to cause no eye irritation (303). Extraction tests in different media showed estertins to be less extractive than an octyl tin. In addition, acute oral toxicity values (LD_{50}) in rats showed estertin compounds to give higher values than octyltin compounds. Due to these very promising data the first-gneration of estertin stabilizers was developed which were four liquid thiotin stabilizers. Naturally, the possibility is that more than one of the estertin stabilizers can be used for applications other than for those originally developed. The four liquid thiotin

stabilizers (the first generation stabilizers) showed promising results in the major applications, viz. extrusion, calendering, injection molding, blow molding, plastisol coating and rotational casting, compared to the octyl, butyl, methyl tin stabilizers as well as barium-cadmium-zinc and cadmium - zinc stabilizers (26).

Direct synthesis of carbonyl group containing organotin compounds and their properties were also reported by Matsuda et al (271, 272). Several other workers also have reported the preparation of functional alkyltin chlorides (273-285). Preparation of $R_qSn[S(CH_2)_mO_2CR']_{4-q}$ (R, R' = C_{1-20} alkyl, cycloalkyl, aryl, aralkyl; m = 2,3 ; q = 1-2] useful as polymer stabilizers have been reported (286). Mack (287) has reported some organotin mercapto di-carboxylic acid esters, useful as PVC stabilizers. A facile route to (β-alkoxy carbonyl) vinyl stannanes has been described by Yasufuku et al (288).

The mechanism of stabilisation of PVC by organotin compounds was studied by ^{119m}Sn Mossbauer spectroscopy of $Bu_2Sn(SCH_2CO_2C_8H_{17})_2$ in thermally degraded PVC (289). Dowrkin (290) reported the preparation of $BuSn(S)CH_2CH_2O_2C(CH_2)_6Me$. Preparation and study of various estertin and other PVC stabilizers have been reported by several workers (291-297). Bis (trialkyl stannyl) derivatives were manufactured for antifouling coatings (298).

The Lewis acidity of estertin chlorides $Cl_3SnCH_2CH_2CO_2R$ (R = Me, Pr^i, Ph and H) and $Cl_2Sn(CH_2CH_2CO_2R)_2$ (R = Me and Pr^i) has been investigated by Wardell et al (299). From the stability constants determined for adducts of these Lewis acids with nitrogen donors, e.g., D = bipy, Phen, Py, quinoline and aniline, it was concluded that (i) $Cl_3SnCH_2CH_2CO_2Me$ appears as a strong Lewis acid as $MeSnCl_3$ towards bidentate ligands and a single Py molecule, (ii) $Cl_3SnCH_2CH_2CO_2Me.D$ (D = monodentate ligand) is a proper acceptor than $MeSnCl_3.D$ but comparable to Me_2SnCl_2 towards D and (iii) $Cl_2Sn(CH_2CH_2CO_2R)_2$ is a weak acceptor than Cl_2SnMe_2 towards Phen and bipy. For $Cl_3SnCH_2CH_2CO_2R$ the sequence of acidity was established as R = Ph > Me > Pr^i > H towards bipy. Adducts of $Cl_3SnCH_2CH_2CO_2Me$ and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ with phen and bipy showed similar Mossbauer parameters to those for other phen and bipy adducts of organotin trichloride and diorganotin dichloride.

Gopinathan et al (300) reported the novel chelated compounds of Bis-(β-carbomethoxy ethyl) tin dichloride with various bi- and tridentate chelating ligands like acetylacetone, salicylaldehyde, 8-hydroxyquinoline, dibenzoylmethane, benzoyl phenyl hydroxy lamine, 2-hydroxy benzophenone, 2-hydroxy 4-methoxy benzophenone

and salicylaldazine. They also reported (301) molecular addition complexes of β -carbaalkoxy ethyltin chlorides with neutral ligands such as pyridine, triphenylphosphine, hexamethylphosphoramide, triphenylphosphine oxide, tri-n-octylphosphine oxide, 1,10-phenanthroline and 2,2'-bipyridyl. Kumar Das et al (302) reported the preparation and spectroscopic studies of the complexes of Bis(β -carbomethoxy ethyl) tin dichloride of formula $(MeO_2CCH_2CH_2)_2SnCl_2L_2$ [L = Ph_3AsO, Ph_3PO, L_2 = 1, 10-phenanthroline, 1,1'-bipyridyl, $[Ph_2P(O)]_2CH_2$], $(MeO_2CCH_2CH_2)_2SnL'_2$ [where L' = oxinate (L^2), S_2CNMe_2, S_2CNEt_2], and $(MeOCCH_2CH_2)_2SnClL^2$.

The compound $(CH_3CO_2CH_2CH_2)_2Sn(Ox)_2$ (OxH = 8-hydroxiquinoline) was reported by Gopinathan et al (300) in 1980 and by Kumar Das et al in 1981 (302). The author of the present investigation also reported the same compound along with a number of other complexes at the 68th Session of Indian Science Congress Association, January, 1981 (communicated during August, 1980). The method of preparation of this compound reported by the author is somewhat different from those reported by Gopinathan et al and Kumar Das et al.