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SYNTHETIC STUDIES IN ORGANOTIN
AND SUBSTITUTED TITANOXANE COMPOUNDS

I wish to express my deep sense of gratitude to Dr. J. Gupta, D.Sc., F.R.S.I., for suggesting the work and giving inspiring guidance.

My sincere thanks to Mr. G. Gopinathan for his ungrudging co-operation and help during the progress of the work; and to my other colleagues in the Organometallic Group.

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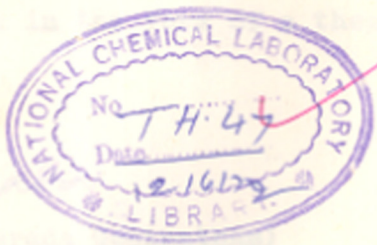
Thesis submitted by
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to the

UNIVERSITY OF POONA

for the degree of

DOCTOR OF PHILOSOPHY

[in Chemistry]



NATIONAL CHEMICAL LABORATORY
POONA 8

-: A C K N O W L E D G M E N T :-

I wish to express my deep sense of gratitude to Dr. J. Gupta, D.Sc., F.N.A., for suggesting the problem and giving inspiring guidance.

My sincere thanks are due to Dr. C. Gopinathan for his ungrudging co-operation and help during the progress of the work; and to my other colleagues in the Organometallic Group. I express my thanks to Dr. C. I. Jose and Dr. K. G. Das for their most helpful discussions in the interpretation of infra-red and mass spectra. My thanks are also due to my colleagues in physical and Organic Divisions of this Laboratory for assistance in infra-red and mass spectra, and carrying out microanalyses of samples.

I thank the Director, National Chemical Laboratory, for his permission to submit this work in the form of a thesis for my Ph.D. degree.

Sarada

Poona 8.

Chelated Ti(IV) No. (Mrs. Sarada Gopinathan)

17 FEB 1972

Dihalotitan chelates 83; Dibutyltin chelates 84; Diethyltin chelates 131; Triphenyltin chelates 104; Reactions of organotin chelates 113.

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SECTION I : GENERAL INTRODUCTION AND SUMMARY

GENERAL INTRODUCTION AND SUMMARY

The main group elements of the Fourth Group in the Periodic System of Elements are carbon, silicon, germanium, tin and lead. The tendency to form organometallic compounds is much stronger among these elements than those of the sub-group consisting of transition metals (Ti, Zr, Hf, Th). In fact, it was the accepted view for over a quarter of the present century that transition metals do not as a rule form organometallic compounds. The reason lies in the fundamental difference in the atomic structure between the two groups of elements as shown below:

Main Group Elements (Gr. IV) Electronic structure of the atom

Atomic Number	Name of Element	Completed Shells	Incomplete Shells
6	Carbon	K	$2s^2 2p^2$
14	Silicon	KL	$3s^2 3p^2 3d^0$
32	Germanium	KLM	$4s^2 4p^2 4d^0 4f^0$
50	Tin	KLM	$4s^2 4p^6 4d^{10} 4f^0 5s^2 5p^2$
82	Lead	KLMN	$5s^2 5p^6 5d^{10} 5f^0 6s^2 6p^2$

Transition Group Elements (Gr. IV)

22	Titanium	KL	$3s^2 3p^6 3d^2 4s^2$
40	Zirconium	KLM	$4s^2 4p^6 4d^2 4f^0 5s^2$
72	Hafnium	KLMN	$5s^2 5p^6 5d^2 5f^0 6s^2$
90	Thorium	KLMN	$5s^2 5p^6 5d^{10} 5f^0 6s^2 6p^6 6d^2 7s^2$

The proximate arrangement of the four outermost electrons ($ns^2 np^2$) in the atoms of the main group suggest the possibility of two (+2 and +4) oxidation states, corresponding to the involvement of either the two p electrons or all the s and p electrons. The bipoisitive state is stabilized because of the presence of the relatively "inert electron pair" (ns^2) of Sidwick.¹ This situation is, however, seldom found in carbon and silicon because of the tendency of these small atoms to saturate themselves covalently, but it becomes increasingly important with increasing atomic size. The bipoisitive species, common in tin and lead, are both known as stable ions in polar solvents.

In the tetrapoisitive state, the elements of this group give rise to compounds which are predominantly covalent and are more acidic than those in the lower oxidation state. Attainment of the higher oxidation state becomes increasingly difficult from carbon to lead with increasing electropoisitive character of the element. Regarding Lewis acidity, carbon does not show acceptor properties in its tetraivalent state owing to octet limitations; others are weak acceptors towards halide or oxy-ions. In the tetra-covalent state, all the elements in this family are characterized by a tetrahedral disposition of the four valencies. Formation of this bond by sp^3 hybridization is facilitated by the proximate presence of the two s and two p electrons in the same valence shell of the atoms of this group, a feature which is absent in the atoms of the transition sub-group elements.

Tin shows the two stable valence states, 2 and 4, in a series of its compounds in which the stannous compounds are more electrovalent in nature. The energy for complete removal of all the four external electrons is high, so tin (IV) compounds tend to be covalent. The valence electrons undergo sp^3 hybridization and the four valencies are symmetrically directed to the corners of a tetrahedron, as in carbon. In the stannous compounds the p electrons effect bonding by two orbitals (p_x and p_y) at an angle of about 90° and the s electrons remain as a free pair.

Within the elements of this group, their bond lengths to carbon increase considerably. C-C 1.54, Si-C 1.94, Ge-C 1.99, Sn-C 2.17 and Pb-C 2.29 $\overset{\circ}{\text{A}}$. The increased bond length for Sn-C explains the increased reactivity and the relatively lower thermal stability of the tin alkyls compared to their silicon and germanium analogues. Long bonds, besides being of low strength, lessen the screening effect of the ligands on the central atom, making the latter more accessible to nucleophilic attack. The relationship is also seen clearly in the dissociation energies of the M-C bonds among the metal tetra alkyls, the mean values being C-C 87, Si-C 70, Ge-C 60, Sn-C 50 and Pb-C 31-37 k cal/mole. Because of the high atomic weight of tin and the relative weakness of the Sn-C bonds, the skeletal vibrations of organotin compounds have low frequencies, generally outside the detection range of the infrared spectrometer with sodium chloride optics (below 600 cm^{-1}).

The availability of empty d orbitals in the tin atom makes possible the expansion of its coordination number to greater than four in many organotin compounds. Donation of electrons by ligands into the empty orbitals is facilitated in tin both for sterical reasons and because of the negligible tendency of any metal-ligand $d\pi-p\pi$ interaction in this element of high atomic number. Five coordination is commonly met with in R_3Sn^{IV} , and six coordination in R_2Sn^{IV} and RSn^{IV} type compounds. In a number of the latter two types, penta-coordination has also been either established or potentially recognized.^{2,3} Penta- and hexa-coordinations have been postulated in the organotin chelates with 8-hydroxyquinoline (oxime) and acetylacetonate as chelating ligands. Triorganotin mono-oxinates are examples of penta-coordination, while dialkyltin dioxinates and di-acetylacetonates of hexa-coordination of the tin(IV) atom. Assuming octahedral geometry for the hexa-coordinates, isomers would be expected in suitable cases. Attempts at resolution of the dialkyl/diaryl-tin oxinates resulted in the isolation of only one form believed to be the trans isomer.⁴

Much less is definitely known, however, about the stereo-chemistry of stannous complexes; and practically no work has been reported on stannous chelates. It is, of course, known generally that the non-bonding electron pair in Sn^{II} is not completely inert in a stereochemical sense and may function as a donor. On the other hand, Sn^{II} halides

dissolve readily in donor solvents (acetone, ethyl acetate pyridine) to give weak complexes which are probably Ψ -tetrahedral (pyramidal). In inorganic complexes, bivalent tin exhibits coordination numbers 4 and 3 in the compounds M_2SnX_4 , $SnCl_2 \cdot 2H_2O$, $SnCl_2 \cdot 2NH_3$, and $MSnX_3$; $SnCl_2 \cdot NH_3$, $MSn(OH)_3$ where M is an alkali metal. Organometallic compounds of Sn^{II} are not well defined; the typical SnR_2 type compounds are believed to be polymers (oligomers)^{5,6}. It was thus of some special interest to synthesize some stannous chelates and examine their molecular complexity.

Catenation, a dominant characteristic of the carbon atom, is considerably weaker in other elements of the group, falling rapidly in the sequence silicon > germanium > tin > lead. Only a few organotin compounds containing more than two catenated tin atoms are well defined. On the other hand, the possibilities of hetero-chain organic derivatives resulting in monomeric as well as polymeric compounds are diverse and extensive with tin. Since such hetero-chain skeleton can result not only from combinations of elements of different electronegativity but also from the utilization of other bond capacities in complex molecules, advantage can be taken of both non-ionogenic and ionogenic bonds. Thus hetero-chain complex compounds can be synthesized containing the tin atom and other organic or organometalloid compounds having electron donor properties.

The inherent chemical instability of homo-chains (other than of carbon) can be partly corrected in hetero-chain compounds by alternating carefully selected elements in the

X-Y- or X-Y-Z chains, selecting elements somewhat more negative than carbon in alternate positions. The compounds thus formed are more resistant to redox processes; and the nearer is the average electronegativity of the hetero-alternates to that of carbon itself, the better is the non-ionogenic character of the bonds formed. The combination of such elements makes it possible to synthesize the interesting poly-organosiloxanes, alumino organosiloxanes and titano organosiloxanes. The idea is continually being extended to synthesize polymers with other hetero-chains.

The general principles enunciated above form the broad basis of our investigations on the nature and type of organo-derivatives of tin including those containing oxygen as the hetero-alternate between tin and carbon, and also tin and titanium (electronegativity values: Ti 1.32, Sn 1.8, C 2.5, O 3.5). In the very rapid development during the last one or two decades of the organic chemistry of tin, prompted mostly by industrial applications of certain types of its compounds, a lack of systematic build-up of knowledge is noticeable, even in respect of relatively simple derivatives. In the present thesis, we have endeavoured a systematic study of some selected areas in organotin chemistry, which can be grouped in the following way:

1. Direct synthesis [of an organotin(IV) halide]
2. Chelated tin(IV) halides, alkyls and aryls
3. Sulphur dioxide insertion compounds of organotin oxides and chelates
4. Stannous chelates
5. Thiényltin(IV) compounds
6. Chelated titano-stannoxanes

The investigations carried out in the above areas have been summed up in the following paragraphs. A somewhat separate though analogous study carried out on oxotitanium chelates has appeared at the end of the summary under serial number 7 for convenience. More detailed reports will be found in the respective sub-sections where experimental results have been discussed.

1. Direct synthesis [of an organotin(IV) halide]

Diorganotin dihalides form an important group of organotin compounds as they are the precursors of several organotin compounds of commercial application. For example, di-n-butyltin oxide, prepared from a di-n-butyltin dihalide by hydrolysis, is the starting material for the manufacture of many dibutyltin stabilizers used by the polymer industry.

A study of literature shows that the common dihalide, viz. dibutyltin dichloride, is not easily obtained in good yields by a direct reaction of butyl chloride on tin metal. Pressure, high temperature (160-180°) and a catalyst are necessary even to get a moderate yield (25-40%) of dibutyltin

dichloride. Unreacted butyl chloride cannot be ^{re-}used as such because of its partial decomposition and isomerization in presence of tin and the catalyst. Butyl bromide, though more reactive than the chloride, does not reportedly give high yields of Bu_2SnBr_2 . The present study was therefore concentrated on the reaction of butyl iodide on tin metal under a variety of conditions, with and without a catalyst. These results have been reported in Section III.1.

It may be seen that yields as high as 95% (based on tin as well as on butyl iodide) are obtainable, and iodine and the unreacted butyl iodide required for the preparation could be recovered and recycled without difficulty. A spongy form of the metal, obtained by precipitation, has been found to be specially reactive. Similar reactions of some other organo iodides with the tin metal have also been studied.

2. Chelated tin(IV) halides, alkyls and aryls

It is well known that titanium tetrachloride reacts with many chelating ligands (LH) containing potential hydroxy groups to give chelated titanium chlorides (L_2TiCl_2 and $LTiCl_3$) and HCl. Under similar conditions, anhydrous stannic chloride, another Lewis acid, gives only addition products. We have noted that chelation can be effected with the elimination of HCl, if a hydrogen chloride acceptor (e.g., sodium methoxide or sodio-derivative of the ligand) is used in the reaction. Big-chelated tin(IV) dihalides are formed in this way. We also observed that the halogen

atoms in these big-chelated tin dihalides did not react with Grignard reagents or lithium alkyls/aryls. Chelated tin alkyls or aryls were prepared by us by the alternate route of reacting chlorotin alkyls/aryls with sodio-derivatives of the chelating ligands.

On the action of halogens or halogen hydracids on chelated organotin, some interesting results, not reported in the literature, were obtained. These and other observations on infrared spectra, molecular weight determinations etc, are presented in Section III.2.

3. Sulphur dioxide insertion compounds of organotin, oxides and chelates

The insertion of a molecule of SO_2 between tin and a metal or tin and a carbon atom in organotins by reacting with sulphur dioxide has been reported in the literature in recent years. The properties and possible structures of the products have also been described. In a similar reaction with chelated organotins we have observed that the latter also take up only one molecule of SO_2 in a medium of liquid sulphur dioxide, and insertion products are formed. Changes that result in the IR spectra of the components have been reported and discussed in Section III.3. Surprisingly, the chelated tin halides failed to react with SO_2 under identical circumstances.

4. Stannous chelates

Literature information is lacking on this type of compounds. Review articles on organotin derivatives do not describe ^{organic} tin(II) compounds in any detail. ^{These} They are generally described as substances difficult to prepare, unstable, and probably polymers having tin-tin bonds.

We have found that tin(II) chelates, on the other hand, are well defined compounds, and can be prepared in good yields from anhydrous stannous chloride and sodio derivatives of the chelating ligands. Our attempts to prepare them by reduction of the chelated tin(IV) compounds were, however, not successful. The tin(II) atom in the chelates is fairly reactive in reduction processes, and as such they may find application in selective reductions in synthetic organic chemistry. Preparation and properties of these chelates have been described in Section III.4.

5. Thienyl tin(IV) compounds

Recent developments in the chemistry and applications of thiophene and its derivatives derived the necessary fillip from the discovery of the synthesis of thiophene from butane and sulphur, thus making thiophene potentially available in unlimited quantities. In the electronic structure of the thiophene molecule, the sulphur atom has been regarded similar to a -CH=CH- group which explains some of the well-known differences between thiophene and furan or pyrrole. The resemblance between the benzene and thiophene ring systems is clearly demonstrated in the new

thienyl tin compounds prepared and studied by us.

α -Iodothiophene was the starting material from which several new α -thienyl tin(IV) compounds were prepared by Grignard reaction on chlorotin compounds. These tin(IV) compounds, in which the metal is linked to the α -carbon atom in thiophene, were found to be exceptionally stable to electron impact in a mass spectrometric analysis. On account of their great stability, they deserve more study and may prove to be good heat-resistant stabilizers in plastics technology. Results of the present investigation have been reported in Section III.5.

6. Chelated titano-stannoxanes

Organotins form metallo-stannoxanes by combining with other elements through oxygen, especially with other members of Gr.IV of the Periodic Table.

Organic derivatives of tin and titanium react among themselves to form titanoxo-stannanes. The first compound containing Ti-O-Sn bond, tetrakis-(triphenyl-stannoxy)-titanium was prepared by reacting tetra-*n*-butyl titanate and triphenyltin hydroxide. Later, dis-(tri-*n*-butyl stannoxy)-diisopropoxy titanium was obtained from tributyltin acetate and tetraisopropyl titanate; it was shown to be a polymeric material useful as reinforcing agent for glass and asbestos fibres. We have prepared a series of new similar compounds by condensing chelated titanium alkoxides with organotin oxides or hydroxides. The products are soluble in benzene and may have properties suitable for their application as stabilizers for plastics. Their IR and possible structure are discussed in Section III.6.

7. Chelated oxotitanium(IV) esters and other derivatives

The (TiO) group in oxotitanium compounds had aroused the interest of several workers in the past. These are prepared either by the hydrolysis of alkoxy titaniums or by the oxidation of titanium(III) compounds. Unlike silicon, a double bond between titanium and oxygen has been postulated in some of these compounds. In our studies, we succeeded after some efforts in developing a general procedure for preparing salicylaldehyde oxotitanium mono alkoxides. The compounds are stable and well defined. An interesting property observed in these mono-esters is the chemical reactivity of their lone alkoxy group. We could introduce other ligands by replacement of this alkoxy group without affecting either the salicylaldehyde or the oxotitanium moiety in the molecule. The (TiO) group, however, readily reacted with thionyl chloride. Preparation procedures, IR spectra and molecular complexity of these chelated oxotitanium compounds have been reported and discussed in Section III.7.

SECTION II : LITERATURE REVIEWS AND CONCLUSIONS

A. Review of relevant literature on organotin compounds

The remarkably sustained interest in organotin chemistry since 1900 to date is reflected in the large number of publications on the subject during the period. It is estimated that the total number of publications (excluding the patent literature) exceeded 3000 by the end of 1965. The part of this literature reviewed here consists of the following groups of organotin compounds : (a) tetraorganotins, (b) organotin hydrides, (c) organotin halides, (d) non-chelates with Sn-O, Sn-N and Sn-S bonds, (e) organotin esters, (f) coordinated adducts, (g) chelated compounds, (h) sulphur dioxide insertion products from Sn-C compounds, (i) metallo-stannoxanes, (j) compounds containing Sn-metal bonds, and (k) applications of organotin compounds.

Since the work reported in this thesis also includes some new oxotitanium chelates, a short review on chelated titanium(IV) compounds with oxygenated ligands has also been included in the literature survey.

(a) Tetraorganotin compounds-

Substitution by organic groups of halogen atom/s bound to tin by the use of other organometallics prepared from metals such as lithium, sodium, potassium, magnesium, zinc or aluminium has been followed as a standard procedure of synthesis from the inception of organotin chemistry.



The reaction between stannic chloride and a Grignard reagent is still used in the laboratory for the preparation of symmetrical organotin compounds in good yields, and even used on a large scale.^{7,8} It has proved to be a general method for preparing fully substituted alkyl (saturated and unsaturated) as well as aryl tin compounds:

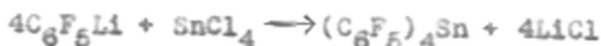


Yields are favoured by the simultaneous addition of stannic chloride and an alkyl halide to magnesium metal suspended in a mixture of heptane and ether.⁹ It has been found possible to make the process a continuous one¹⁰ and also to use tin alkoxides¹¹ in place of stannic chloride.

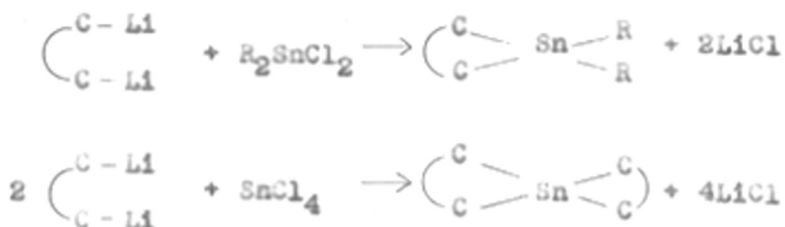
Unsymmetrical compounds of the types R_3SnR^1 and $R_2SnR_2^1$ are easily made by the reaction between an organotin mono- or di-halide and a Grignard reagent.¹²⁻¹⁵ A Grignard reagent made from an equimolar mixture of two alkyl halides, when treated with stannic chloride, gives $R_2SnR_2^1$ as the main product.¹⁶ Organotin compounds containing functional groups are also synthesised with the help of Grignard reagents:¹⁷



An organolithium compound has been found in some cases to be better than the Grignard reagent for the synthesis of an organotin. For example, tetra-perfluorophenyltin was prepared from perfluorophenylmagnesium bromide and stannic chloride in 13 per cent yield, but in 91 per cent yield from perfluorophenyl lithium and stannic chloride:¹⁸



Cyclic organotin compounds are prepared in good yields using dilithium reagents: ¹⁹⁻²⁶

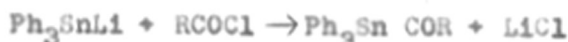


Though organo-magnesium and organo-lithium reagents have been quite generally used for introducing Sn=C bonds, similar organo-derivatives of aluminium, ²⁷⁻²⁹ sodium, ^{30,31} potassium, ³² mercury ³³⁻³⁵ and zinc ³⁶ have found specific applications in organotin chemistry.

Vander Kerk and Luijten ³⁷ reported wurtz-type synthesis of tetrabutyltin by the use of sodium metal:



The yield was low (35%) on account of other side reactions. The yield could be increased to 54 per cent by using a tin-magnesium alloy of the composition Mg₂Sn. Aryltin compounds were prepared in moderate yields from an aryl chloride, stannic chloride and sodium by Srivastava and Bhattacharyya. ³⁸ Acyl aryltin compounds were obtained from triphenyltin lithium and acid chlorides: ^{39, 40}



Electrolytic methods have also been used to obtain tetraalkyltin compounds. Good yields have been reported⁴¹ by the electrolysis of Grignard reagents in ethers with tin anode and mercury cathode in presence of catalysts. A solution of sodium tetraalkyl borate⁴¹ or potassium tetraalkyl aluminate⁴² has also been electrolysed successfully for this purpose to obtain tetraalkyltins.

Van der Kerk⁴³ has shown that hydrostannation of unsaturated compounds also gives new tin-carbon bonds:



Fully substituted alkyl- and aryl-tin compounds are colourless substances, generally of high thermal and chemical stability. Tetraaryltin compounds are crystalline substances whereas tetraalkyltins are liquids, the lower ones being distillable at atmospheric pressure without decomposition. All of them are soluble in common organic solvents.

(b) Organotin hydrides-

Organotin hydrides form a small group of highly reactive and versatile compounds. They are being increasingly used in organic synthesis as reducing agents for special purposes. They are conveniently prepared by the reduction of an organotin halide by lithium aluminium hydride:

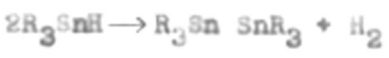


Sodium aluminium hydride and dialkyl aluminium hydride may also be used in place of lithium aluminium hydride. Organotin di- and tri-hydrides are prepared by similar methods.

Trialkyltin formates on decarboxylation under reduced pressure also give hydrides: ^{45, 46}



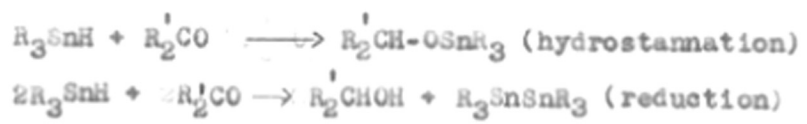
Organotin hydrides are stable at room temperature in the absence of catalysts, silicone grease, metals and acids. ⁴⁷⁻⁴⁹ On storage they slowly decompose into tetraorganotin, hydrogen and tin metal. Organotin hydrides decompose in presence of an amine, liberating hydrogen:



⁵⁰ Van der Kerk found that an organotin hydride could be added to a carbon-carbon double bond. Several new compounds with Sn-C bonds were thus prepared:



Not only olefins but acetylenes and organometallic compounds with unsaturated functional groups also react in this manner with organotin hydrides. ⁵¹⁻⁵⁵ Aldehydes and ketones, and compounds with C=N, C=S and N=N bonds undergo hydrostannation and/or reduction with organotin hydrides:



TH 47

Organic halides are reduced by organotin hydrides, selectively and in good yields, under mild conditions:



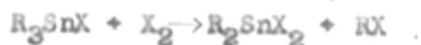
Organotin deuterides have also been used in the synthesis of deuterated organic compounds:⁵⁹



(c) Organotin halides-

Organotin halides are prepared mainly by one of the three synthetic routes: (i) cleavage reaction, (ii) redistribution reaction and (iii) direct synthesis from an alkyl halide and tin metal.

(i) Cleavage by nucleophilic attack with a halogen is a convenient method for the preparation of organotin mono- and di-halides:

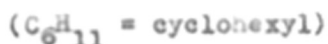
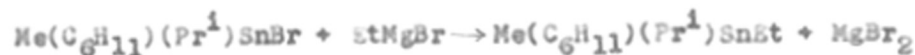
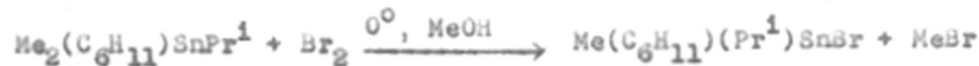
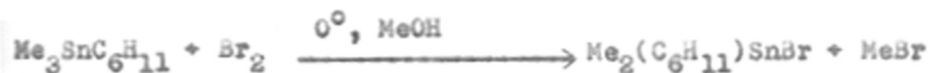


Among the halogens, iodine reacts slowly and requires heating in a solvent. Bromine solutions react in the cold, usually at 0° , and the yields are good. Much less work has been done with chlorine.

Organic groups attached to tin show marked differences in their reactivity towards the halogen. When unsymmetrical organotin compounds are reacted, it is often possible to predict

which group would be preferentially replaced by the halogen. From a study of the cleavage reactions of many unsymmetrical compounds of the types R_3SnR' and $R_2SnR'_2$, sequences have been established indicating the relative ease with which the organic group R and R' are cleaved by the halogen from the tin atom. Gilman⁶⁰ arranged the ease of replacement of different groups in the following order: o-tolyl > p-tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > isobutyl > butyl > isoamyl > amyl > hexyl > heptyl > octyl.

However, deviations from the above sequence are not uncommon,⁶¹ because it is possible to induce cleavage reactions under a variety of experimental conditions. For example, the effect of solvent upon the product of some cleavage reactions has been reported by Gielen and Nasielski⁶¹⁻⁶³. They studied the kinetics of cleavage reactions of Me_3SnR using bromine and iodine in polar, nucleophilic solvents such as methanol or acetic acid. The cleavage was considered to occur by S_N2 mechanism, and the reactivity sequence observed for the group R was $R=Me > Et > Bu > Pr > Pr^i > Bu^t$. Differences among the rate constants were considerable, indicating a high degree of selectivity for the cleavage reactions in polar solvents. The first synthesis of a fully unsymmetrically substituted tetraalkyltin compound was achieved through successive and selective cleavage reactions in methanol, alternating with Grignard syntheses:^{64, 65}



In a less polar and weakly nucleophilic solvent such as chlorobenzene, the observed reactivity sequence for the group R in Me_3SnR was $\text{R} = \text{Bu}^t > \text{Me} = \text{Pr}^i > \text{Pr} = \text{Bu}$ with nearly equal rate constants. In general, there is not much difference in the reactivities of different alkyl groups,⁶² and conflicting results have been reported^{66,67} regarding the products of cleavage reactions.

Hydrogen halides have also been used to a limited extent for preparing organotin halides from tetraorganotin compounds.⁶⁸



(X = Cl, Br, I; R = allyl;

R' = methyl, ethyl, propyl, phenyl)

(11) Many organotin halides have been prepared by a redistribution reaction between tetraorganotin compound and the calculated amount of a stannic halide. Stannic chloride reacts more readily than the bromide. The method is unsuitable for the preparation of iodo compounds.⁶⁹ Usually this reaction is carried out at about 200^o, sometimes under pressure⁷⁰ or in presence of a catalyst⁷¹:



where R = alkyl or aryl; X = Cl or Br.

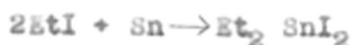
None of the organic groups is lost in the reaction, and this is a definite advantage over the halogen cleavage method. However, because of the high temperature used, yields are somewhat lowered by thermal decomposition of the reactants. Also, since a mixture of products is usually obtained, further separation by suitable methods becomes necessary. In spite of these difficulties, the method has been widely used for the manufacture of tributyl- and triphenyltin chlorides and butyl- and phenyl-tin trichlorides.^{72, 73}

Unsymmetrical tetraorganotin compounds also undergo redistribution reactions:⁷⁴



Reviews on the redistribution reactions^{75, 76} and their studies by the use of gas chromatography⁷⁷ and NMR spectroscopy^{69, 78} have appeared in the literature.

(iii) Frankland prepared the first organotin compound in 1849 by direct synthesis by reacting ethyl iodide with tin metal:⁷⁹



To-day, direct synthesis has proved to be the method of choice for the manufacture of several diorganotin dihalides. A catalyst, often a Lewis base, is required for the reaction. The reactivity of the alkyl halide varies in the order $\text{RI} > \text{RBr} > \text{RCl}$. An exception is benzyl chloride, which reacts even without a catalyst and gives dibenzyltin dichloride or tribenzyltin chloride, depending on the medium used for the reaction.⁸⁰ Metallic iodides in traces⁸¹, zinc⁸² and lithium⁸³ are sometimes added with the tin to improve the yield. Amines,^{84,85} tetrabutyl ammonium iodide in diglyme⁸⁶, a Lewis base with a metallic salt⁸⁷, have all been found to catalyse the reaction of an alkyl halide with tin metal. The reaction has been extended by Matsuda *et al.*⁸⁸⁻⁹⁶ to halo-carboxylic esters such as halo-succinates, malonates, β -halo-isobutyrate, β -halo-propionamides and several other esters.

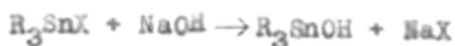


It has been reported that irradiation with γ -rays induces alkyl bromides to react with tin metal.^{97,98}

(d) Sn-O, Sn-N and Sn-S bonded organics (non-chelates)-

(1) Sn-O bonded organics: These include organotin hydroxides, oxides, alkoxides, phenoxides and esters (carboxylates). The esters, which are technically important, are discussed under a separate section (e).

When a triorganotin monohalide is treated with dilute alkali, the hydroxide is obtained:



(X = Cl, Br, I)

The hydroxides differ in their stabilities. For example, dibutyl vinyltin hydroxide decomposes at room temperature:²⁹



Triphenyltin hydroxide loses water on storage.¹⁰⁰ However, the lower trialkyltin hydroxides can be distilled under reduced pressure without much decomposition, and are converted into their oxides (hexa-organo distannoxanes) by dehydrating with sodium and benzene. Once formed, these oxides (except the methyl) do not hydrate in contact with water. Several of the hydroxides and oxides absorb carbon dioxide to form the carbonates, and react with acids to give the salts and water. However, organic isocyanates undergo condensation with hexa-organo distannoxanes, giving useful polymeric products.

Diorganotin oxides, not hydroxides, are directly obtained by treating diorganotin dihalides with dilute alkali:



These are polymeric, non-melting substances, soluble in organic acids forming esters. They react with other organotin chlorides forming oligomeric chlorostannoxanes:^{101, 102}



Organostannoic acids are prepared from organotin trihalides and excess of dilute alkali:

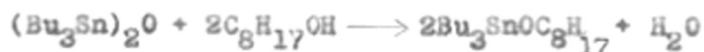


They are infusible polymeric substances soluble in strong alkali and also in dilute acids. On dehydration, they form compounds with the empirical formula $\text{R}_2\text{Sn}_2\text{O}_3$.¹⁰³

Organotin alkoxides and phenoxides are readily obtained from an organotin halide by reaction with an alcohol (in presence of a base)¹⁰⁴, an alkali metal alkoxide,¹⁰⁵⁻¹⁰⁷ or phenoxide:¹⁰⁸



Alternatively, an organotin oxide may be reacted directly with a higher boiling alcohol or phenol in boiling benzene or toluene, the water formed being removed azeotropically:¹⁰⁹⁻¹¹³



They may also be prepared from an organotin oxide and dialkyl carbonate:¹¹⁰



Organotin alkoxides are more sensitive to moisture than the phenoxides. Phenoxides of the more acidic phenols, e.g. nitrophenols, are less readily hydrolysed.^{108,112} Derivatives of dihydric phenols are thermally more stable.¹¹⁴

(ii) Sn-N bonded organics: Van der Kerk¹¹⁵ and Jones and Lappert¹¹⁶ have reviewed these organotin compounds. Two important types of compounds of this class are (1) organostannylamines, $R_{4-n}Sn(NR'R'')_n$ and (2) organostannylamides, $R_{4-n}Sn(NR'COR'')_n$. Compounds of the first type are prepared by the transmetalation reaction between lithium or other metal derivatives of the amine and an organotin halide:¹¹⁶⁻¹¹⁸



where $R' = H$, $R'' = \text{alkyl or aryl}$ and $n = 1, 2, 3$.

Similarly, $3R_3SnCl + Li_3N \rightarrow (R_3Sn)_3N + 3LiCl$



(ref. 121-123)

where $n = 1, 2, 3$.

Related compounds with Sn-N-Si and Sn-N-Ge are reported in the literature.^{124,125}

To convert one organostannylamine into another, use is made of a transamination reaction by treatment with an amine:

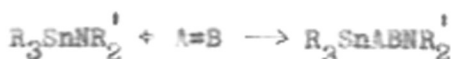


The progress of this reaction is dependent upon steric factors as well as on volatility of the products formed.^{116,117}

Organostannylamines are sensitive to moisture and carbon dioxide:



They add to unsaturated systems:¹²⁶



They undergo metathetical reactions also:¹²⁷⁻¹²⁹



Because of their high reactivity, they are sometimes used in the synthesis of other non-amine compounds such as trialkylstannyl phosphines and acetylenes.^{116,127}

Organostannylamides, on the other hand, are prepared in several ways. An organotin hydroxide reacts with an acid imide such as phthalimide or saccharin¹³⁰ to form an amide:



In an analogous manner, Davies and co-workers^{131,132} prepared a number of stannylamides by the following reactions:



where R = Me, Et, Ph and R' = H, Me.

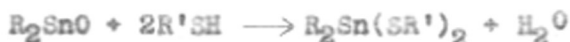
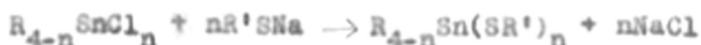
The amides are also formed by addition reactions of isocyanates with organotin hydrides:¹³³



Organostannylamides are sensitive to moisture and acids.

(iii) Sn-S bonded organics: These organotin derivatives have attracted considerable attention because of their marked stabilizing action on polyvinyl chloride against slow degradation. Some 270 organotin-sulphur compounds were already known in 1967,¹³⁴ and their number is still increasing at a rapid rate.

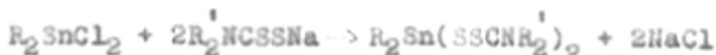
Organotin mercaptides, $\text{R}_{4-n}\text{Sn}(\text{SR}')_n$, containing the Sn-S-C grouping, are prepared by the reaction between an organotin chloride/oxide/hydroxide/alkoxide and sodium mercaptide. The reaction is carried out in ethanol, in dilute sodium hydroxide¹³⁵ or in presence of a base such as pyridine or triethylamine:¹³⁶⁻¹³⁸



These compounds are also formed when organotin hydrides react with thiols:¹³⁹



Dithiocarbamates are obtained from an organotin chloride and sodium dithiocarbamate:



and also by in situ reaction:



Organotin compounds with Sn-S-Sn bonds are formed by the action of an alkali sulphide on an organotin chloride:



or by passing hydrogen sulphide into a water suspension or acetone solution of the organotin hydroxide or oxide:



Yet another method is directly to react carbon disulphide and the tin organotin oxide.¹⁴⁰



The organotin mercaptides are thermally stable compounds. Strong alkali solutions break the Sn-S bond:¹⁴¹



They are also attacked by boron trichloride,¹⁴¹ phosphorus trichloride¹⁴² and mercuric chloride.¹⁴¹

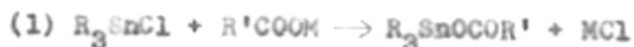
(e) Organotin esters of carboxylic acids-

By far the largest single use of organotin compounds to-day is for stabilizing vinyl chloride polymer (PVC) against degradation. A large number of organotin esters of carboxylic acids have been reported in the literature and their PVC stabilization properties studied by different workers for commercial exploitation. Much of the available information is in the form of patents.

These esters are prepared from the organotin oxide or hydroxide and a carboxylic acid or its anhydride: ¹⁴³⁻¹⁴⁹



other less important methods are:



¹⁵⁰ Verity Smith in his monograph gives a brief survey of organotin stabilizers, their preparations and their probable mode of stabilization action on PVC. Some of the important organotin components of commercial PVC stabilizing compositions are dibutyltin dilaurate and maleate, big(dibutyltin mono-laurate) maleate, dibutyltin big(mono-octyl-maleate) / big(mono-2-ethyl-hexylmaleate) / big(S-dodecyl-3-mercaptoisobutyrate); dibutyltin esters of thiolauroic, thiomaleic and thioglycollic acids; mercaptides and sulphides such as dibutyltin didodecyl mercaptide,

diphenyl mercaptide, dimercaptobenzthiazole; dibutyltin dimercapto acid amides and derivatives of thio polyesters and mercapto alcohols.

Dibutyltin dilaurate, prepared from dibutyltin oxide and pure lauric acid, melts at 30° ; but when prepared from crude lauric acid, (e.g., distilled coconut fatty acids), it has a much lower setting point (-2°). This crude dibutyltin dilaurate of commerce has a superior stabilizing action to the pure compound and is more readily soluble in plasticizers.

Dibutyltin maleate, prepared from dibutyltin oxide and maleic acid or its anhydride, is a solid mixture of trimeric and tetrameric forms.^{151, 152} They have low solubility in organic solvents.

In spite of their excellent properties, dibutyltin stabilizers are not used in food containers on account of their slight toxicity. Van der Kerk and collaborators¹⁵³ reported the application of dioctyltin compounds as stabilizers for PVC in place of the dibutyl compounds because dioctyltin stabilizers show negligible mammalian toxicity, and these have now been accepted for use in PVC containers for food packing. As expected, this has stimulated research on the preparation of dioctyltin stabilizers on lines similar to dibutyltin compounds.

(f) Coordinated adducts of tin(IV) compounds-

The tendency of stannic halides to form addition complexes with a variety of organic compounds has been well known. This tendency stems from the availability of low-energy outer d-orbitals, providing conditions for the tetravalent tin atom to expand its coordination number from 4 to 6. Stannic chloride, a Lewis acid, readily forms adducts by accepting electron pairs from donor molecules. The acceptor strength of the tin(IV) halides are in the order $\text{SnCl}_4 > \text{SnBr}_4 > \text{SnI}_4$ ¹⁵⁴, all of which form stable adducts of the type $\text{SnX}_4 \cdot 2\text{L}$ ^{155,156} with suitable ligands. The capacity of stannic halides to form coordinated adducts, however, diminishes in substituted organotin halides. In general, the relative acceptor strength of tin(IV) in the substituted halides for the same donor molecule declines in the order shown below:^{154,157,158}



Coordinated adducts are easily prepared by mixing solutions of the organotin halides with the ligands in inert solvents which are removed afterwards. Sometimes the ligand itself may act as the solvent medium.

The majority of the donor ligands are oxygen, nitrogen or sulphur compounds, though a few have been described containing phosphorus and arsenic as the donor atoms. The compositions of the adducts formed from two common ligands are as follows:



(L = pyridine and dimethyl sulphoxide and

R = Me, Bu, Ph)

Paul and co-workers¹⁵⁶ have prepared some addition compounds of tin(IV) chloride alkoxides with oxygen- and nitrogen- containing donors.

(g) Organotin chelates-

Tin(IV) forms chelated halides and other compounds less readily than does titanium. Literature survey shows only scanty reports on these compounds, and no review has so far been published on the subject.

Stannic chloride, unlike titanium tetrachloride, does not react directly with ligands to form chelated chloro compounds, but forms adducts. Nelson and Martin¹⁵⁹ prepared some chelated tin(IV) dichlorides by effecting Sn-C (phenyl) cleavage by a chelating ligand. They reacted diphenyltin dichloride with a large excess of the ligand at 100° and isolated the products by adding petroleum ether. Derivatives of some diketones, salicylaldehyde and 8-hydroxyquinoline were thus prepared. These are stable and well defined chelates, some being soluble in benzene. No mono chelated tin trichloride or tris-chelated tin monochloride is known.

Chelated tin(IV) alkyls and aryls have been better studied. They are examples of penta- and hexa- coordination in the structural chemistry of tin. Acetylacetonone as a chelating ligand has been studied in detail. Its compounds are prepared from an organotin chloride and sodio-derivative of the ligand or from organotin alkoxide and the ligand itself.¹⁶⁰⁻¹⁶⁴ Chelated metal halides are formed when an alkyltin halide reacts directly with acetylacetonone.¹⁶⁴ Acetylacetonone and other similar ligands form compounds of the type R_3SnL and R_2SnL_2 but tropolone alone forms a compound of the type $RSnL_3$.^{165,166} A chelated distannoxane derivative, symmetrical tetraalkyl bis(1-nitroso 2-naphthoxy) distannoxane, was prepared by Mehrotra¹⁶⁷ from dialkyltin diisopropoxide and 1-nitroso 2-naphthol. Some diaryltin bis-acetylacetonates were prepared and their properties studied by Srivastava and Saxena.¹⁶⁸ The smaller separation, compared to the ligand itself, between the C=O and C-C stretching vibrations suggests a fair degree of stability of these compounds. A new penta-coordinated tin complex was prepared by Paul and co-workers¹⁶⁹ from dibutyltin oxide and o-amino benzoic acid in boiling xylene. The compound appears to contain one Sn-H bond, a rare example of a strong metal-hydrogen bond formed by coordination. Organotin chelates of stannous tin are not reported in the literature.

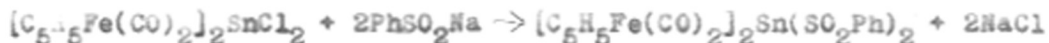
(n) Sulphur dioxide insertion into Sn-C bonds-

Reactions involving the insertion of small but reactive molecules into organometallic structures have become a topic of considerable interest in recent years. Several of them have been found to insert themselves,¹⁷⁰ into Sn-N and Sn-O bonds;¹⁷⁰

e.g., olefins have been inserted into metal-metal bonds, and carbon monoxide and sulphur dioxide into transition metal-carbon bonds.^{173, 174} In an attempt to insert sulphur dioxide into Sn-Fe bond in $[C_5H_5Fe(CO)_2]_2SnPh_2$, Edmondson and Newlands¹⁷⁵ found that the sulphur dioxide got inserted into the Sn-C bond forming a $\overset{Sn-O-S-C}{\curvearrowright}$ bond: structure



The course of the reaction was confirmed by the independent synthesis of an identical product from bis(cyclopentadienyl dicarbonyl iron) dichlorotin and sodium benzene sulphinate in methanol:



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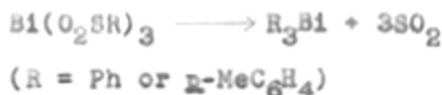
Lindner and co-workers found recently that tetraorganotin react with liquid sulphur dioxide. Tetramethyl- and tetraethyl-tin each absorbs one mole of sulphur dioxide at -20° to yield the corresponding colourless, stable trialkyltin alkane sulphinates, R_3SnO_2SR ($R = Me, Et$). Penta- and hexa-coordinated dimeric O-sulphinato complexes of the type Ph_3SnO_2SR , $Ph_2Sn(O_2SR)_2$ and $Me_2Sn(O_2SR)_2$ were obtained respectively by the action of Ph_3SnCl , Ph_2SnCl_2 and Me_2SnCl_2 on sodium organo-sulphinates.

Reviews on the insertion of sulphur dioxide into metal-carbon bonds have been made by Kitching and Fong¹⁷⁷ and by Lappert.¹⁷⁸ They describe the sulphur dioxide insertion as a general reaction of the Sn-C system. Mono-insertion is the general feature:



However, tetraphenyltin reacts with sulphur dioxide under pressure to give $\text{Ph}_2\text{Sn}(\text{O}_2\text{SPh}_2)_2$.¹⁷⁹
 Linderand Kunze¹⁸⁰ studied the behaviour of tetra-ethyl- and tetrabutyl-tins towards aqueous sulphur dioxide at 60° under pressure and isolated dialkyltin sulphites. Correct formulation of the insertion products was arrived at from vibrational, NMR and mass spectrometric analysis. The products are O-sulphinates, aggregated in the solid phase and in solution. The tin atom achieves a coordination number of 5 with an essentially planar R_3Sn moiety.¹⁸¹ Rearrangement of the allyl group sometimes accompanies the sulphur dioxide insertion process.¹⁸²

Insertion of sulphur dioxide into metal-carbon bonds in mercury,¹⁸³ lead,¹⁸⁴ silicon,¹⁸⁵ iridium and rhodium¹⁸⁶ organics and into palladium-oxygen bonds¹⁸⁷ have been reported. Deacon^{188,189} observed the formation of bismuth-carbon bonds by sulphur dioxide elimination:



(1) Metallo-stannoxanes-

Organotin moieties are known to form strong bonds through oxygen, sulphur, selenium and tellurium with other main group elements of Gr.IV. A recent review has been published by Harrison.¹⁹⁰ Among the metallo-stannoxanes, sila-stannoxanes have been more widely studied. The first synthesis of a polymer containing a Sn-O-Si linkage was

accomplished by the cohydrolysis of diethyltin dichloride and dialkyl (aryl) dichlorosilane in toluene by 10% aqueous ammonia at 50-55°, ^{191, 192}



Cohydrolysis can also be used to prepare organo silastannoxanes with definite structures. Trimethylsiloxy-trialkyltin compounds have been isolated as colourless oils by the cohydrolysis of the respective halides in benzene with aqueous ammonia. ¹⁹¹



Another method is the reaction between an alkoxide of organotin and a chloro-metal compound, ¹⁹³ or vice versa:

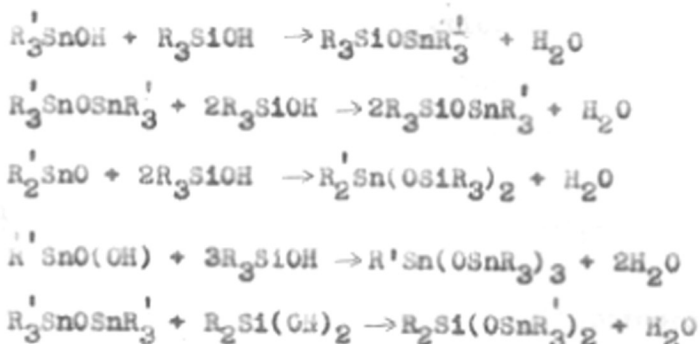


¹⁹⁴ Andrianov, and ¹⁹⁵ Ruidisch and Schmidt have prepared the above compounds in good yields by this method and studied their properties.

Trans-esterification reaction between an organotin acetate and an organosilicon ester gives moderate yield of siloxy-tin compounds: ¹⁹⁶



Substituted silanols react readily with organotin oxides/hydroxides in a suitable solvent to give good yields of the siloxy-tin compounds: ¹⁹⁶⁻¹⁹⁸



Germastannoxanes are prepared by the methods used for the silastannoxanes. Hexamethylgermastannoxane is obtained from lithium trimethylgermoxane and trimethyltin chloride in ether. ¹⁹⁵



Triphenylgermanol, like the corresponding silanol, reacts with triorganotin hydroxides giving triphenyl germatriorganostannoxanes which are monomeric in benzene: ¹⁹⁷



Stannoxysilanes are toxic, unpleasant smelling liquids or low melting solids. ^{193, 196} Their stabilities and physical properties are inferior to those of organopolysiloxanes. ^{199, 200}

Of the transitional elements in Gr. IV, titanium and zirconium are known to form Sn-O-M linkages. The first compound containing Sn-O-Ti bond, tetrakis-(triphenylstannoxy) titanium was reported by Cohen ²⁰¹ who prepared it as a pale

yellow solid by reacting butyl titanate with triphenyltin hydroxide:



²⁰²
Cohen has also described the preparation of phenyl stannyl nitrilotriethylene titanate obtained from nitrilotriethylene isopropyl titanate and triphenyltin hydroxide:



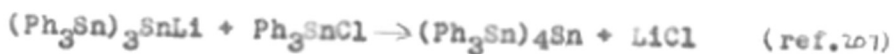
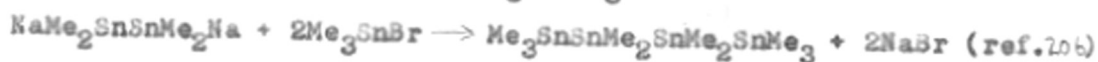
The preparation of big-(tributylstannoxy)-diisopropoxy titanium from tributyltin acetate and tetraisopropyl titanate was described in a British Patent.²⁰³ This was claimed to be a polymeric material useful in reinforcing glass and asbestos fibre. Some metallostannoxanes have been reported to act as stabilizers for plastics, and as corrosion inhibitors, biocides, and fungicides.

(j) Organotin compounds containing tin-metal bonds-

Earliest examples of these compounds are those containing Sn-Sn bonds only. In recent years, compounds have been synthesized in which the tin atom is bonded with practically all the elements of Gr. IV and several elements from the other groups of the Periodic Table. For example, published literature describes Sn-M organics where the metal M is one of the alkali metals, magnesium, zinc, cadmium, mercury, silicon, germanium, tin, lead, titanium, zirconium, hafnium, arsenic, antimony, bismuth, selenium, tellurium, chromium, molybdenum, tungsten, manganese, rhenium, iron or cobalt.

Catenated tin compounds reviewed by Gilman and Mackay

fall into two types, namely, open-chain poly-organostannanes, $\text{Sn}_x\text{R}_{2x+2}$ and cyclic compounds $(\text{R}_2\text{Sn})_x$. Compounds containing up to 9 tin atoms have been identified, but catenation is much more limited with tin than with silicon. These are generally prepared by reacting lithium- or sodium-derivatives of organotins with organotin halides:



Neumann observed that hydrostannolysis with organotin hydrides of aminotin compounds²⁰⁸ or of organotin oxides²⁰⁹ also gives similar compounds:



Base-catalysed elimination of hydrogen from organotin monohydrides also gives di-tin compounds:²¹¹



Cyclic polyorganostannanes, $(R_2Sn)_x$, were observed to form in the attempted synthesis of divalent organotins. Neumann^{5,6} found that the 'diphenyltin' obtained by reacting phenyl magnesium bromide with stannous chloride in ether is, in fact, a polymer of the empirical formula $(Ph_2Sn)_x$. Also, when diorganotin dihydrides are decomposed in presence of a base, cyclic organostannanes^{an} are formed:



They are also formed in the following reaction:



These compounds containing Sn-Sn bond are stable substances. Except the lower alkyl compounds, others are solids. However, iodine or hydrogen halides readily cleave the Sn-Sn bonds, the reaction being often used for their identification.

²¹³
Kazuyaev has recently reviewed the chemistry of compounds containing tin bonded to another main group metal. Organotin-alkali metal compounds are highly reactive and are very useful in the synthesis of other organotins. Earlier, these were prepared by reacting an organotin halide with the alkali metal in liquid ammonia:²¹⁴



A more convenient method of preparation is in THF:²¹⁵



²¹⁶
 Gilman observed that an alkyl lithium (3 moles) and anhydrous stannous chloride (1 mole) could also be used:



These alkali metal derivatives react with alkyl halides, organotin halides and organosilicon halides in the expected manner:



Magnesium, like lithium, also reacts with triphenyltin chloride in TiF_4 ²¹⁷



Compounds containing Sn-Zn and Sn-Cd bonds were isolated in good yields by the hydrostannolysis of chelated complexes of alkyl-zinc and alkyl-cadmium: ²¹⁸



(R = Me, Et; M = Zn, Cd; D = N,N,N',N'-tetramethyl ethylene diamine, 2,2'-bipyridyl)

Big-(triphenylstannyl) mercury was isolated from the following reactions: ²¹⁹



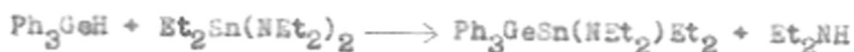
Products containing Sn-Si²²⁰, Sn-Ge²²⁰ and Sn-Pb²²¹ bonds are prepared as follows:



Creemers and co-workers²²² carried out hydrostannolysis with tetrakis(dimethylamino) derivatives of titanium and zirconium:



They also carried out similar reactions with triphenyl germanium hydride:²²³

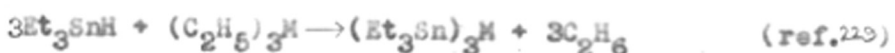


Stable, coloured compounds with Sn-Ti and Sn-Zr bonds were obtained by Coutts and Wailes²²⁴ by reacting triphenyltin sodium in THF with bis-cyclopentadienyl titanium(III) chloride, bis-cyclopentadienyl titanium(IV) dichloride and bis-cyclopentadienyl zirconium dichloride.

Compounds with Sn-Zr(IV) and Sn-Hf(IV) bonds were obtained as their cyclopentadienyl derivatives by the following reactions:²²⁵



Some compounds containing Sn-P(III) Sn-As(III), Sn-Sb(III), and Sn-Bi(III) bonds have been prepared as shown below, and reported by different workers:



²³⁰
Schumann and co-workers have prepared some compounds containing Sn-Se-Ge and Sn-Te-Pb bonds:



The synthesis of a triorganostannyl cobalt tetra-carbonyl was carried out as follows:²³¹



Similar methods were applied to prepare compounds containing tin bonded directly with various other metals such as chromium, molybdenum, tungsten, manganese, rhenium and iron.

For example,



(M = Cr, Mo, W)



(M = Mn, Re)



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Maxfield has recently reported the preparation of several tin-(transition metal) compounds from tetra-allyltin. Reactions of triorganotin hydrides with iridium and rhodium complexes were reported by Travers²³⁷ to give binuclear compounds. Several of these compounds are stable at room temperature, have sharp melting points and are attacked by halogens and hydrogen halides. Compounds containing tin-(transition metal) bonds are readily oxidized by atmospheric oxygen. The structures of only the carbonyl derivatives have been studied in detail^{238, 239} by infrared and mass spectral analysis.

(k) Applications of organotin compounds-

Estimates by the Tin Research Institute, Greenford, put world production of organotin compounds at 10,000 tons for the year 1968. Most of the applications are as polymer stabilizers, insecticides, fungicides and catalysts.

(i) Polymer stabilizers: In the absence of a good stabilizer, polyvinyl chloride gets degraded even at room temperature by ultraviolet light. This is due to

dehydrochlorination which, once commenced, appears to proceed automatically causing chain scission.

Compounds of the type R_2SnX_2 are well known stabilizers for PVC, neoprene, chlorinated polyethylenes, vinyl copolymers, silicones, polyamides and other polymers. Colourless transparent PVC foils and discs and rigid PVC articles are made using organotin stabilizers. Dibutyltin-dilaurate and -maleate were the first two compounds to be used, but now a large number of organotin compounds are mentioned in patent literature. They include derivatives of hydroxy compounds, thioglycollic acid esters, mercaptides and other similar sulphur compounds. Dioctyltin compounds are recommended particularly for PVC sheets or coatings used for food packaging, because they are non toxic.

(ii) Insecticides and fungicides: The notable lack of toxicity of inorganic tin compounds makes organotin fungicides superior to those containing other metals such as Hg, Cu, Cd and Zr. The "biological half-life" of most of the organotin compounds used as insecticides and fungicides is comparatively short. For example, for triphenyltin acetate it is only about 3-4 days in the open and 7-8 days under glass. Water and light degrade it to inorganic tin compounds.

Compounds of the type R_2SnX_2 show less fungicidal activity than the R_3SnX type. The activity is at its maximum when the alkyl groups contain a total of 9-12 carbon atoms. A large number of aliphatic and aromatic organotins have been tested for their activities against various micro organisms.

As a rule, aromatic organotins are less phytotoxic than aliphatic ones. ²⁵³ Triphenyltin acetate or hydroxide is used to combat fungus diseases in leaves or in root crops like tobacco, potato and sugar-beet. ^{254, 255} Triphenyltin chloride and tributyltin oxide are added to paints, to impregnate potato sacks (jute), manila ropes, textiles, leather, canvas and nets against attack by moulds, fungi and algae. Triethyltin hydroxide, tributyltin acetate and tributyltin oxide dissolved in mineral oil are recommended as preservatives for wood. ²⁵⁶⁻²⁵⁸ Tripropyl- and tributyl-tin fluorides have antiseptic action on non-metallic surfaces. ²⁵⁹ Dibutyltin dilaurate and maleate are used in veterinary medicines. ²⁶⁰

(iii) Catalysts : Organotin compounds such as dibutyltin dilaurate catalyse the reaction of isocyanates with alcohols (forming urethans) ²⁶¹⁻²⁶⁴ and esterification of epoxy resins with fatty acids. ²⁶⁵ Polyurethane foams with improved physical and chemical resistant properties are prepared by using alkyltin halides as catalysts. ²⁶⁶ Organotin compounds are used commercially in Ziegler catalyst systems for polyolefin production; ²⁶⁷ a combination of titanium tetrachloride and organotin hydride gives polymers of high molecular weights under mild conditions. Polymerization of styrene by the use of vanadium oxychloride-tetrapropyltin catalyst has been reported. ²⁶⁸ Tributyltin lithium is an effective catalyst for the solution polymerization of conjugated dienes giving transparent polymers. ²⁶⁹ An organotin ester such as dibutyltin dilaurate is useful in the

'cold curing' of organopolysiloxanes having terminal hydroxy groups. ²⁷⁰⁻²⁷⁴ These compounds are also used for the production of polysiloxane elastomers, ²⁷⁵⁻²⁷⁹ surface coatings, acrylate-silicone copolymers ²⁸⁰ and for hardening epoxy resins. ^{281,282} Tetraorganotins are useful ballistic additives for solid rocket engine fuels. ²⁸³ Hexa alkyl distannes ²⁸⁴ are additives for gasoline. They are also used for corrosion prevention of metals, as water-repellents, in paints and varnishes and as primer for coating glass. ²⁸⁵

B. Chelated compounds of titanium(IV) with oxygenated ligands

Titanium forms chelated complexes with β -diketones, β -ketoesters, salicylaldehyde, esters of salicylic acid etc. These are easily obtained by mixing the required amount of the chelating agent in each case with an ortho ester of titanium in a suitable solvent, and distilling off the alcohol liberated in the course of the reaction. Yamamoto and Kambara ²⁸⁶ prepared two acetylacetonates from acetylacetone and an alkyl titanate. Rust and Takimoto ²⁸⁷ prepared diisopropoxy bis-dibenzoylmethane titanium and diisopropoxy bis-8-hydroxy-quinolino titanium from isopropyl titanate and the respective ligands. Similar compounds were prepared by Puri and Mehrotra ²⁸⁸ from alkyl titanates by reaction with acetylacetone as well as benzoylacetone. Alkyl titanates and acetoacetic esters ^{286,289,290} react to give similar chelated compounds. Two salicylaldehyde derivatives, salicylaldehyde trialkoxytitanium and

big-salicylaldehyde dialkoxytitanium, were prepared by Varma and Mehrotra.²⁹¹ Similar compounds were also prepared by Yamamoto and Kambara²⁹² from alkyl titanate and salicylaldehyde as well as methyl salicylate ligands.

An alternative procedure for preparing chelated titanium compounds is to react the ligand with titanium tetrachloride in a suitable solvent medium. The reactions of titanium tetrachloride with acetylacetone and benzoylacetone were reported by Dilthey,²⁹³ who obtained the corresponding dichloro-titanium chelates. Rosenheim and co-workers²⁹⁴ prepared trichloro-titanium acetylacetonate, and Pande and Mehrotra²⁹⁵ trichloro- and di-chloro-titanium acetylacetonates by similar procedure. Puri and Mehrotra^{296,297} reported the preparation of the trichloro- and dichloro-titanium derivatives of benzoylacetone and ethylacetoacetate, and of big-salicylaldehyde dichloro-titanium.²⁹¹ Yamamoto and Kambara²⁹² prepared big-salicylaldehyde and big-methylsalicylate dichlorotitaniums. Lutschinsky^{296,297} prepared big-o-nitrophenoxy dichlorotitanium. Dibenzoylmethano chloro-titanium compounds were reported by Nyholm and co-workers.²⁹⁸

Several chelated titanium methylsulphates have been synthesized by Gopinathan and Gupta by reacting dimethyl sulphate with chelated dichloro-titaniums. Chelated titanium sulphates and oxalates were prepared by reacting the ligands with dichloro-titanium sulphate and oxalate respectively. Chelated derivatives of $\text{ClTi}(\text{SO}_4)(\text{CH}_3\text{SO}_4)$ also were obtained by similar methods. Several hexa-coordinated phenol, resorcinol and catechol derivatives of di-substituted chelated titanium dichlorides have also been reported.^{299,300}

The alkoxy-titanium acetylacetonates are orange to red viscous liquids soluble in organic solvents. They hydrolyse in water forming oxy-titanium acetylacetonates. The ethyl-acetoacetato, benzoylacetonato, dibenzoylmethano and salicylaldehyde derivatives are yellow to orange-red low-melting solids or viscous liquids, soluble in benzene. Among the chloro titanium chelates, the trichloro-titanium compounds of acetylacetone, ethylacetoacetate, benzoylacetonato and dibenzoylmethane are chocolate to dark red solids which melt or decompose at high temperatures. The dichloro-titanium compounds are red powders except the salicylaldehyde chelate, which is a chocolate solid. The trichloro compounds are more hygroscopic than the corresponding dichlorides. Only acetylacetone and ethylacetoacetato chloro-titanium compounds are soluble in benzene; but all of them dissolve in alcohol, some with chemical reaction. Trichloro-titanium acetylacetonate reacts with ethanol giving acetylacetone ethoxy dichloro-titanium. Dichloro-titanium big-acetylacetonate reacts with isopropanol in presence of dry ammonia gas to give di-isopropoxytitanium big-acetylacetonate; this, when reacted with dry hydrogen chloride gas, gives back the original dichloride.

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Bradley and Holloway³⁰¹ have carried out structural studies on big-acetylacetone dialkoxy titanium(IV). The results obtained show that they have the big-configuration. Recently Fay and Lowry³⁰² have prepared and studied the structure of big-(acetylacetone) diiodo titanium.

Some tetrachelated titanium(IV) compounds have been reported by Frazer and co-workers³⁰³, e.g. tetra-8-quinolinato titanium, di-8-quinolinato di-salicylaldehyde titanium and tetra-salicylaldehyde titanium.

Among oxotitanium compounds, the oxotitanium alkoxides were described by Bradley and co-workers^{304, 305} as polymeric compounds obtained by the controlled hydrolysis of the alkyl titanates; and by Nesmeyanov and co-workers³⁰⁶ as the products of oxidation of trialkoxytitaniums. Both types show identical IR spectra.³⁰⁷ Dimeric big-acetylacetonoxotitanium was prepared by Yamamoto and Kambara²⁸⁶ by the hydrolysis of big-acetylacetonodialkoxo titanium and also by Beattie and Fawcett³⁰⁸ by the oxidation of titanium(III) acetylacetonate. Recently the acetylacetonocompound $(C_5H_7O_2)(TiO)Cl$ has been prepared by Collis³⁰⁹ by the oxidation procedure of Nesmeyanov³⁰⁶ and shown to be a dimer also.

The above survey of the literature on organotin and organotitanium compounds, mostly relevant to the work reported in this thesis, shows that though considerable work has been done on organotin and chelated titanium compounds generally, information is relatively scanty in certain areas, e.g., on chelated tin compounds, oxo-titanium chelates and chelated titanoxo stannanes. Following more specific points may be noted:-

1. In spite of the large number of patents on the direct synthesis of organotin halides, available precise information is inadequate. Apparently, there is scope for examining new methods, especially for making some industrially important intermediates such as dibutyltin dihalides.

2. In comparison with that of titanium(IV), the literature on chelated tin(IV) halides is very limited; chelates of tin(II) seem to be unknown. It seems desirable, therefore, to examine possible methods of synthesis of these and related compounds, and to study the properties of the products obtained.

3. Only one or two thienyl derivatives of tin have so far been reported.^{310, 311} It is conceivable that thiophene may form very stable organotin compounds with sulphur atom in the heterocyclic ring.

4. Cleavage of the tin-carbon bond in tetraorganotins by halogens has been widely studied; but the action of halogens on chelated organotin compounds is yet to be reported.

5. A field of recent interest in organotin chemistry is the study of insertion of sulphur dioxide into tin-carbon bonds. No attempt has so far been made to study the action of sulphur dioxide on chelated organotin compounds.

6. Only a few titanoxo stannanes are known. Chelated titanoxo stannanes are expected to be stable, and are also interesting from the structural point of view.

7. Organoxo titanium oxides and chelated oxotitanium compounds have not attracted much attention so far. More information on the organophilic nature of these compounds would be worthwhile.

SECTION III : EXPERIMENTAL RESULTS AND DISCUSSIONS

1. Direct Synthesis of Diorganotin Diodides

Direct Synthesis of Diorganotin Diiodides

A. Discussion and Results

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Frankland's method (1849) of direct synthesis of diethyltin diiodide from ethyl iodide and tin metal remained uninvestigated for a long time. In recent years, however, it forms the basis of manufacture of several diorganotin dihalides. Different organic halides have been tried by different workers. For the direct synthesis of dialkyl tin dihalides the order of reactivity of the alkyl halide appears to be in the order of RI > RBr > RCl. A catalyst (generally a Lewis base) is almost always necessary for the progress of the reaction, the only known exception being the reaction with benzyl chloride. A wide variety of other catalysts such as metallic iodides, zinc, lithium, organic amines, tetrabutyl ammonium iodide and even irradiation with γ -rays have been reported by different workers. The tin metal has been used in the forms of foil, granules or powder.

Dibutyltin oxide is an important intermediate for making polymer stabilizers. In the absence of adequate literature on an efficient method for its preparation, it was decided to re-examine the reaction between a *n*-butyl halide and tin metal with a view to obtaining high yields of dibutyltin dihalide, a precursor of dibutyltin oxide. From preliminary considerations, the iodide was the halide of choice for its known greater activity, and also

because of its relatively high boiling point (131°) which would facilitate the reaction being carried out at a higher temperature under atmospheric pressure. The physical state of the tin metal, a factor not sufficiently stressed by previous workers, was also included in the study. A spongy variety of the metal, chemically very reactive, was prepared by treating a solution of stannous chloride with slightly less than the stoichiometric quantity of zinc metal powder, and has been used in addition to the other forms of tin. It was observed at the very outset that none of the forms of the metal reacted appreciably with butyl iodide in the absence of a catalyst. Search for a suitable chemical catalyst was, therefore, essential.

As stannic halides and organotin halides are both known to form coordinated addition compounds of varying stabilities with donor molecules (e.g., molecules containing a tertiary nitrogen atom), some tertiary nitrogen bases were tried as catalysts. With pyridine or triethylamine as the catalyst, the spongy tin reacted better than all the other varieties of the metal, and the product was nearly pure dibutyltin diiodide. Since the addition products of tertiary amines with butyl halides are quaternary compounds, salts of the tertiary bases (e.g., pyridine hydrochloride and triethylamine hydrochloride) were also tried as catalysts. As expected, the spongy variety of tin was found more reactive than all the other forms of tin here also, and the metal reacted (dissolved) to a maximum of 95%. The product formed, even on varying the proportion of the reactants, was essentially dibutyltin diiodide, and the excess of either reactant used could be recovered unchanged.

Even though the reaction took place in the molar ratio 1:2 of tin to butyl iodide, an excess of the latter was found advantageous to keep the product in solution. The minimum amount of the catalyst to be used was determined by trial and was fixed at 1/40th mole fraction of the tin metal taken, any less amount proving insufficient for maximum reaction. Larger amounts did not appreciably increase either the rate of the reaction or the yield of the dibutyl compound.

Bases such as piperidine, quinoline, isoquinoline and sodamide were tried without much success for catalysing the reaction between spongy tin and butyl iodide.

Other organic iodides such as *n*-amyl iodide, *n*-hexyl iodide, 2-ethylhexyl iodide and *n*-octyl iodide reacted with spongy tin in the presence of pyridine hydrochloride and gave corresponding diorganotin diiodides. The amount of tin reacted (16-30 per cent) was, however, much less than that in the case of butyl iodide. Only negligible quantities (2-5 per cent) of tin metal dissolved during reactions of spongy tin with cyclohexyl iodide, iodobenzene and 4-iodothiophene in presence of the same catalyst. The results are summarized in Tables 1 and 2.

Table 1

Reaction between tin (0.04 mole) and butyl iodide (0.12 mole)
in presence of catalysts (0.001 mole) at 130-140°

Form of tin metal used	Catalyst	Reaction time (hrs.)	Tin reacted (%)
1. Granulated	nil	6	4.2
2. Foil	nil	6	4.2
3. Sponge	nil	6	6.3
4. Granulated	pyridine	6	8.4
5. Foil	"	6	10.5
6. Sponge	"	6	69.0
7. Granulated	pyridine hydrochloride	6	44.2
8. Foil	"	6	36.8
9. Sponge	"	2	94.0
10. Sponge	triethylamine	6	63.2
11. Sponge	triethylamine hydrochloride	2	94.0
12. Granulated	"	6	44.2
13. Foil	"	6	36.8
14. Sponge	pyridine hydrochloride	6	76.4
15. Sponge	"	6	68.0
16. Sponge	"	6	79.0

Other experimental conditions:-

- Experiments 1-13 - Components mixed together and heated to 130-140° under reflux.
- Experiment 14 - Catalyst added to boiling mixture of butyl iodide and tin.
- Experiment 15 - Tin added in small lots to boiling butyl iodide and catalyst.
- Experiment 16 - Done in boiling xylene (130°).

Table 2

Reaction between tin sponge (0.04 mole) and organic iodides (0.12 mole) in presence of pyridine hydrochloride (0.001 mole) catalyst

No. Organic iodide used	Reaction time (hrs.)	Temp. (°C)	Tin reacted (%)
1. n-Butyl	2	130-140	94
2. n-Amyl	6	150-160	36.4
3. n-Hexyl	6	160-170	21.0
4. 2-Ethylhexyl	6	190-200	16.0
5. n-Octyl	6	190-200	25.1
6. Cyclohexyl	6	150-200	2-5
7. Phenyl	6	"	"
8. α -Thienyl	6	"	"

From the pattern of reactivity recorded in the two Tables, it seems probable that the quaternary ammonium type compounds are good catalysts. When the hydrochloride was replaced by another hydrohalide of the same base it was found that the effect remained the same, showing that the quaternary ammonium group was the effective moiety.

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Sisido et al have proposed a radical mechanism for the direct reaction between benzyl chloride and tin metal in absence of a catalyst. However, for the reaction of butyl iodide with tin in presence of quaternary ammonium salts, an ionic reaction mechanism has been considered more probable by some other Japanese workers.³¹²

B. Experimental Data1.1 Preparation of starting materials-1.1.1 Alkyl and other iodides-

n-Butyl iodide was obtained from red phosphorus, iodine and n-butanol. The quality was good and the yield better than that reported by Vogel.³¹³ n-Amyl, n-hexyl, cyclohexyl, 2-ethylhexyl and n-octyl iodides were prepared from the respective alcohols and hydriodic acid. Iodobenzene (B.D.H. Laboratory Reagent grade) was dried and distilled. p-Iodothiophene was prepared according to the method given by Wirth et al.³¹⁴

1.1.2 Spongy tin-

This active variety was prepared by treating a solution of stannous chloride (analytical grade) in dilute hydrochloric acid with not more than the stoichiometric quantity of pure zinc metal powder. After allowing sufficient time to dissolve the latter, the precipitated tin metal was filtered, washed with distilled water, dried and preserved in a stoppered bottle.

1.1.3 Pyridine and triethylamine hydrochlorides-

Equivalent amounts of the base and concentrated hydrochloric acid were mixed in a flask with strong cooling, after which the solution was evaporated on a water bath under reduced pressure. When the contents in the flask showed signs of crystallization, the solution was cooled and the lumps formed were broken into small pieces. The solid was dried at 120° under reduced pressure (5 mm) till no more water came out. Yields were nearly quantitative.

- 1.2 Reaction between tin (in different forms) and n-butyl iodide
- 1.2.1 Granulated tin metal (analytical grade, 4.75 g; 0.04 mole) and n-butyl iodide (22 g; 0.12 mole) were slowly heated in oil bath with stirring in an atmosphere of dry nitrogen. Very little reaction took place even after refluxing at 130-140° for six hours. Amount of tin reacted 0.2 g (4.2 per cent).
- 1.2.2 Tin foil (analytical grade, 4.75 g; 0.04 mole) cut into small pieces and n-butyl iodide (22 g; 0.12 mole) were heated under reflux in a similar manner for six hours. Only about 0.2 g of the metal dissolved.
- 1.2.3 Tin sponge and n-butyl iodide (same quantities as above) were mixed and reacted as in 1.2.1. The metal got coated with a yellow deposit. After removing this deposit by washing with acetone, the tin dissolved was found to be 0.3 g.
- 1.3 Reaction between tin and n-butyl iodide in presence of catalysts
- 1.3.1 Pyridine-
Granulated tin (4.75 g; 0.04 mole) and n-butyl iodide (22 g; 0.12 mole) were mixed and pyridine (0.08 g; 0.001 mole) added. The mixture was slowly heated to refluxing point with constant stirring and kept at that temperature for six hours. Metal dissolved was 0.4 g (8.4 per cent).
- 1.3.2 Above experiment was repeated with tin foil. The amount of tin dissolved was 0.5 g (10.5 per cent).

1.3.3 When spongy tin was substituted for tin granules in expt. 1.3.1 the metal dissolved was 3.3 g (69 per cent). After removing the undissolved tin, the solution was first treated with cold dilute hydrochloric acid (2N, 30 ml) and then extracted thrice with carbon tetrachloride. The extract was dried over fused calcium chloride and fractionally distilled. The solvent and the unreacted butyl iodide first distilled over. The fraction distilling between 143-144^o/5 mm. was collected separately. Yield 9.2 g (47 per cent on the metal taken).

Analysis: Found Sn 24.24, I 52.45; calculated for $(C_4H_9)_2SnI_2$, Sn 24.39, I 52.19 per cent.

Pale yellow, heavy liquid; turns red on exposure to light and air; soluble in common organic solvents.

1.3.4 Triethylamine-

In place of pyridine in expt. 1.3.3 triethylamine (0.101 g; 0.001 mole) was used as the catalyst. The metal dissolved was 3 g (63.16 per cent), and the yield of dibutyltin diiodide was 9.5 g (48.8% on the metal taken).

1.3.5 Pyridine hydrochloride-

A mixture of n-butyl iodide (22 g; 0.32 mole), spongy tin (4.75 g; 0.04 mole) and dry pyridine hydrochloride (0.115 g; 0.001 mole) was heated slowly with vigorous stirring. Tin dissolved quickly and the reaction was complete within an hour. Heating and stirring were continued for another hour, after which the mixture was cooled, decanted from the solid residues

and processed as in 1.3.3. The residue containing the unreacted tin metal was washed with acetone, dried and weighed (about 0.3 g; 6 per cent). The acetone washings on evaporation gave a red solid (about 1 g) which was purified and identified as stannic iodide. The yield of dibutyltin diiodide was 14.68 g (76.4 per cent on the metal taken).

1.3.6 Triethylamine hydrochloride-

This salt (0.137 g; 0.001 mole) was substituted for pyridine hydrochloride in 1.3.5. The clear red liquid was decanted and processed for dibutyltin diiodide as in 1.3.5.

Yield 14.1 g (74.8 per cent on the metal taken). After washing with acetone, the tin metal in the residues weighed 0.3 g (6 per cent) and the acetone washings gave stannic iodide (1 g).

1.3.7 Granulated tin (4.75 g; 0.04 mole) and *n*-butyl iodide (22 g; 0.12 mole) were reacted in presence of pyridine hydrochloride (0.115 g; 0.001 mole) as in expt. 1.3.5. After six hours of refluxing and stirring, tin remaining unreacted was 2.1 g (44.21 per cent). A similar result was obtained by substituting triethylamine hydrochloride in place of pyridine hydrochloride.

1.3.8 Experiment 1.3.7 was carried out by substituting small pieces of tin foil in place of granulated tin. After allowing a period of six hours to react, the tin remaining undissolved was 1.75 g (36.84 per cent). A similar result was obtained by using triethylamine hydrochloride as catalyst in place of pyridine hydrochloride in this reaction.

- 1.3.9 Spongy tin (4.75 g; 0.04 mole) and *n*-butyl iodide (22 g; 0.12 mole) were mixed well and heated to refluxing temperature. Pyridine hydrochloride (0.115 g; 0.001 mole) was added to this mixture under vigorous stirring. After six hours the metal remaining unreacted was 1.12 g (23.6 per cent). Yields of dibutyltin diiodide and stannic iodide were 10.32 g (53 per cent) and 4.5 g respectively.
- 1.3.10 To a boiling mixture of *n*-butyl iodide (22 g; 0.12 mole) and pyridine hydrochloride (0.115 g; 0.001 mole), spongy tin (4.75 g; 0.04 mole) was added in small amounts within a period of 30 minutes. After six hours the metal remaining unreacted was 1.52 g (32 per cent) and the yield of dibutyltin diiodide 8.3 g (47.7 per cent). Stannic iodide (1 g) also was obtained.
- 1.3.11 Spongy tin and *n*-butyl iodide (quantities same as above) were mixed well, pyridine hydrochloride added and the temperature slowly increased with continuous stirring. Reaction proceeded smoothly at a fast rate and was complete within an hour. The metal dissolved was 95 per cent and the yield of dibutyltin diiodide 15 g (77 per cent). Some stannic iodide also was obtained (1 g).
- 1.3.12 Experiment 1.3.5 was carried out in a medium of xylene. Reaction was slow in this case and took six hours for completion. The unreacted tin was 0.97 g (21 per cent) and the yield of dibutyltin diiodide was 14.6 g (60 per cent).

- 1.3.13 In expt. 1.3.5, the catalyst was added in small quantities (10 mg each time) during one hour. Reaction started slowly and the tin metal taken reacted fully only when all the required amount of catalyst (0.12 g; 0.001 mole) was added. Further addition of catalyst did not increase the rate of the reaction. Tin dissolved was 94 per cent.
- 1.3.14 The molar ratio of tin and butyl iodide the expt. 1.3.5 was varied. For ratios 1:1, 2:3, 1:2, 1:3, 1:4 and 1:6, the product was dibutyltin diiodide. When tin metal was in excess, the reaction product was a sticky solid, which made the isolation of any pure compound difficult.
- 1.3.15 Other catalysts-
Piperidine, quinoline, isoquinoline and sodamide (0.001 mole each) were used in turn to catalyse the reaction between spongy tin and *n*-butyl iodide in expt. 1.3.3. The amount of tin dissolved in each case was negligible (0.5 per cent).
- 1.4 Reaction of tin with other organic iodides
- 1.4.1 *n*-Amyl iodide-
Tin metal sponge (4.75 g; 0.04 mole), *n*-amyl iodide (23.76 g; 0.12 mole) and pyridine hydrochloride (0.115 g; 0.001 mole) were mixed and slowly heated to 150-160° with stirring. The reaction being slow, a period of six hours was given for the materials to react. The metal dissolved was 1.75 g (36.84 per cent). The dark red liquid was processed for the diiodide similar to the dibutyl derivative in 1.3.3.

Di- η -amyltin diiodide obtained was 6.2 g (30 per cent).

Analysis: Found Sn 22.11, I 49.73; calculated for $(C_5H_{11})_2SnI_2$, Sn 23.10, I 49.41 per cent.

Pale yellow liquid, b.p. $135^\circ/5$ mm.

1.4.2 η -Hexyl iodide-

Tin metal sponge (4.75 g; 0.04 mole), η -hexyl iodide (26.44 g; 0.12 mole) and catalyst pyridine hydrochloride (0.115 g; 0.001 mole) were reacted in the same manner as in expt. 1.4.1. for six hours at $160-170^\circ$. Tin dissolved was 0.96 g (21 per cent) and the diiodide obtained was 3.25 g (14.9 per cent).

Analysis: Found Sn 21.11, I 47.36; calculated for $(C_6H_{13})_2SnI_2$, Sn 21.91, I 48.86 per cent.

1.4.3 2-Ethylhexyl iodide-

Spongy tin (4.75 g; 0.04 mole) and 2-ethylhexyl iodide (28.8 g; 0.12 mole) were reacted in presence of catalyst pyridine hydrochloride (0.115 g; 0.001 mole) at $190-200^\circ$ for six hours. The metal reacted was 0.72 g (16 per cent) and the diiodide obtained was 2.63 g (11 per cent).

Analysis: Found Sn 18.97, I 42.79; calculated for $(C_8H_{17})_2SnI_2$, Sn 19.86, I 42.47 per cent.

Colourless liquid, b.p. $168-170^\circ/1$ mm.

1.4.4 n-Octyl iodide-

n-Octyl iodide (28.8 g; 0.12 mole) was reacted with the same amounts of spongy tin and catalyst as in expt. 1.4.3. Tin reacted was 1.2 g (25.1 per cent) and the diiodide obtained was 4.17 g (17.5 per cent).

Analysis: Found Sn 19.28, I 43.06; calculated for $(C_8H_{17})_2SnI_2$, Sn 19.86, I 42.47 per cent.

Pale red liquid, b.p. 190-192°/5 mm.

1.4.5 Only negligible quantities (2-5 per cent) of the tin metal dissolved during reactions of spongy tin with cyclohexyl iodide, iodobenzene and α -iodothiophene in presence of the above-mentioned catalysts.

2. Chelated Tin(IV) Halides, Alkyls and Aryls

Chelated tin(IV) halides, alkyls and arylsA. Discussion and Results

Stable chelated tin(IV) compounds, arising out of simultaneous coordination and proton replacement of potentially acidic OH group of acetylacetone, benzoylacetone and salicylaldehyde, are reported in literature. Nelson and Martin¹⁵⁹ prepared some chelated tin dichlorides by cleavage of the phenyltin bond by some chelating ligands, and noted that a large excess of the ligand was necessary; also, yields were low in many cases. We have succeeded in preparing bis-chelated tin(IV) dihalides by reacting the sodio-derivative of a ligand and anhydrous stannic halide in an inert solvent. Compounds prepared are of the type L_2SnCl_2 where LH = salicylaldehyde, methylsalicylate, acetylacetone, benzoylacetone, dibenzoylmethane, benzoylethylacetate, acetoacetanilide and 8-hydroxyquinoline. Stannic iodide was also found to react with the sodio-derivatives of chelating ligands forming chelated tin(IV) iodides, but the products were insoluble in solvents and hence difficult to purify. Bis-chelated tin(IV) iodides were prepared by us by the alternate route of addition of iodine to bis-chelated tin(II) compounds. In all the reactions carried out by us, it was observed that even when the molar ratio of the reactants was varied, only the bis-chelated tin(IV) dihalides were obtained.

Bis-chelated tin(IV) dihalides are coloured, non-hygroscopic and stable solids, some showing sharp melting points while others decomposing at higher temperatures. Some of them are sufficiently soluble in hot benzene and their molecular weights show that they are monomers. Salicylaldehyde gave two isomers, yellow and red, on crystallization from benzene and chloroform respectively. These had identical infrared spectra but their molecular weight determinations by ebullioscopy indicated that the yellow variety was a monomer and the red one a dimer. Compounds are listed in Table 3.

The two halogen atoms in the chelated tin halides were found to be less chemically reactive than those in tin tetrachloride or alkyl/aryl-tin halides. When reacted with dry hydrogen chloride, bromine in solvent, phenyllithium, Grignard reagent, phenol, water or dilute alkali, no well-defined product could be isolated.

Though tetravalent tin does not form a chelated penta-coordinated halide of the type $LSnX_3$, (LH is a bidentate ligand), it is known that stable penta (and hexa)-coordinated compounds are obtained when the halogen is replaced by an alkyl or aryl group. Bis-chelated tin(IV) dihalides did not show reactivity towards organolithium compounds or Grignard reagents, but chelated tin(IV) alkyls and aryls could be prepared by reacting the alkyl/aryl tin halides with sodio-derivatives of ligands. The organotin halides used were di-*n*-butyl- and di-*n*-octyl-tin dichlorides and triphenyltin chloride;

and the ligands were salicylaldehyde, methyl salicylate, acetylacetone, benzoylacetone, dibenzoylmethane and 8-hydroxyquinoline. No replacement of alkyl or aryl groups by the ligand was observed during the reaction. Yields were good, and the products were coloured, stable solids soluble in common organic solvents and having sharp melting points. Ebullioscopy in benzene showed that they were monomeric in solution. (Tables 4 and 7).

The cleavage of organic groups attached to tin in a tetraorganotin (symmetrical and unsymmetrical) molecule by halogens has become a topic of recent interest to several workers.^{60,64,65} When the chelated organotins prepared by us were subjected to the action of bromine under mild conditions (e.g., as dilute solutions in methylene chloride at -20°) some interesting results were obtained. Bromine reacted successively with the organic moieties in the compound, leaving the chelating ligand intact. Thus, big-chelated dibutyltin gave big-chelated monobutyl monobromotin; chelated triphenyltin gave a monobromo- and then a dibromo-derivative by successive replacement of the phenyl groups only. Excess of bromine had no further action either on the last phenyl group attached to tin or on the ligand under the experimental conditions described. The weakly nucleophilic solvent methylene chloride provided conditions for the electrophilic substitution of the alkyl or phenyl groups in these metal chelates leaving the chelating ligand unaffected. Compounds prepared in this way are tabulated in Table 5.

Furthermore, it is well known that HCl cleaves organic groups attached to tin in tetraorganotins, forming organotin chlorides.⁶⁸ When similar experiments were carried out using dry HCl and chelated tin alkyls/aryls in benzene, it was observed that the chelating ligands were removed; an organotin chloride and the free ligand were identified in the reaction products. No further substitution, e.g., of the organic groups, was noticed under the experimental conditions.

IR Spectra

A large number of IR absorption spectra for the 600-2000 cm^{-1} region have been recorded and reported here in the experimental section, especially of the new compounds synthesized, to provide basic physical data for identification. It is not the purpose of this thesis to make a complete vibrational analysis of the recorded spectra. As is well known, such an exercise requires comparative analysis of supplementary data from the corresponding Raman spectra and, in many cases, from the spectra of the deuterio-substituted derivatives.

However, an attempt has been made here to analyse the spectrum only in the range 1500-1750 cm^{-1} for two reasons. (Table 6) Firstly, the frequencies in this region are relatively insensitive to large variations in the substituent groups in a molecule; secondly, the C-C and C=O vibrations appear as absorption peaks in this region, which are of the greatest interest to the chemist in the structure of metal chelates. The attempted analysis is empirical and is based on relative values of the absorption peaks in the IR spectra of the compounds rather than on any rigorous analysis from considerations of molecular symmetry.

(a) Big-(salicylaldehyde) complexes

Regarding the carbonyl frequency in these complexes, (Table 6) it is known³¹⁵ that a shift in this frequency is a direct function of the stability of the salicylaldehyde chelate. It would thus be reasonable to assign the frequency 1661 cm^{-1} to the hydrogen-bonded C=O group in salicylaldehyde. With the tin metal replacing hydrogen, the frequency is damped further, especially when the metal itself is sigma-bonded to an electro-negative atom such as Cl, Br or I ($\nu_{\text{CO}} = 1613, 1621, 1661 \text{ cm}^{-1}$). replacement of the halogen atom by an alkyl causes the electron density to shift towards the tin atom with loosening of the bond of chelation and consequent increase in the C=O value, the effect being more pronounced in the octyl- than in butyl-tin compound.

The two frequencies, viz., 1576 and 1616, appear to be ring oscillations in the salicylaldehyde molecule. They persist in all the tin complexes of salicylaldehyde and even in the corresponding titanium complexes. (vide Section III.6) A similar reduction in these values is observed when the metal atom is attached to different groups. The frequencies are absent in the spectra of acetylacetonone. Of the four frequencies 1576, 1616, 1647 and 1661 cm^{-1} in the ligand, 1647 appears to be a $\delta(\text{OH})$ oscillation because it does not appear in any of the metal complexes of salicylaldehyde. The assignment, however, needs to be confirmed by deuteration of the OH group.

(b) Bis-(methylsalicylato) complexes

Proceeding on the above line of reasoning, the following inferences can be made about methyl salicylate and its chelates from a study of the absorption peaks in the same region. (Table 6)

(1) In the ligand itself, the damping effect of hydrogen bonding on the CO frequency is about the same as in the case of salicylaldehyde.

(2) The corresponding further lowering in the metal complexes is, however, small and the differential effect of increasing or decreasing electron density on the tin atom by linking the latter with a halogen or an alkyl group is insignificant. This indicates that the carbonyl oxygen in methyl salicylate is a relatively weaker donor of electrons (to tin metal) compared to salicylaldehyde itself.

(c) Bis-(acetylacetonato) complexes

The strong effect of replacing the hydrogen atom by tin is particularly evident here. As expected from the above tentative analysis of the bis-salicylaldehyde complexes, the effect is most pronounced with the dichloro and least with dioctyl complexes. The unusually broad character of the CO band is probably a resonance effect arising out of conjugate chelation in this strongly chelating 1-3 diketone.³¹⁶ The doublet at about $1710_{\pm 15} \text{ cm}^{-1}$ also indicates the presence of the unchelated keto-form in the pure ligand, which disappears in the metal complexes.

(d) Big-(benzoylacetono) complexes

Benzoylacetone gives a clear picture of a strongly chelating ligand. Its ring vibrations 1513 and 1627 cm^{-1} undergo damping effect in a manner similar to that observed in salicylaldehyde complexes. The damping of the ketonic frequency in the metal complexes is in direct variation with the electronegativity of the X atom or group attached to the metal.

(e) Big-(benzoylethylacetato) complexes

Hydrogen bonding in this ligand is weak, and the ligand appears to exist at room temperature in both its keto and enol forms (1739, 1695 cm^{-1}). Disappearance of the higher frequency in the metal complexes indicates that the latter are chelates like those of the other ligands.

(f) Big-(dibenzoylmethano) complexes

Unlike acetylacetone, the carbonyl group frequency at 1720 cm^{-1} is absent in this symmetrical 1:3 diketone. The larger number of recorded frequencies in 1500-1700 cm^{-1} region is noteworthy, and may indicate that the ligand exists in more than one form, though the metal complex probably has one structure. Two forms of the ligand, yellow and red, have been isolated by workers using different solvents for crystallization.³¹⁷ The reduction in the frequency of the H-bonded ketonic group as a result of metal substitution in place of hydrogen is considerable, indicating high stability of the metal chelates.

(8) dig-(8-hydroxyquinolino) complexes

The ligand exists as a strong hydrogen chelate. The single peak at 1587 cm^{-1} in the ligand is split into two sharp peaks in the complexes, probably as a result of augmentation of the C=N frequency which was previously superimposed on the ring C=C vibrations. Chelated C=N frequencies for chloride, bromide, butyl and octyl tin compounds ($1615, 1606, 1600, 1600\text{ cm}^{-1}$) indicate significant coordination of C=N with the metal.

In the triphenyltin monochelates prepared by us and listed in Table 8, salicylaldehyde, acetylacetone and benzoyl ethylacetate show fairly strong chelation between the carbonyl group and the metal as indicated by the shift in the carbonyl frequencies in the complex and in the ligands. Carbonyl frequencies comparable to those of ligands themselves are observed in complexes of methyl salicylate, benzoylacetone and dibenzoylmethane. If the carbonyl group in these ligands had not coordinated with the metal at all, it should have shown an absorption peak in the neighbourhood of 1700 cm^{-1} . Absence of such a band indicates coordination of the CO group of the ligand with metal comparable in strength to that of hydrogen bonding in these ligands. In the 8-hydroxyquinoline derivative, two bands (at 1587 and 1600 cm^{-1}) in place of only one (at 1587 cm^{-1}) in the ligand probably indicates coordination of the nitrogen atom with the tin metal and consequent separation of the C=N frequency from the C=C frequency in the ring. ³¹⁸

All these triphenyltin mono-chelates were found soluble in warm benzene, and their molecular weights determined by ebullioscopy in this solvent indicated their monomeric nature. The IR spectra of a solution of salicylaldehyde triphenyltin in benzene (5% w/w) showed a peak at 1667 cm^{-1} corresponding to that of free salicylaldehyde, indicating weak coordination with the metal as compared to that in the solid compound (1616 and 1626 cm^{-1} in Nujol).

Conditions favourable to penta-coordination around tin have been formulated by van der Kerk.^{2,3} Compounds with penta-coordinate tin atoms tend to become more stable if the tin atom is rendered more positive by attachment with one or more negative ligands, and also in the presence of a powerful donor solvent. In triphenyltin mono-chelates reported above, these conditions appear to be fulfilled, so it is also possible that tin may exist as penta-coordinate in these compounds.

It can perhaps be stated generally that the strength of chelation of ligands with the metal, as measured in the shift in the carbonyl frequency from their original values, determines the thermal (and chemical) stability of these chelates. Though enough data have not been collected by us on the mono-chelates, it appears that big-chelates are stabler, and a trans structure (with a centre of symmetry at the site of the metal) seems probable.

Table 3

Reaction products of tin tetrachloride/bromide (1 mole) and
sodio-derivatives of ligands (2.2 mole)

Stannic halide	Reactants		Mol. wt. Found (calc.)	m.p. °C
	Ligand	Products**		
SnCl ₄	Salicylaldehyde	(C ₇ H ₅ O ₂) ₂ SnCl ₂	445 (yellow) 848 (red) (432)	> 260 d
"	Methyl salicylate	(C ₈ H ₇ O ₃) ₂ SnCl ₂ *	499 (492)	104
"	Acetylacetone	(C ₅ H ₇ O ₂) ₂ SnCl ₂	398 (388)	204
"	Benzoylacetone	(C ₁₀ H ₉ O ₂) ₂ SnCl ₂	520 (512)	221
"	Dibenzoylmethane	(C ₁₅ H ₁₁ O ₂) ₂ SnCl ₂	626 (636)	265
"	Benzoylethylacetate	(C ₁₁ H ₁₁ O ₃) ₂ SnCl ₂ *	-	130
"	Acetoacetanilide	(C ₁₀ H ₁₀ O ₂ N) ₂ SnCl ₂ *	-	210
"	8-Hydroxyquinoline	(C ₉ H ₆ ON) ₂ SnCl ₂	-	> > 300 d
SnBr ₄	Salicylaldehyde	(C ₇ H ₅ O ₂) ₂ SnBr ₂ *	-	250
"	Acetylacetone	(C ₅ H ₇ O ₂) ₂ SnBr ₂ *	475 (477)	181
"	Benzoylacetone	(C ₁₀ H ₉ O ₂) ₂ SnBr ₂ *	597 (601)	190
"	Dibenzoylmethane	(C ₁₅ H ₁₁ O ₂) ₂ SnBr ₂ *	726 (725)	266 d
"	8-Hydroxyquinoline	(C ₉ H ₆ ON) ₂ SnBr ₂ *	-	250 d

* New compounds

** Based on chemical analysis

d decomposes at this temperature

Table 4

Reaction products of di-n-butyl/di-n-octyl tin dichloride (1 mole)
and sodio-derivatives of ligands (2.2 mole)

Tin compound	Reactants		Products **	Mol. wt.	
	Ligand			Found (calc.)	m. p. °
Dibutyltin dichloride	Salicylaldehyde		$(C_4H_9)_2Sn(C_7H_5O_2)_2$	475 (475)	143
"	Methyl salicylate		$(C_4H_9)_2Sn(C_8H_7O_3)^*$	540 (535)	45
"	Acetylacetone		$(C_4H_9)_2Sn(C_5H_7O_2)_2$	421 (431)	30
"	Benzoylacetone		$(C_4H_9)_2Sn(C_{10}H_9O_2)_2$	548 (555)	sticky solid
"	Dibenzoylmethane		$(C_4H_9)_2Sn(C_{15}H_{11}O_2)_2$	678 (678)	93
"	Benzoyl ethylacetate		$(C_4H_9)_2Sn(C_{11}H_{11}O_3)^*$	590 (615)	viscous liquid
"	Acetoacetanilide		$(C_4H_9)_2Sn(C_{10}H_{10}O_2)^{\ddagger}$	588 (585)	140
"	8-Hydroxyquinoline		$(C_4H_9)_2Sn(C_9H_6ON)_2$	524 (521)	149
Diocetyl tin dichloride	Salicylaldehyde		$(C_8H_{17})_2Sn(C_7H_5O_2)^*$	594 (587)	85
"	Acetylacetone		$(C_8H_{17})_2Sn(C_5H_7O_2)^*$	585 (543)	liquid
"	Dibenzoylmethane		$(C_8H_{17})_2Sn(C_{15}H_{11}O_2)^*$	805 (791)	66
"	8-Hydroxyquinoline		$(C_8H_{17})_2Sn(C_9H_6ON)^*$	645 (633)	205

* New compounds

** Based on analysis and molecular weight.

Table 6

Reaction product of organotin(IV) chelate (A) and bromine (B)
(in methylene chloride solvent)

Organotin compound	Molar ratio	Products**	Mol. wt. Found (calc.)	m.p. °C
oig-salicylaldehyde dibutyltin	1:2	$(C_4H_9)_2SnBr(C_7H_5O_2)_2$	500 (497)	82
oig-dibenzoylmethano dibutyltin	1:2	$(C_4H_9)_2SnBr(C_{15}H_{11}O_2)_2$	705 (701)	52
oalicylaldehyde triphenyltin	1:2	$(C_6H_5)_2SnBr(C_7H_5O_2)$	475 (473)	103
"	1:4	$(C_6H_5)_2SnBr_2(C_7H_5O_2)$	478 (476)	97
Dibenzoylmethano triphenyltin	1:2	$(C_6H_5)_2SnBr(C_{15}H_{11}O_2)$	576 (575)	112
"	1:4	$(C_6H_5)_2SnBr_2(C_{15}H_{11}O_2)$	580 (578)	80

** Based on analysis and molecular weight.

All are new compounds, not previously reported.

Table 6

IR Spectra of big-chelated tin(IV) compounds

Compound	Frequencies in the range 1500-1750 cm^{-1}
Salicylaldehyde	1575(s), 1616(s), 1642 ⁷ (sh), 1661(s)
Cl_2SnL_2	1526(s), 1575(s), 1613(s)
Br_2SnL_2	1527(s), 1562(s), 1621(s)
I_2SnL_2	1538(m), 1600(m), 1639(s), 1661(s)
Bu_2SnL_2	1545(m), 1600(s), 1653(s), 1667(s)
$(\text{Oct})_2\text{SnL}_2$	1538(m), 1603(s), 1661(s,br)
Methyl salicylate	1600(s), 1626(s), 1689(s)
Cl_2SnL_2	1527(m), 1582(m), 1613(s), 1675(s)
Bu_2SnL_2	1521(s), 1575(s), 1587(s), 1613(s), 1675(m)
Acetylacetone	1613(s), 1704(s), 1727(m)
Cl_2SnL_2	1538(s, Br)
Br_2SnL_2	1527(s), 1650(s, Br)
Benzoylacetone	1513(m), 1527(s), 1562(s), 1600(s)
Cl_2SnL_2	1515(s), 1538(m), 1587(w)
Br_2SnL_2	1504(s), 1538(s), 1582(m)
Bu_2SnL_2	1515(s), 1662(s), 1603(s)

.....6 (contd.)

Table 6 (contd.)

Compound	Frequencies in the range 1500-1750 cm^{-1}
Benzoylacetate	1572(m), 1587(m), 1626(s), 1695(s), 1739(s)
Cl_2SnI_2	1527(s), 1562(s), 1600(s)
Bu_2SnI_2	1515(s), 1575(m), 1639(s)
Dibenzoylmethane	1520(s), 1550(sh), 1570(s), 1600(s), 1681(s)
Cl_2SnI_2	1522(s), 1540(sh), 1587(m)
Br_2SnI_2	1515(s), 1535(s), 1587(m)
Bu_2SnI_2	1538(s), 1562(s), 1605(s)
8-Hydroxyquinoline	1504(s), 1587(s)
Cl_2SnI_2	1504(s), 1587(s), 1615(s)
Br_2SnI_2	1500(s), 1580(s), 1605(s)
I_2SnI_2	1502(s), 1575(s), 1600(s)
Bu_2SnI_2	1500(s), 1580(s), 1600(s)
$(\text{Oct})_2\text{SnI}_2$	1504(s), 1580(s), 1600(s)

Table 7

Reaction products of triphenyltin chloride (1 mole) and
sodio-derivatives of ligands (1.1 mole)

Ligand	Products **	Mol. wt. Found (calc.)	m.p. °C
Salicylaldehyde	$(C_6H_5)_3Sn(C_7H_5O_2)$	470 (471)	166
Methyl salicylate	$(C_6H_5)_3Sn(C_8H_7O_3)^*$	512 (501)	107
Acetylacetone	$(C_6H_5)_3Sn(C_5H_7O_2)$	456 (449)	110
Benzoylacetone	$(C_6H_5)_3Sn(C_{10}H_8O_2)^*$	521 (511)	sticky solid
Dibenzoylmethane	$(C_6H_5)_3Sn(C_{15}H_{11}O_2)$	568 (573)	145
Benzoylethylacetate	$(C_6H_5)_3Sn(C_{11}H_{11}O_3)^*$	555 (541)	viscous liquid
Acetoacetanilide	$(C_6H_5)_3Sn(C_{10}H_{10}O_2N)^*$	521 (526)	59
8-Hydroxyquinoline	$(C_6H_5)_3Sn(C_9H_6OH)^*$	489 (494)	143

* New compounds

** Based on analysis and molecular weight

Table 8Triphenyltin chelates (Ph_3SnL)

Absorption peaks in the range 1500-1750 cm^{-1}		
Ligand (L)	Pure ligand	Complex Ph_3SnL
Salicylaldehyde	1575(s), 1616(s), 1642(sh), 1661(s)	1550(m), 1613(s), 1626(s)
Ethyl salicylate	1600(s), 1626(s), 1689(s)	1587(m), 1675(s)
Acetylacetone	1613(s), 1704(s), 1727(m)	1531(s), 1580(s)
Propylacetone	1513(m), 1527(s), 1562(s), 1600(s)	1504(s), 1587(s), 1613(s), 1631(w)
Benzoylmethane	1520(s), 1550(sh), 1570(s)	1527(s), 1567(m), 1605(s)
Propylethylacetate	1572(m), 1587(m), 1626(s), 1695(s), 1739(s)	1527(s), 1587(m), 1653(s)
2-Hydroxyquinoline	1504(s), 1587(s)	1587(s), 1600(m)

B. Experimental Data

Purification of starting materials

Anhydrous stannic chloride: Commercial Riedel product was purified as described by Hildebrand and Carter.³¹⁹ It was filtered through glass wool to remove solid hydrate, refluxed over phosphorus pentoxide for several hours and distilled in an all-glass apparatus which had been flame-dried in nitrogen before the distillation. The distillate collected between 114 and 114.2°C was used for the experiments.

Triphenyltin hydroxide, triphenyltin chloride and dioctyltin oxide: These three products of Alpha Inorganics Inc. U.S.A. were dried under reduced pressure and their melting points checked.

A few other known organotin compounds were also prepared and purified by methods given in the literature. Solid organic reagents were generally purified by recrystallization, and liquid reagents by distillation, under reduced pressure where necessary. Solvents were purified and dried by procedures given by Weissburger.³²⁰ Salicylaldehyde, methyl salicylate, acetylacetone and ethyl acetoacetate were dried with anhydrous sodium sulphate and fractionally distilled under reduced pressure.

Extreme care was taken to exclude moisture at all stages. Experiments were done in a dry, oxygen-free nitrogen atmosphere in all-glass apparatus fitted with standard ground joints. Reagents and chemicals were preserved under a dry atmosphere when not in use.

Dichloro tin(IV) chelates - Reactions of sodio-derivatives
of ligands with anhydrous stannic chloride

Reaction with salicylaldehyde -

Clean sodium (0.506 g; 0.022 mole) was dissolved in absolute methanol (10 ml) and the excess of alcohol removed under reduced pressure. Sodium methoxide thus formed was suspended in dry benzene (50 ml) and reacted with salicylaldehyde (2.68 g; 0.022 mole). A yellow precipitate was formed, which was stirred vigorously and the mixture refluxed for an hour. The solvent and the liberated alcohol were then removed under reduced pressure. The dry sodio-derivative of the ligand thus obtained was then again suspended in dry benzene (50 ml), cooled and anhydrous stannic chloride (2.6 g; 0.01 mole) diluted with benzene (10 ml) was added dropwise to it with constant stirring. The deep yellow mixture so formed was stirred for an hour and then gently boiled for 30 minutes. Since big-salicylaldehyde dichloro tin was only sparingly soluble in benzene, most of it remained in the precipitate of sodium chloride and excess of the sodio-ligand. The undissolved mixture was dried under reduced pressure, divided into two parts, and soxhleted separately with (a) chloroform, which gave red crystals; and (b) benzene, which gave deep yellow crystals. The crystals were washed with hexane and dried under reduced pressure at 60°. Total yield 3.9 g (91 per cent).

Analysis: For the red compound, Found C 40.09, H 2.82, Cl 16.45, Sn 27.31; for the yellow compound, found Cl 16.38, Sn 27.23 per cent. Calculated for $(C_7H_5O_2)_2SnCl_2$, C 38.91, H 2.32, Cl 16.43, Sn 27.51 per cent.

Both the red and yellow varieties were non-hygroscopic solids, soluble in alcohol, fairly soluble in hot benzene and chloroform, and insoluble in hexane. Both decompose above 260° without melting. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4-1.2% w/w) found for the yellow variety 446 and for the red variety 848; calculated for the monomer 432. Both have identical IR spectra, with the following absorption maxima (in cm^{-1}) in Nujol:

2899s, 1613s, 1675s, 1526s, 1460s, ^{1428s}1390s, 1370sh, 1205s, 1190sh, 1143s, 1130m, 1026w, 905s, 869w, 790m, 767s.

2.1.2

Reaction with methyl salicylate-

Dry sodium methoxide, prepared from sodium (0.506 g; 0.022 mole) and dry methanol (10 ml), was reacted with methyl salicylate (3.34 g; 0.022 mole) as in 2.1.1. To a cool and stirred suspension of sodio methyl salicylate in benzene (50 ml), stannic chloride (2.6 g; 0.01 mole) in benzene (10 ml) was added and the mixture refluxed for an hour. The insoluble material was then filtered off and the filtrate concentrated to crystallization. The white crystals formed were washed with hexane and dried in vacuum at 60° . Yield 4 g (81 per cent).

Analysis: Found C 38.61, H 2.97, Cl 14.11, Sn 24.13;
 Calculated for $(\text{C}_8\text{H}_7\text{O}_3)_2\text{SnCl}_2$, C 39.04, H 2.85, Cl 14.44, Sn 24.14 per cent.

White crystalline solid, non-hygroscopic, soluble in benzene and insoluble in hexane. M.p. 104° . Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 499; calculated 492.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2899s, 1675s, 1613s, 1582m, 1527m, 1460s,br, 1370s, 1325w, 1290s,
 1260s, 1212s, 1162s, 1140sh, 1087s, 1031w, 1008m, 961br,m,
 871s, 850m, 837m, 802w, 757s, 704m.

2.1.3 Reaction with acetylacetone-

Sodium derivative of acetylacetone, prepared from sodium (0.506 g; 0.022 mole), methanol (10 ml) and acetylacetone (2.2 g; 0.022 mole) as already described, was reacted with stannic chloride (2.6 g; 0.01 mole) in benzene medium, and processed as in 2.1.2. Yield 2.8 g (72 per cent).

Analysis: Found Cl 17.98, Sn 29.95, calculated for $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCl}_2$, Cl 18.31, Sn 30.72 per cent.

Grey, crystalline solid, m.p. 204° . Soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 398; calculated 388.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2941s, 1638s,br/^{1471s}1429m, 1370m, 1351s, 1290s, 1198w, 1031s,
 939s, 813s, 685w.

2.1.4 Reaction with benzoylacetone-

Benzoylacetone (3.58 g; 0.022 mole) was treated with sodium methoxide prepared from sodium (0.506 g; 0.022 mole) and methanol (10 ml) in benzene. The sodio-derivative thus obtained was further reacted with stannic chloride (2.6 g; 0.01 mole) as in 2.1.2. Yield of big-benzoylacetone dichlorotin was 5 g (98 per cent).

Analysis: Found Cl 14.02, Sn 23.11; Calculated for $(C_{10}H_9O_2)_2SnCl_2$, Cl 13.88, Sn 23.20 per cent.

Pale yellow crystals, soluble in benzene and insoluble in hexane. M.p. 220-221°. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 520; calculated 512.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1687w, 1638m, 1515s, 1496s, 1460m, 1449m, 1370m, 1350s, 1307m, 1183w, 1105m, 1030w, 1015w, 1000m, 952m, 856m, 816w, 787w, 781m, 706m.

2.1.6 Reaction with dibenzoylmethane-

The sodio-derivative of dibenzoylmethane, prepared from sodium (0.506 g; 0.022 mole), dry methanol (10 ml) and the ligand (4.93 g; 0.022 mole) was reacted with stannic chloride (2.6 g; 0.01 mole) in benzene medium as in 2.1.2.

Big-dibenzoylmethano dichlorotin obtained was 5.5 g (86.5 per cent).

Analysis: Found C 57.03, H 4.11, Cl 11.32, Sn 18.46; calculated for $(C_{16}H_{11}O_2)_2SnCl_2$, C 56.62, H 3.46, Cl 11.17, Sn 18.67 per cent.

Pale yellow, non-hygroscopic crystals, m.p. 265°. Soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 625; calculated 636.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2899s, 1687m, 1540sh, 1522s, 1481s, 1357s, 1312s, 1230m, 1183w, 1160w, 1124w, 1064m, 1026m, 1003w, 938m, 823w, 775s, 718s, 683w.

11.6 Reaction with benzoylethylacetate-

This ligand (4.22 g; 0.022 mole) was treated with sodium methoxide prepared from sodium (0.506 g; 0.022 mole) and methanol (10 ml) in benzene and the sodio-derivative was further reacted with stannic chloride (2.6 g; 0.01 mole) as in 2.1.2. Yield of big-benzoylethylacetato dichlorotin was 5 g (87 per cent).

Analysis: Found Cl 13.11, Sn 20.69; calculated for $(C_{11}H_{11}O_3)_2SnCl_2$, Cl 12.41, Sn 20.75 per cent.

Pale yellow crystals, m.p. 129-130°; soluble in alcohol, slightly soluble in benzene and insoluble in hexane.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1739s, 1689s, 1600s, 1562s, 1527s, 1503s, 1460s, 1439s, 1379s, 1299s, 1258m, 1220s, 1196sh, 1160w, 1111s, 1081m, 1042sh, 1030s, 990m, 975w, 917m, 810m, 780s, 789m, 725w, 699s.

11.7 Reaction with acetoacetanilide-

Sodium derivative of this ligand was prepared from acetoacetanilide (3.8 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml), and reacted with stannic chloride (2.6 g; 0.01 mole) as in 2.1.2. Yield of big-acetoacetanilido dichlorotin was 4.8 g (89 per cent).

Analysis: Found Cl 13.02, Sn 21.76; calculated for $(C_{10}H_{10}O_2N)_2SnCl_2$, Cl 13.11, Sn 21.92 per cent.

White crystalline powder, non-hygroscopic, m.p. 210°, soluble in alcohol, slightly soluble in benzene and insoluble in hexane.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 3390s, 2941s, 1739w, 1681m, 1613s, 1662s, 1615s, 1449s, 1408s,
 1390w, 1332s, 1325s, 1299m, 1266s, 1198s, 1198w, 1170w, 1093s,
 1025s, 966s, 921w, 835w, 800s, br, 760s, 694m.

2.1.8 Reaction with 8-hydroxyquinoline-

The ligand (3.19 g; 0.022 mole) was first reacted with sodium methoxide, prepared from sodium (0.666 g; 0.022 mole) and methanol (10 ml), to get the sodio-derivative. This was then suspended in benzene and reacted with stannic chloride (2.6 g; 0.01 mole). The deep yellow dichloro derivative formed was completely insoluble in benzene and it was found difficult to separate it from the sodium chloride formed during the reaction. After removing the solvent by filtration and drying the residue, the latter was washed with cold water several times, then with ether and hexane, and dried. The deep yellow powder thus obtained was 4.6 g (93 per cent).

Analysis: Found Cl 14.89, Sn 24.51; calculated for $(\text{C}_9\text{H}_6\text{ON})_2\text{SnCl}_2$, Cl 14.87, Sn 24.84 per cent.

Deep yellow powdery material; decomposes above 300° without melting; soluble in alcohol and insoluble in benzene, chloroform and hexane.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2900s, 1613m, 1587m, 1504s, 1471s, 1389s, 1333s, 1274m, 1235m,
 1176w, 1149w, 1111s, 1036w, 976w, 889w, 833s, 810m, 794m, 755s,
 727w.

The ligands ethylacetoacetate, benzoylacetylacetone and dibenzoylacetylacetone gave viscous products which were difficult to purify and were of indefinite composition.

2.2 Dibromo tin(IV) chelates: Reactions of sodio-derivatives of bidentate ligands with anhydrous stannic bromide

2.2.1 Salicylaldehyde-

Sodio-salicylaldehyde, prepared from sodium (0.506 g; 0.022 mole), methanol (10 ml) and salicylaldehyde (2.68 g; 0.022 mole) as in 2.1.1, was suspended in benzene (50 ml), cooled and stirred. To this ^{suspension} suspension, stannic bromide (4.38 g; 0.01 mole) in benzene (10 ml) was added dropwise. A bright yellow product separated and the reaction was completed by refluxing for two hours. The product being only slightly soluble in benzene, the entire solid mixture was dried under reduced pressure and soxhleted with benzene. Yellow crystals, obtained by concentrating the benzene extract, were washed with hexane and dried at 60° in vacuum. A portion was recrystallized from hot benzene. Yield 4.8 g (92 per cent).

Analysis: Found Br 30.46, Sn 22.67; calculated for $(C_7H_5O_2)_2SnBr_2$, Br 30.70, Sn 22.81 per cent.

Bright yellow crystals, non-hygroscopic, m.p. 250°, soluble in alcohol, slightly soluble in benzene and chloroform and insoluble in hexane.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2857s, 1621s, 1562s, 1527s, 1460s, 1429s, 1398s, 1290m, 1212s, 1185s,
1156s, 1130m, 1020m, 906s, 865m, 790m, 758s.

2.2.2 Acetylacetone-

The sodium derivative of acetylacetone prepared from sodium (0.506 g; 0.022 mole), methanol (10 ml) and acetylacetone (2.2 g; 0.022 mole) was dried, suspended in benzene (50 ml) and reacted with stannic bromide (4.38 g; 0.01 mole) diluted with the same solvent (10 ml). After stirring and refluxing for two hours, the mixture was filtered and the filtrate concentrated to crystallization. The crystals were washed with hexane and dried at reduced pressure at 60°. The yield of big-acetylacetono dibromo-tin was 30 g (63 per cent).

Analysis: Found Br 33.11, Sn 23.7; calculated for $(C_5H_7O_2)_2SnBr_2$, Br 33.54, Sn 24.91 per cent.

Grey crystals, stable in air, m.p. 181°, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 475; calculated 477.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2890s, 1550s, br, 1527s, 1449s, 1415s, 1361s, 1330s, 1274s, 1190w, 1070w, 1015s, 935s, 850w, 807s, 722w, 683m.

2.2.3 Reaction with benzoylacetone-

Benzoylacetone (3.56 g; 0.022 mole) was reacted with sodium methoxide obtained from sodium (0.506 g; 0.022 mole) and methanol (10 ml). From this product big-benzoylacetono dibromo-tin was prepared by reacting it with stannic bromide (4.38 g; 0.01 mole) in benzene as in 2.2.1. The product being

soluble in benzene was separated from sodium chloride and excess of sodio-ligand by filtration. The crystals obtained by concentrating the benzene filtrate were washed with hexane and recrystallized from hot benzene. Yield 3 g (50 per cent).

Analysis: Found Br 25.98, Sn 19.71; calculated for $(C_{10}H_9O_2)_2SnBr_2$, Br 26.61, Sn 19.76 per cent.

Light yellow crystals, m.p. 189-190°, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 597; calculated 601.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2899s, 1582m, 1538s, 1504s, 1481m, 1449m, 1439s, 1342s, 1299s, 1209w, 1179m, 1156w, 1105m, 1070w, 1029w, 1005w, 998m, 975w, 953m, 932w, 854m, 841w, 813w, 780m, 760w, 705s, 693w, 682w.

2.2.4 Reaction with dibenzoylmethane-

Sodio-derivative of the ligand was prepared from ligand (4.93 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml) and reacted with stannic bromide (4.38 g; 0.01 mole) in benzene medium as in 2.2.1. The yellow product was soluble in hot benzene and the filtrate on cooling gave yellow crystals of the dibromide. The crystals were washed with hexane and dried at 60° under reduced pressure. Yield 6 g (83 per cent).

Analysis: Found Br 21.79, Sn 16.23; calculated for $(C_{15}H_{11}O_2)_2SnBr_2$, Br 22.06, Sn 16.39 per cent.

Orange crystals, stable in air, soluble in warm benzene, insoluble in hexane, melts with decomposition (265-266°). Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 726, calculated 725.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1687m, 1535s, 1515s, 1481s, 1361s, 1304s, 1299sh, 1227m, 1183w, 1157w, 1124w, 1096w, 1064m, 1024w, 1000w, 936m, 823w, 769m, 715s, 673m.

2.2.6 Reaction with 8-hydroxyquinoline-

Sodio-derivative of this ligand was prepared in a manner similar to that of salicylaldehyde in 2.1.1 from ligand (3.19 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml). This was suspended in dry benzene and stannic bromide (4.38 g; 0.01 mole) was added. Reaction was completed by boiling and stirring for two hours. The yellow precipitate formed was insoluble in benzene and other similar solvents. So this was processed like the dichloro derivative of this ligand in 2.1.8 by washing with water. Yield 4.5 g (79 per cent).

Analysis: Found Br 28.9, Sn 20.15; calculated for $(\text{C}_9\text{H}_6\text{ON})_2\text{SnBr}_2$; Br 28.21, Sn 20.96 per cent.

Deep yellow powder, melts with decomposition at 250°, insoluble in benzene and slightly soluble in alcohol. Stable towards cold water.

Infrared absorption maxima (in cm^{-1}) are given below: 2899s, 1605m, 1580m, 1497s, 1453s, 1370s, 1319s, 1266m, 1229m, 1212w, 1176w, 1138w, 1105s, 1075w, 1031w, 969w, 882w, 828s, 806m, 787m, 753s, 746s.

2.2.1 Diiodotin(IV) chelates

Reaction of stannic iodide with sodio-derivatives
of ligands-

Stannic iodide was found to be less reactive than corresponding chloride or bromide towards the sodio-derivatives of ligands. The chelated tin(IV) iodides formed by the reaction were sparingly soluble in most solvents. Though the reactions took place under conditions described for stannic chloride and bromide, pure products could not be obtained from the reacted mixture.

2.3 Di-n-butyltin(IV) chelates: Reactions of di-n-butyltin dichloride with sodio-derivatives of ligands-

2.3.1 Reaction with salicylaldehyde-

Salicylaldehyde (2.68 g; 0.022 mole) was reacted with sodium methoxide prepared from sodium (0.506 g; 0.022 mole) and dry methanol (10 ml) as in 2.1.1. The dry sodio-derivative was suspended in benzene (50 ml) and dibutyltin dichloride (3.03 g; 0.01 mole) dissolved in benzene (10 ml) was added to it. The mixture was stirred well and gently refluxed for two hours. After cooling, sodium chloride (with any other insoluble material) was filtered off and the filtrate concentrated to crystallization. The crystals were washed with hexane and dried under reduced pressure. Yield 3.2 g (67 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 55.71, H 6.02, Sn 25.13; calculated for $(C_4H_9)_2Sn(C_7H_5O_2)_2$; C 55.62, H 5.9, Sn 25.01 per cent.

Yellow crystals, m.p. 143° , soluble in benzene but insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 475; calculated 475.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2900s, 2740m, 1667s, 1653s, 1600s, 1545m, 1460s, 1445s, 1445s,
 1399s, 1380m, 1342m, 1333w, 1299s, 1193m, 1180s, 1155s, 1124m,
 1080w, 1047w, 1034w, 965w, 906s, 895s, 843w, 782w, 770w, 755s, 730w.

2.3.2 Reaction with methyl salicylate-

The sodio-derivative of methyl salicylate was prepared in a manner similar to that of salicylaldehyde from methyl salicylate (3.34 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml). This was reacted with dibutyltin dichloride (3.03 g; 0.01 mole) in benzene. The product being soluble in benzene, the insolubles were removed and the filtrate was concentrated to a viscous syrup. This was repeatedly washed with hexane finally to give a solid which was dried under reduced pressure. Yield 3.2 g (60 per cent).

Analysis: Found C 53.11, H 6.58, Sn 21.49; calculated for $(C_4H_9)_2Sn(C_8H_7O_3)_2$, C 54.01, H 6.01, Sn 22.01 per cent.

White solid, m.p. 45° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 540; calculated 535.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2924s, 1676m, 1613s, 1587s, 1575s, 1521s, 1488s, 1471s, 1449s, 1389s, 1348m, 1321s, 1307m, 1250s, 1242s, 1220m, 1163s, 1149m, 1096w, 1081w, 1045w, 1031w, 985w, 893m, 865m, 833m, 813m, 760s, 749s, 704s.

2.3.3 Reaction with acetylacetone-

Bis-acetylacetone dibutyltin was prepared from acetylacetone (2.2 g; 0.022 mole), sodium (0.506 g; 0.022 mole), methanol (10 ml) and dibutyltin dichloride (3.03 g; 0.01 mole) in a manner similar to 2.3.2. The viscous liquid material obtained after the reaction, was washed repeatedly with hexane

and dried under reduced pressure, but could not be obtained as a solid powder. It decomposed when distillation under reduced pressure was attempted, and also in a chromatographic alumina column. Yield 2.6 g (60 per cent).

Analysis: Found Sn 27.28; calculated for $(C_4H_9)_2Sn(C_5H_7O_2)_2$, Sn 27.51 per cent.

Colourless viscous liquid, solidifying at 29-30°. Hygroscopic, soluble in benzene, but insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 421; calculated 431.

Infrared absorption maxima (in liquid film) are given below (in cm^{-1}) 2941s, 1687s, 1524s, 1449s, 1379s, 1258s, 1198m, 1156m, 1081m, 1021s, 966m, 930s, 880m, 848m, 775s, 748w.

2.3.4 Reaction with benzoylacetone-

Bis-benzoylacetone dibutyltin was prepared in a manner similar to the methyl salicylate derivative described in 2.3.2 from benzoylacetone (3.56 g; 0.022 mole), sodium (0.506 g; 0.022 mole), methanol (10 ml) and dibutyltin dichloride (3.03 g; 0.01 mole). The reaction product remained a pale yellow, sticky solid even after washing with hexane and drying under reduced pressure. Further purification without decomposition was difficult. Yield 2.8 g (50 per cent).

Analysis: Found Sn 21.93; calculated for $(C_4H_9)_2Sn(C_{10}H_9O_2)_2$, Sn 21.40 per cent.

Pale yellow sticky solid becoming liquid at about 60°; soluble in benzene but in soluble in hexane. Molecular weight

(ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 548; calculated 555. On keeping at 150° at 1 mm. pressure it becomes a white powder showing no melting point.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2941s, 1603s, 1562s, 1515s, 1458s, 1484s, 1379s, 1300s, 1279s,
 1209m, 1179m, 1155w, 1107m, 1073m, 1031s, 1010sh, 1000s,
 952m, 880w, 861m, 796w, 764s, 711s, 684m.

1.3.6 Reaction with dibenzoylmethane-

Dibutyltin dichloride (3.03 g; 0.01 mole) was reacted with the sodio-derivative obtained from dibenzoylmethane (4.93 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml). The product, being soluble in benzene, was separated from insolubles by filtration. The benzene filtrate was concentrated to crystallization and the crystals were washed with hexane. Yield 5 g (74 per cent). A portion was further purified by recrystallization from benzene.

Analysis: Found C 67.92, H 6.73, Sn 17.13; calculated for $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{C}_{15}\text{H}_{11}\text{O}_2)_2$, C 67.19, H 5.89, Sn 17.49 per cent.

Pale yellow crystals, m.p. 93°, stable in air, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 678; calculated 678.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2941s, 1605s, 1562s, 1538s, 1488s, 1471s, 1389s, 1316s, 1299s,
 1236s, 1190m, 1170m, 1136m, 1099w, 1075m, 1058m, 1036sh,m,
 1031m, 1005m, 983w, 943m, 889w, 852w, 816w, 793m, 762s, 720s, 688s.

2.3.6 Reaction with benzoylethylacetate-

benzoylethylacetate (4.22 g; 0.022 mole) was converted into the sodio-derivative as in the case of other ligands and reacted with dibutyltin dichloride (3.03 g; 0.01 mole). After the reaction, the insolubles were filtered off and the benzene filtrate on concentration gave a thick liquid. This was washed with hexane and dried, but the product remained a pale yellow thick liquid. Yield 3 g (48 per cent). The product could not be purified either by chromatography or by distillation under reduced pressure.

Analysis: Found Sn 18.72; calculated for $(C_4H_9)_2Sn(C_{11}H_{11}O_3)_2$
Sn 19.30.

Pale yellow viscous liquid, hygroscopic, soluble in benzene and slightly soluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 590; calculated 615.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2899s, 1639s, 1575m, 1515s, 1460s, 1372s, 1290w, 1253s, 1190s,
1176s, 1112s, 1072m, 1034m, 1020s, 965w, 920w, 840s, 801w,
776s, 720m, 706sh, 694m.

2.3.7 Reaction with acetoacetanilide-

Sodio-derivative of this ligand was prepared from acetoacetanilide (3.8 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml) and reacted with dibutyltin dichloride (3.03 g; 0.01 mole) in benzene in a similar way as in 2.3.1. Yield of big-aceto-

acetanilido dibutyltin was 4.2 g (72 per cent). A portion was recrystallized from benzene.

Analysis: Found C 57.31, H 6.6, Sn 19.85; calculated for $(C_4H_9)_2Sn(C_{10}H_{10}O_2N)_2$, C 57.46, H 6.5, Sn 20.31 per cent.

Pale yellow shining crystals, m.p. 140° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4-1.2% w/w) found 588; calculated 585.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 3300s, 2941s, 1718s, 1678s, 1613s, 1570s, 1515s, 1471s, 1449s, 1418s, 1383s, 1361s, 1316s, 1263m, 1239m, 1174s, 1087m, 1070m, 1048w, 1032w, 1006m, 966m, 905m, 885m, 864m, 750s, 693s.

1.3.8 Reaction with 8-hydroxyquinoline -

Sodio-derivative of this ligand was prepared from 8-hydroxyquinoline (3.19 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml). This was dried and reacted with dibutyltin dichloride (3.03 g; 0.01 mole) in benzene. A deep yellow product obtained from benzene filtrate was washed with hexane and dried at 60° at one mm pressure. Yield 4 g (77 per cent) A portion was recrystallized from benzene for analysis.

Analysis: Found C 60.05, H 5.61, Sn 22.27; calculated for $(C_4H_9)_2Sn(C_9H_6ON)_2$, C 59.91, H 5.38, Sn 22.79 per cent.

Yellow crystals, m.p. 149° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 524; calculated 521.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}); 2960s, 1600m, 1575s, 1538w, 1504s, 1471s, 1379s, 1333s, 1282s, 1242m, 1227m, 1176w, 1139w, 1111s, 1080m, 1055w, 1034m, 1020w, 966w, 951w, 909w, 869w, 830s, 809s, 806s, 754s, 736s.

Di-n-octyltin(IV) chelates: Reactions of di-n-octyltin dichloride with sodio-derivatives of ligands

2.4.1 Reaction with salicylaldehyde-

Salicylaldehyde (2.68 g; 0.02 mole) was reacted with sodium methoxide prepared from sodium (0.506 g; 0.022 mole) and dry methanol (10 ml) as in 2.1.1. The dry sodio-derivative was suspended in benzene (50 ml) and dioctyltin dichloride (4.16 g; 0.01 mole) dissolved in benzene (10 ml) was added to it. The mixture was stirred well, refluxed for two hours and processed as in 2.3.1. Yield 4.4 g (75 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 60.9%, H 7.87, Sn 20.26; calculated for $(C_8H_{17})_2Sn(C_7H_6O_2)_2$, C 61.37, H 7.50, Sn 20.23 per cent.

Pale yellow crystals, soluble in benzene and slightly so in hexane. M.p. 85° . Molecular weight (ebullioscopy in benzene in the concentration range of 0.5 - 1.2% w/w) found 594; calculated 587.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1661s, 1603s, 1538m, 1460s, 1399s, 1376m, 1339w, 1295s, 1271s, 1227w, 1198m, 1171m, 1149s, 1121m, 1110w, 1031m, 901s, 895s, 885m, 846w, 824w, 760s, 722m.

2.4.2 Reaction with acetylacetone-

Di-g-acetylacetone dioctyltin was prepared from acetylacetone (2.2 g; 0.022 mole), sodium (0.506 g; 0.022 mole), methanol (10 ml) and dioctyltin dichloride (4.16 g; 0.01 mole) similar to method adopted for other ligands. The liquid obtained after the reaction

was washed with cold hexane and dried under reduced pressure. The viscous liquid residue could not be recrystallized. It decomposed when distillation was attempted under reduced pressure and also in a chromatographic alumina column. Yield 2 g (37 per cent).

Analysis: Found Sn 20.69; calculated for $(C_8H_{17})_2Sn(C_5H_7O_2)_2$, Sn 21.87 per cent.

Pale yellow liquid, does not solidify on cooling, hygroscopic and miscible with benzene. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 585; calculated 543.

Infrared absorption maxima (in liquid film) are given below (in cm^{-1}): 2941s, 1600s, 1515s, 1471s, 1449s, 1389s, 1297sh, 1258s, 1198s, 1149m, 1107m, 1020s, 929s, 823w, 775s, 716m.

2.4.3 Reaction with dibenzoylmethane-

Diocetyl tin dichloride (4.16 g; 0.01 mole) was reacted with the sodio-derivative obtained from dibenzoylmethane (4.93 g; 0.022 mole), sodium (0.506 g; 0.022 mole) and methanol (10 ml). The product, being soluble in benzene, was separated from insolubles by filtration. The benzene filtrate was concentrated to crystallization and the crystals were washed with hexane. Yield 6.6 g (76 per cent). A portion was further purified by recrystallization from benzene for analysis.

Analysis: Found C 70.24, H 7.21, Sn 14.72; calculated for $(C_8H_{17})_2Sn(C_{15}H_{11}O_2)_2$; C 69.81, H 7.08, Sn 15.02 per cent.

Yellow viscous solid, m.p. 66° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 805; calculated 791.

1.4.4 Reaction with 8-hydroxyquinoline-

Sodio-derivative of this ligand was prepared from 8-hydroxyquinoline (3.19 g; 0.022 mole) sodium (0.506 g; 0.022 mole) and methanol (10 ml). This was dried and reacted with dioctyltin dichloride (4.16 g; 0.01 mole) in benzene and the product isolated as in 2.3.8. Yield 5 g (79 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 65.69, H 7.12, Sn 19.48; calculated for $(C_8H_{17})_2Sn(C_9H_6OH)_2$; C 64.49, H 6.96, Sn 18.76 per cent.

Deep yellow crystals, m.p. 205° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range 0.4 - 1.2% w/w) found 645; calculated 633.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2941s, 1600s, 1580s, 1504s, 1479s, 1391s, 1337s, 1297s, 1250s,
 1236s, 1174w, 1111s, 1049w, 1028m, 957w, 897w, 818s, 797s,
 784s, 778s, ^{743s}/727s.

2.3 Triphenyltin(IV) chelates: Reaction of triphenyltin chloride with sodio-derivatives of ligands

4.5.1 Reaction with salicylaldehyde-

Salicylaldehyde (1.34 g; 0.011 mole) was treated with dry sodium methoxide prepared from sodium (0.253 g; 0.11 mole) and dry methanol (10 ml) in benzene. The dried sodio-derivative of the ligand was then suspended in benzene (50 ml) and triphenyltin chloride (3.85 g; 0.01 mole) dissolved in benzene (10 ml) was added drop by drop with constant stirring. When the addition was over the mixture was refluxed for one hour, then cooled and filtered. The filtrate on concentration gave yellow crystals which were washed with hexane and kept under reduced pressure at 60°. Yield 4.2 g (89 per cent).

A portion was recrystallized from benzene for analysis.

Analysis: Found C 63.69, H 4.59, Sn 25.33; calculated for $(C_6H_5)_3Sn(C_7H_5O_2)$, C 63.74, H 4.25, Sn 25.23 per cent.

Deep yellow crystalline solid, m.p. 166°, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 470; calculated 471.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2899s, 1626s, 1613s, 1550w, 1468s, 1429m, 1379s, 1333m, 1282w, 1240s, 1182m, 1163m, 1155s, 1099w, 1080m, 1031w, 1000w, 877m, 860w, 824m, 778w, 766m, 730s, 699s.

2.5.2 Reaction with methyl salicylate-

The sodio-derivative of the ligand was prepared from methyl salicylate (1.67 g; 0.011 mole) in a manner similar that of salicylaldehyde in 2.5.1. This was reacted with triphenyltin chloride (3.85 g; 0.01 mole) and the product crystallized from the benzene filtrate. This was washed with hexane and kept under reduced pressure at 60°. Yield 3 g (60 per cent). A portion of this was recrystallized from benzene for analysis.

Analysis: Found C 61.85, H 4.92, Sn 23.09; calculated for $(C_6H_5)_3Sn(C_8H_7O_3)$, C 62.32, H 4.39, Sn 23.73 per cent.

White crystalline solid, m.p. 106-107°, soluble in benzene and slightly soluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 512; calculated 501.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2924s, 1675m, 1587w, 1471s, 1429s, 1379s, 1342w, 1316w, 1299w, 1258m, 1212m, 1160m, 1083m, 1026w, 1000m, 969w, 913m, 901s, 870w, 852w, 756w, 735s, 727s, 694s.

2.5.3 Reaction with acetylacetone-

Acetylacetone triphenyltin was prepared from acetylacetone (1.1 g; 0.011 mole), sodium (0.263 g; 0.011 mole), methanol (10 ml) and triphenyltin chloride (3.85 g; 0.01 mole) in a manner similar to the method adopted for other ligands. The benzene filtrate gave a viscous liquid which became solid on cooling and washing with hexane. This was kept at 60° under reduced pressure. Yield 4 g (89 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 62.24, H 5.30, Sn 27.14; calculated for $(C_6H_5)_3Sn(C_5H_7O_2)$, C 61.51, H 4.903, Sn 26.45 per cent.

Pale yellow crystals, m.p. 110° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 456; calculated 449.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2941s, 1724w, 1639w, 1580m, 1531m, 1486m, 1471s, 1439s, 1383s, 1339m,
1304w, 1263w, 1195w, 1163w, 1083s, 1026m, 970m, 917m, 901m,
854w, 778s, 727s, 696s.

2.6.4 Reaction with benzoylacetone-

Benzoylacetone triphenyltin was prepared from the sodio-derivative of the ligand which was prepared from the ligand (1.78 g; 0.011 mole) sodium (0.253 g; 0.011 mole) and methanol (10 ml) and triphenyltin chloride (3.85 g; 0.01 mole). The product obtained by concentrating the filtrate remained a sticky solid even after washing with hexane. Further purification without decomposition was difficult. Yield 3.7 g (72 per cent).

Analysis: Found Sn 22.87; calculated for $(C_6H_5)_3Sn(C_{10}H_9O_2)$, Sn 23.25 per cent.

Pale yellow sticky solid, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 521; calculated 511.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2941s, 1681m, 1613s, 1587s, 1504s, 1460s, 1418s, 1379m, 1307m,
1274s, 1205m, 1176w, 1156w, 1105m, 1075m, 1026s, 1005s, 957m,
844s, 812m, 781m, 763s, 733sh, 725s, 699s.

4.5.6 Reaction with dibenzoylmethane-

Triphenyltin chloride (3.85 g; 0.011 mole) was reacted with the sodio-derivative of the ligand obtained from dibenzoylmethane (2.46 g; 0.011 mole) sodium (0.253 g; 0.011 mole) and methanol (10 ml). The product which was soluble in benzene was crystallized by concentrating the filtrate. The crystals were washed with hexane and dried. Yield 5 g (87 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 69.72, H 4.91, Sn 20.48; calculated for $(C_6H_5)_3Sn(C_{15}H_{11}O_2)$, C 69.15, H 4.54, Sn 20.73 per cent.

Pale yellow powder, m.p. 145° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 568; calculated 573.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1605s, 1567s, 1527s, 1497s, 1481s, 1439m, 1370s, 1340w, 1316m, 1290m, 1227m, 1188w, 1167w, 1124w, 1093w, 1075m, 1064m, 1026m, 1015w, 1000m, 947m, 930w, 862w, 849w, 816w, 790w, 745s, 730s, 703s, 680m.

4.5.6 Reaction with benzoyl ethylacetate-

Benzoyl ethylacetate (2.11 g; 0.011 mole) was converted into the sodio-derivative as in the case of salicylaldehyde in 2.5.1. and reacted with triphenyltin chloride (3.85 g; 0.01 mole). After the reaction, the insolubles were filtered off and the benzene solution when concentrated gave a thick liquid. This product remained a colourless thick liquid even after washing with

hexane and removing the solvent under reduced pressure. Yield 3.6 g (60 per cent). It decomposed when attempted to distil under reduced pressure or in a chromatographic alumina column.

Analysis: Found Sn 21.90; calculated for $(C_6H_5)_3Sn(C_{11}H_{11}O_3)$, Sn 21.96 per cent.

Viscous, colourless liquid does not solidify in ice, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 566; calculated 541.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1653s, 1587m, 1527s, 1471s, 1439s, 1370s, 1333w, 1307m, 1260s, 1198s, 1183s, 1163w, 1117m, 1081s, 1070w, 1047w, 1026m, 1000m, 971w, 921w, 868w, 844m, 788s, 733s, 722sh, 699s.

2.5.7 Reaction with acetoacetanilide-

Sodio-derivative of acetoacetanilide was prepared from the ligand (1.9 g; 0.011 mole), sodium (0.253 g; 0.011 mole) and methanol (10 ml) and reacted with triphenyltin chloride (3.85 g; 0.01 mole) in benzene in a manner similar to 2.5.1. Yield of acetoacetanilido triphenyltin was 4 g (76 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 65.24, H 4.69, Sn 22.09; calculated for $(C_6H_5)_3Sn(C_{10}H_{10}O_2N)$, C 65.24, H 4.75, Sn 22.58 per cent.

Orange crystals, m.p. 59° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 521; calculated 526.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 3268m, 2941s, 1724w, 1630w, 1587w, 1550w, 1515w, 1481m, 1460s,
 1439s, 1429s, 1370s, 1320w, 1290m, 1258m, 1149m, 1070m, 1031m,
 1000w, 962m, 905w, 755m, 730s, 697m.

2.6.8 Reaction with 8-hydroxyquinoline-

8-Hydroxyquinoline (1.6 g; 0.011 mole) was reacted with sodium methoxide prepared from sodium (0.263 g; 0.011 mole) and methanol (10 ml). The sodio-derivative of the ligand thus obtained was then reacted with triphenyltin chloride (3.85 g; 0.01 mole) in benzene and the product isolated from the benzene filtrate as in 2.5.1. Yield of 8-hydroxyquinolino triphenyltin was 3.2 g (67 per cent). A portion was recrystallized from benzene for analysis.

Analysis: Found C 65.75, H 4.23, Sn 23.62; calculated for $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{C}_9\text{H}_6\text{ON})$, C 65.63, H 4.052, Sn 24.04 per cent.

Pale yellow crystals, m.p. 143° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 489; calculated 494.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2941s, 1600m, 1587m, 1493s, 1460s, 1429m, 1370s, 1316s, 1274m,
 1236w, 1180w, 1105s, 1075m, 1031w, 1000w, 862m, 810w, 790m,
 763w, 744s, 730m, 700s.

2.6 Reactions of organotin(IV) chelates2.6.1 Bromine substitution reactions-

A solution of pure bromine (10 g) in dry methylene chloride (100 ml) was used for these studies.

2.6.1a With bis-salicylaldehyde dibutyltin-

The compound (0.95 g; 0.002 mole) was dissolved in methylene chloride (25 ml), stirred and cooled in ice and salt. To this solution, bromine (0.32 g; 0.004 mole) in the same solvent was added drop by drop. The colour of bromine disappeared and when the addition was over, stirring was continued for 30 minutes. The clear solution obtained was concentrated under reduced pressure, the crystals formed were washed with cold hexane and recrystallized from methylene chloride. Yield 0.5 g (50 per cent).

Analysis: Found Br 16.58, Sn 24.12; calculated for $(C_7H_5O_2)_2(C_4H_9)SnBr$, Br 16.05, Sn 23.85 per cent.

Pale yellow crystals, m.p. 80-82°, slightly hygroscopic, easily soluble in benzene and in methylene chloride.

Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 500; calculated 497.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2887s, 1653s, 1613m, 1560w, 1460s, 1378s, 1333m, 1274s, 1220m,
1202s, 1172s, 1149s, 1130m, 1111w, 1081m, 1070m, 1031m, 1015w,
961w, 921w, 897s, 885s, 875sh, 830s, 766s, 737s, 704s, 677s.

2.6.1b With bis-dibenzoylmethano dibutyltin-

The compound (1.36 g; 0.002 mole) and bromine (0.32 g; 0.004 mole) were reacted in methylene chloride in the same manner as in 2.6.1a. Yield 0.55 g (40 per cent).

Analysis: Found Br 11.94, Sn 16.33; calculated for $(C_{15}H_{11}O_2)_2(C_4H_9)SnBr$, Br 11.39, Sn 16.92 per cent.

Colourless crystals, m.p. 50-52°, hygroscopic, soluble in benzene and methylene chloride. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 705; calculated 701.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1681s, 1667s, 1696m, 1587m, 1527w, 1460s, 1449s, 1379s, 1342w, 1326m, 1282s, 1250m, 1188s, 1163w, 1155w, 1104w, 1081w, 1034w, 1000s, 948w, 873w, 816m, 798m, 765s, 740m, 696sh, 685s.

2.6.1c With salicylaldehyde triphenyltin-

(a) A solution of this compound (0.94 g; 0.002 mole) in methylene chloride was reacted with bromine (0.32 g; 0.004 mole) in the same manner as in 2.6.1a and product isolated.

Yield 0.38 g (40 per cent).

Analysis: Found Br 16.09, Sn 24.61; calculated for $(C_7H_5O_2)(C_6H_5)_2SnBr$, Br 16.90, Sn 25.07 per cent.

Pale yellow crystals, m.p. 102-103°, hygroscopic and soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 475; calculated 473.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2900s, 1667s, 1621s, 1572s, 1480s, 1471s, 1429s, 1370s, 1333s,
 1300s, 1280s, 1222s, 1202s, 1176s, 1148s, 1130w, 1111w, 1064s,
 1031w, 1020s, 1000s, 897m, 887s, 860w, 833m, 769s, 732s,
 714m, 692s.

(b) Salicylaldehyde triphenyltin (0.95 g; 0.002 mole) was reacted with bromine (0.64 g; 0.008 mole) in the same manner as in 2.6.1a. Yield 0.4 g (40 per cent).

Analysis: Found Br 34.49, Sn 25.16; calculated for $(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_6\text{H}_5)_2\text{SnBr}_2$, Br 33.54, Sn 24.91 per cent.

Yellow solid, m.p. 96-97°, very soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 478; calculated 476.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2900s, 1667m, 1621s, 1572w, 1471m, 1429m, 1370w, 1333w, 1279s,
 1222m, 1202w, 1176s, 1148m, 1130w, 1064m, 1020m, 1000s, 897w,
 887m, 833m, 769br, 732s, 714m, 692s

2.6.1d With dibenzoylmethane triphenyltin-

(a) A solution of this substance (1.15 g; 0.002 mole) was reacted with bromine (0.32 g; 0.004 mole) in the same manner as in 2.6.1a, and product isolated. Yield 0.6 g (55 per cent).

Analysis: Found Br 14.20, Sn 21.03; calculated for $(\text{C}_{15}\text{H}_{11}\text{O}_2)(\text{C}_6\text{H}_5)_2\text{SnBr}$, Br 13.88, Sn 20.62 per cent.

Orange solid, m.p. 111-112°, hygroscopic, soluble in benzene. Molecular weight ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 576; calculated 575.

(b) Bromine (0.64 g; 0.008 mole) was added to a solution of dibenzoylmethano triphenyltin (1.16 g; 0.002 mole) in methylene chloride and the product isolated as in previous experiments. Yield 0.46 g; (40 per cent).

Analysis: Found Br 28.57, Sn 21.07; calculated for $(C_{15}H_{11}O_2)(C_6H_5)_3SnBr_2$, Br 27.63, Sn 20.62 per cent.

Red crystals, m.p. 80° , hygroscopic and soluble in benzene. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 580; calculated 578.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2976s, 1724m, 1681s, 1608s, 1587s, 1538w, 1488m, 1458s, 1446s, 1385w, 1361w, 1330s, 1311w, 1285s, 1252s, 1220m, 1190s, 1163m, 1109w, 1079m, 1026w, 1006s, 946w, 938w, 869w, 808m, 790w, 763s, 732s, 689s.

2.6.2 Reactions with hydrogen chloride

2.6.2a Di-salicylaldehyde dibutyltin-

Dry hydrogen chloride gas was bubbled through a solution of di-salicylaldehyde dibutyltin (1.9 g; 0.004 mole) in benzene (25 ml) for 15 minutes at room temperature. The yellow solution turned colourless and upon evaporation under reduced pressure gave a pale yellow viscous product. This was chromatographed through alumina (Grade I) using hexane as elutant. The hexane solution on concentration gave colourless crystals, m.p. 42° (reported for dibutyltin dichloride, 43°) yield 0.6 g (50 per cent).

2.6.2b Bis-dibenzoylmethano dibutyltin-

This compound (2.72 g; 0.004 mole) was reacted with dry hydrogen chloride in the same manner as in 2.6.2a. Yield of dibutyltin dichloride 0.7 g (60 per cent).

2.6.2c Salicylaldehyde triphenyltin-

This compound (1.88 g; 0.004 mole) was reacted with dry hydrogen chloride gas in the same manner as in 2.6.2a. The product after purification by chromatography showed a melting point of 104° (reported for triphenyltin chloride, 106°). Yield 0.8 g (54 per cent).

2.6.2d Dibenzoylmethano triphenyltin-

Dry hydrogen chloride was bubbled through a solution of dibenzoylmethano triphenyltin (2.3 g; 0.004 mole) in benzene in the same manner as in 2.6.2a. Yield of triphenyltin chloride was 0.8 g (54 per cent).

3. Sulphur Dioxide Insertion Compounds of Organotin(IV)
Oxides and Chelates

Sulphur dioxide insertion compounds of
organotin oxides and chelates

A Discussion and Results

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According to Kitching¹, the insertion of one molecule of sulphur dioxide in a Sn-C system by electrophilic attack is a fairly general reaction, e.g.,



It has been shown that identical products are obtained from the above reaction and one between an appropriate organotin chloride and sodium organic sulphinate:



From this, the inference has been made that the products of SO₂ insertion are O-sulphinates, probably aggregated in such a manner that the tin atom achieves a stable coordination number (usually five).

SO₂ insertion products of unsymmetrical tetraorganotins and other compounds containing M-C bonds (M = Li, Mg, Zn, Cd, Hg, Al, Si, Ge, Pb, Bi, Fe, Mn, W, Ni, Pd, Pt) have been reported. No information, however, is available on possible insertion reactions between SO₂ and chelated organometallic compounds. Our studies reported here with

several chelated organotin compounds have shown that the latter undergo similar insertion cleavage reactions when allowed to react with liquid sulphur dioxide at -20° . Expected mono-insertion products were obtained in all the cases. The products are fairly stable at room temperature. A few of them tended to decompose gradually in a day or two, but even these could be preserved indefinitely under liquid sulphur dioxide. Usually, the SO_2 molecule is tenaciously retained by these insertion products at room temperature, and is not given up even under reduced pressure or by dissolving in a solvent and warming. However, on treatment with dilute hydrochloric acid, SO_2 was evolved, and the original organotin chloride and the free ligand could be isolated from the products of decomposition.

The SO_2 insertion products of organotin chelates reacted quantitatively with aqueous iodine, a reaction which has been conveniently used by us for the volumetric estimation of SO_2 content of these compounds. Many of the compounds show sharp melting points without decomposition, and are soluble in common organic solvents. In some cases molecular weights could also be determined by ebullioscopy in benzene (Table 9).

Any proposed structure for these SO_2 reaction products of chelated organotins must seek to clarify the following points:

1. whether SO_2 enters between tin and the organo-
or between tin and the chelate;
2. whether the tin compounds so obtained are
O-sulphinates (Sn-O-S bonded) or S-sulphinates
(Sn-S-O bonded); and
3. whether there has been a change in the nature of
sulphur-oxygen bonds of sulphur dioxide in these
compounds.

IR Spectra

The carbonyl frequency in the IR spectra, damped to a value of 1613 cm^{-1} in salicylaldehyde triphenyltin, is restored to 1661 cm^{-1} , (observed in the spectrum of the free ligand) in the SO_2 insertion compounds. Other vibrations, ascribed to the salicylaldehyde group in the chelate (1366 , 1240 and 1182 cm^{-1}), are also observed to return to the free ligand values in the insertion compound. From this apparent breakdown of the metal-chelate ring, it would be reasonable to assume that the SO_2 molecule has entered between the metal and the chelating ligand, i.e., the Sn-O bond is more susceptible to electrophilic attack than the Sn-C bond. This assumption is supported by the observation that decomposition of the insertion compounds with hydrochloric acid gives the organotin chloride, the free chelating ligand and sulphur dioxide. The observation also supports the view that the insertion compound is an O-sulphinate, with the metal linked to an oxygen atom of the sulphur dioxide molecule.

A considerable change in the SO_2 spectrum is, therefore, to be expected in the insertion compounds and has, indeed, been observed (Table 10). The original SO_2 absorption bands find no place in the spectra of these compounds; instead, two (or three) new peaks appear in the $820\text{-}980\text{ cm}^{-1}$ region which were not present in the original organotin chelates. Absorption in this region does not appear in the IR spectra of organic sulphoxides, sulphites and sulphinates (1060 , 1200 , 1130 cm^{-1} respectively).³²¹⁻³²⁴

At this stage, it would be relevant to examine the observation made by previous workers on the SO_2 insertion compounds of tetraorganotins. These were shown to have the O-sulphinate structure.¹⁷⁷ At least in one case, this was established by X-ray crystallographic analysis.³²⁵ In the insertion compound $\text{Me}_3\text{Sn}(\text{SO}_2)\text{Ph}$, the values of the (SO_2) vibrations¹⁷³ have been shown to be in the region $850\text{-}1100\text{ cm}^{-1}$. A strong (SO) absorption peak in the region $950\text{-}990\text{ cm}^{-1}$ has been observed in the SO_2 insertion products of unsymmetrical organotins containing the allyl group, and an intermolecular coordination of oxygen to a tin atom has been postulated by Kitching.¹⁸² In the dimethylsulphoxide addition compound of Me_2SnCl_2 , where a coordination of the $\text{S}=\text{O}$ oxygen to the tin atom can be assumed, the $\text{S}=\text{O}$ stretching frequency 1063 cm^{-1} suffers a reduction in value by 120 cm^{-1} .^{326,327}

Thus, from a study of the IR spectra of the new SO_2 -insertion compounds of chelated organotins, and a literature study of the work reported on similar compounds of pure organotins, it is possible to infer that the new compounds are structurally similar to organic sulphites. The usually assigned $\text{S}=\text{O}$ stretching frequency at about 1200 cm^{-1} in organic sulphites appears, however, in the spectra at considerably reduced values ($820\text{-}980 \text{ cm}^{-1}$). In fact, two or three absorption peaks are recorded in this region which can be ascribed to the stretching vibrations of the bidentate $-\text{O}(\text{SO})\text{O}-$ group as a whole. The large lowering of frequency can conceivably be caused by any one of the following two factors:

1. A redistribution in electron density over the entire $-\text{SO}_3-$ group on account of the strongly electropositive organotin group [$(\text{Ph}_3\text{Sn}$ group in case of the salicylaldehyde chelate insertion compound)] to which it is attached, resulting in a lengthening of the $\text{S}=\text{O}$ bond.
2. A coordination of the oxygen atom of the $(\text{S}=\text{O})$ group with a tin atom, similar to one postulated by Kitching.

Since the compounds are mostly insoluble in organic solvents, a determination of their molecular weights to understand their molecular complexity was not possible. In the few cases where the compounds were soluble, monomer values were obtained in boiling benzene, and IR spectra in

benzene retained all the features of those taken in Nujol indicating their stability in the solvent. Thus, explanation 1 above appears to be more probable, which can also explain the easy rupture of the coordination of the C=O oxygen to the tin atom. The alternative explanation would lead to the postulation of an intramolecular coordinate bond from (S=O) oxygen to the tin atom, making the metal atom a five-coordinate. Though 5-coordinate tin complexes of the R_3Sn - type are well known, it would not be easy to understand in this case why the (SO) \rightarrow Sn coordination is favoured where (CO) \rightarrow Sn coordination bond has been ruptured in these compounds.

B. Experimental Data

General method of preparation of sulphur dioxide insertion compounds of organotin oxides and oxo-chelates

Sulphur dioxide from a cylinder was dried by bubbling it through sulphuric acid wash bottles at a medium rate, and condensed into liquid in a long necked flask [in which the organotin compound (0.5-1 g) was already kept] by keeping the flask immersed in ice-salt mixture. Care was taken to avoid moisture entering into the reaction flask. After an hour when about 10 ml of liquid sulphur dioxide had collected over the sample in the flask, the rate of releasing sulphur dioxide from the cylinder was reduced. Reaction was in several cases accompanied by rapid change in colour and change in the physical nature of the compound. The mixture in the flask was shaken occasionally and allowed to remain in the slow stream of gas for two hours. Then the flask was taken out of the refrigerant and liquid sulphur dioxide allowed to evaporate. Finally the substance was dried at room temperature under reduced pressure (0.5 mm). Samples for analysis were drawn within 1-2 hours of isolating the compound.

Properties

The sulphur dioxide insertion products were mostly stable at room temperature. Some of them decomposed slowly during one or two days, but they could be kept under liquid sulphur

dioxide for much longer periods. Compounds once decomposed at room temperature could not be regenerated on contacting with liquid sulphur dioxide. Sulphur dioxide was not given out from the insertion compounds at room temperature even under reduced pressure or by dissolving in a solvent and warming. However, sulphur dioxide was lost on heating the compounds with dilute hydrochloric acid; the corresponding organotin chloride and the free ligand could be isolated as products of decomposition. The sulphur dioxide insertion products reacted quantitatively with aqueous iodine, a reaction which could be used for the rapid volumetric estimation of sulphur dioxide in these compounds. Many of the insertion compounds were stable enough to show sharp melting points and solubility in solvents without decomposition. In some cases, molecular weights also were determined by ebullioscopy in benzene.

Results obtained by the action of liquid sulphur dioxide on a number of organotin compounds, mostly chelates, are shown in Table 9.

Table 9

Sulphur dioxide mono-insertion products

10. Organotin compound used	Colour of product (m.p.)	Analysis Found(calc)		Molecular weight* Found(calc.)
		Sn %	SO ₂ %	
1. <i>o</i> -salicylaldehyde dibutyltin	pale yellow (190° d)	21.70 (22.04)	12.21 (11.88)	
2. <i>o</i> -methylsalicylate dibutyltin*	white (105°)	20.12 (19.83)	11.23 (10.69)	600 (599)
3. <i>o</i> -dibenzoylmethane dibutyltin	yellow (110°)	15.57 (16.00)	8.13 (8.63)	
4. <i>o</i> -acetoacetanilido dibutyltin	yellow (160°)	18.22 (18.30)	10.20 (9.87)	
5. <i>o</i> -8-hydroxyquinolino dibutyltin	yellow (200° d)	19.98 (20.30)	9.73 (20.30)	
6. Salicylaldehyde triphenyltin*	white (135°)	21.97 (22.20)	10.96 (11.97)	548 (535)
7. Methylsalicylate triphenyltin*	white (143°)	20.56 (21.02)	10.87 (11.33)	558 (566)
8. Benzoylacetone triphenyltin*	white (151°)	20.56 (20.66)	11.19 (11.14)	581 (575)
9. Dibenzoylmethane triphenyltin*	yellow (149°)	18.38 (18.64)	10.78 (10.06)	648 (637)
10. Acetoacetanilido triphenyltin*	yellow sticky solid	19.52 (20.13)	9.35 (10.85)	
11. 8-Hydroxyquinolino triphenyltin*	yellow (205°)	20.71 (21.28)	12.04 (11.48)	543 (558)
12. Dibutyl tin oxide	white non-melting	38.51 (37.96)	21.79 (20.46)	
13. Hexabutyl distannoxane	semi solid			
14. Hexaphenyl distannoxane	white (161°)	14.10 (15.24)	7.35 (8.22)	

The SO₂ insertion products of these compounds are soluble in benzene.
Determined by ebullioscopy in benzene.

Table 10

(SO₂) Group frequencies in SO₂-insertion products of
chelated organotins and related compounds

Compound	IR absorption values in cm ⁻¹
Ph ₃ Sn(Sal)SO ₂	823, 858, 935
Ph ₃ Sn(Ba)SO ₂	830, 860, 937
Ph ₃ Sn(Dbm)SO ₂	843, 860, 937
Ph ₃ Sn(Hq)SO ₂	864, 934
(Ph ₃ Sn) ₂ SO ₃	826, 935
Bu ₂ Sn(Sal) ₂ SO ₂	850, 930
Bu ₂ Sn(Mesal) ₂ SO ₂	870, 880, 897, 980
Bu ₂ Sn(Dbm) ₂ SO ₂	873, 900
Bu ₂ Sn(Aaa) ₂ SO ₂	870, 908
Bu ₂ Sn(Hq) ₂ SO ₂	823, 976
(Bu ₃ Sn) ₂ SO ₃	824, 877, 935, 980
Bu ₂ SnSO ₃	820, 980

SalH- salicylaldehyde, BaH- benzoylacetone,
DbmH- dibenzoylmethane, HqH- 8-hydroxyquinoline,
MesalH- methyl salicylate, AaaH- acetoacetanilide

Infrared absorption frequencies in sulphur dioxide

Solid SO ₂	1144, 1310, 1322
Gaseous SO ₂	1151, 1360
Aqueous SO ₂	1132, 1157

323, 336

4. Stannous Chelates

Stannous Chelates

A Discussion and Results

Stannous chelates form one of the least studied class of tin organics. While organotin(II) compounds are not easy to isolate and characterize in the pure state, we have found that the chelates of tin(II) are well defined, stable in dry air, and show sharp melting points. They are chemically reactive and may find application as mild reducing agents in organic synthesis, and as intermediates for the preparation of other chelated tin compounds.

The stannous chelates were prepared by reacting the sodio-derivatives of the chelating ligands (2.2 moles) with anhydrous stannous chloride (1 mole) in an inert solvent such as benzene. The compounds so formed were soluble in benzene at the time of preparation, but often became insoluble after their isolation as solids, making their molecular weight determination difficult. Big-acetylacetonato tin(II), which was isolated as a viscous liquid soluble in benzene, was found to be a tetramer. The compounds prepared using salicylaldehyde, methyl salicylate, acetylacetonone, benzoylacetonone, dibenzoylmethane and 8-hydroxyquinoline are shown in Table II.

The tin(II) atom in these chelates is quite reactive towards bromine and iodine (as solutions in methylene chloride), which convert the big-chelated tin(II) compounds to big-chelated tin(IV)-dibromide and -diiodide respectively.

The ligands remained unaffected (Table 12). However, when hydrogen sulphide was bubbled through cold methylene chloride solutions of the chelated tin(II) compounds, brown stannous sulphide was precipitated, and free ligand was isolated from the filtrate. Tin(II) chelates were found to reduce ferric ions quantitatively to ferrous, a reaction which has been used for the volumetric estimation of tin(II) in the tin(II) chelates prepared. Reactions with ammonia, dry hydrogen chloride phenyllithium and phenylmagnesium bromide gave products of indefinite composition.

Attempts to prepare compounds of the type $LSn(II)Cl$ from one mole of sodio-derivative of the ligand and one mole of stannous chloride were not successful. The reaction gave the chlorine-free big-chelated tin(II) compound in all cases.

In acetylacetonone and benzoylacetonone complexes of tin(II) the observed carbonyl absorption peak at 1687 cm^{-1} indicates strong chelation of the carbonyl group of the ligand with the metal atom (Table 13). In the complexes of salicylaldehyde, methyl salicylate and dibenzoylmethane the carbonyl absorptions of the free ligands are still observed. If the carbonyl group were free as a result of the replacement of the hydrogen atom of the chelate by metal, one would expect the absorption to be in the neighbourhood of 1700 cm^{-1} . Absence of such a feature in the spectrum indicates a relatively weaker coordination bond of the carbonyl group with the metal, the strength of which is of the order of a hydrogen bond.

Molecular weight determination of the soluble big-acetylaceton tin(II) in boiling benzene showed the compound to be a polymer, probably a tetramer with the tin atom assuming a coordination number of 6. Polymerization of stannous diphenyl has been reported in literature.^{5,6} Unlike the tin-tin bonds postulation in the diphenyl polymer, dative bonds are more likely in the case of these chelate polymers between the oxygen atom of the C-O-Sn group of one metal chelate molecule and the tin atom of another. There will be two such oxygen atoms in each molecule $[\text{Sn(II)}L_2]$ of a metal chelate, which may coordinate with the tin atoms of two other molecules forming a polymeric, cage-like structure.

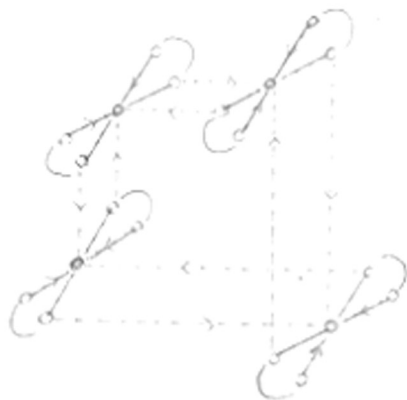


Table 11

Reaction products* of tin(II) chloride (1 mole) and
sodio-derivatives of ligands (2.2 moles)

Ligand	Product**	Mol. wt. Found (calc.)	m.p. °C
Salicylaldehyde	$(C_7H_5O_2)_2Sn$	330(377)	96
Methyl salicylate	$(C_8H_7O_3)_2Sn$	361(408)	116
Acetylacetone	$(C_5H_7O_2)_2Sn$	1200(317)	viscous liquid
Benzoylacetone	$(C_{10}H_9O_2)_2Sn$		150 (d)
Dibenzoylmethane	$(C_{15}H_{11}O_2)_2Sn$		135
8-Hydroxyquinoline	$(C_9H_6ON)_2Sn$		235 (d)

* These are new compounds, not previously reported.

** Based on chemical analysis.

Table 12

Reaction products of bis-chelated tin(II) compounds (1 mole)
and bromine/iodine (2 moles) in methylene chloride.

Reacting halogen	Chelated tin(II) compound	Product formed	Mol. wt. Found (calc.)	m.p. °C
Bromine	<u>Bis</u> -salicylaldehyde tin(II)	$(C_7H_5O_2)_2SnBr_2$		250
"	<u>Bis</u> -methyl salicylate tin(II)	$(C_8H_7O_3)_2SnBr_2$	575(581)	(d)
"	<u>Bis</u> -acetylacetonone tin(II)	$(C_8H_7O_2)_2SnBr_2$	486(477)	181
"	<u>Bis</u> -benzoylacetonone tin(II)	$(C_{10}H_9O_2)_2SnBr_2$	600(601)	189-190
"	<u>Bis</u> -dibenzoylmethane tin(II)	$(C_{15}H_{11}O_2)_2SnBr_2$	715(725)	265-270
"	<u>Bis</u> -8-hydroxyquinolino tin(II)	$(C_9H_6ON)_2SnBr_2$		> 250(d)
Iodine	<u>Bis</u> -salicylaldehyde tin(II)	$(C_7H_5O_2)_2SnI_2$		> 250 (d)
"	<u>Bis</u> -8-hydroxyquinolino tin(II)	$(C_9H_6ON)_2SnI_2$		> 250 (d)

Table 13

IR Frequencies in the range 1500-1750 cm^{-1} in
big-chelated tin(II) compounds

Ligand LH	Frequencies observed in LH	Frequencies observed in L_2Sn
Salicylaldehyde	1595(s), 1616(s), 1642(sh), 1661(s)	1538(w), 1600(s), 1667(s)
Methyl salicylate	1600(s), 1626(s), 1689(s)	1562(s), 1605(s), 1667(s)
Acetylacetone	1613(s), 1704(s), 1727(m)	1548(s), 1587(s)
Benzoylacetone	1513(m), 1527(s), 1562(s), 1600(s)	1515(s), 1538(s), 1587(s)
Dibenzoylmethane	1520(s), 1550(sh), 1570(s), 1600(s), 1681(s)	1520(s), 1562(s), 1600(s)

B Experimental Data

4.1 Preparation of bis-chelated tin(II) compounds:

Reaction of anhydrous stannous chloride with sodio-derivatives of ligands

Anhydrous stannous chloride-

This was prepared from the crystalline hydrate (analytical reagent grade). It was first dried for several hours at 110°C at 10 mm. pressure, after which the crystals were carefully heated at a higher temperature in a slow stream of dry hydrogen chloride gas for two hours.

4.1.1 Reaction with salicylaldehyde-

Dry sodium methoxide was prepared by dissolving sodium (0.506 g; 0.022 mole) in absolute methanol and removing the excess of methanol under reduced pressure. This was reacted with salicylaldehyde (2.68 g; 0.022 mole) in boiling benzene. To a suspension of this sodio-derivative of salicylaldehyde in benzene, finely powdered anhydrous stannous chloride (1.89 g; 0.01 mole) was added, stirred vigorously and the mixture refluxed gently for two hours. A deep yellow solution and a white precipitate were formed. The cooled mixture was centrifuged, and the clear yellow solution (free from chlorine) was evaporated under reduced pressure. The yellow powder thus obtained was washed with hexane and kept at 60° under reduced pressure for drying. Bis-salicylaldehyde tin(II) obtained was 3.2 g (88 per cent).

Analysis: Found C 44.37, H 2.98, Sn 32.85 (gravimetry, by ignition) and 32.66 (volumetry); calculated for $(C_7H_5O_2)_2Sn$, C 44.68, H 2.77, Sn 32.92 per cent.

Yellow powder, m.p. $95-96^\circ$, decomposes in moist air, insoluble in benzene and hexane; reacts with bromine and iodine and reduces ferric ions to ferrous quantitatively.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1667s, 1600s, 1538w, 1460s, 1379s, 1307sh, 1274s, 1242m, 1198w, 1183w, 1149m, 1124w, 1026m, 897m, 885m, 766s, 758s, 719m.

4.1.2 Reaction with methyl salicylate-

Dry sodium methoxide, prepared from sodium (0.506 g; 0.022 mole) and methanol (10 ml), was reacted with methyl salicylate (3.34 g; 0.022 mole). Big-methylsalicylate tin(II) was obtained from this sodio-derivative of the ligand and powdered dry stannous chloride (1.89 g; 0.01 mole) by reacting the two in refluxing benzene, filtering the mixture and concentrating the filtrate. The product was a viscous liquid, which solidified on cooling and washing with hexane. Yield 3.8 g (90 per cent).

Analysis: Found C 45.61, H 3.83, Sn 28.35 (gravimetry, by ignition) and 28.72 (volumetry); calculated for $(C_8H_7O_3)_2Sn$, C 45.63, H 3.33, Sn 28.22 per cent.

Buff coloured solid, m.p. $115-116^\circ$, decomposes in moist air, insoluble in benzene and hexane; reacts with bromine and iodine and reduces ferric ions to ferrous quantitatively.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2899s, 1667s, 1606s, 1562s, 1471s, 1443s, 1379s, 1333s, 1307s,
 1260s, 1227s, 1196m, 1163s, 1143m, 1087s, 1049s, 961w, 865m, 858m,
 813m, 803w, 761s, 705m.

4.1.3 Reaction with acetylaceton-

Big-acetylaceton tin(II) was prepared by reacting anhydrous stannous chloride (1.89 g; 0.01 mole) with sodium acetylacetonate obtained from sodium (0.506 g; 0.022 mole), methanol (10 ml) and acetylaceton (2.2 g; 0.022 mole) similar to the method described for salicylaldehyde in 4.1.1. The benzene filtrate was concentrated under reduced pressure to give a pale yellow liquid which did not solidify on cooling. Yield 2.4 g (75 per cent). The liquid decomposed on contact with moist air and also on a chromatographic alumina column. When attempted to distil under reduced pressure, it changed into a white insoluble powder.

Analysis: Found Sn 36.96 (gravimetry, by ignition) and 37.52 (volumetry); calculated for $(\text{C}_8\text{H}_7\text{O}_2)_2\text{Sn}$, Sn 37.48 per cent.

Pale yellow viscous liquid, soluble in benzene. It did not show any appreciable elevation in the boiling point of benzene in the concentration range of 0.1 - 1.2% w/w, but determinations at higher concentrations (2 - 3% w/w) indicated the molecular weight to be about 1200 (calculated for monomer 317). The liquid reacted with bromine and iodine and reduces ferric ions to ferrous quantitatively.

Infrared absorption maxima (in-liquid film) are given below (in cm^{-1}):
 2941s, 1587s, 1538s, 1475s, 1429w, 1370s, 1282m, 1170w, 1026m,
 938m, 787w, 725w.

4.1.4 Reaction with benzoylacetone-

Sodium methoxide, prepared from sodium (0.506 g; 0.022 mole) and methanol (10 ml) was reacted with benzoylacetone (3.56 g; 0.022 mole). The sodio-derivative of the ligand was then reacted with dry stannous chloride (1.89 g; 0.01 mole) in refluxing benzene with constant stirring for two hours. When cold, the mixture was centrifuged and the benzene filtrate on concentration gave pale yellow crystals, which were washed with hexane before drying. Yield 4 g (90 per cent).

Analysis: Found C 55.02, H 4.52, Sn 26.63 (gravimetry, by ignition) and 27.29 (volumetry); calculated for $(\text{C}_{10}\text{H}_9\text{O}_2)_2\text{Sn}$,
 C 54.45, H 4.08, Sn 26.94 per cent.

Pale yellow solid, hygroscopic, decomposes at 150° , insoluble in benzene and hexane; reacts with bromine and iodine and reduces ferric ions to ferrous quantitatively.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2941s, 1587s, 1538s, 1515s, 1479s, 1453s, 1351s, 1290m, 1166m,
 1193w, 1174w, 1151w, 1099w, 1081w, 1068w, 1026m, 1000m, 952m,
 841w, 806w, 763s, 705m.

4.1.5 Reaction with dibenzoylmethane-

Sodium methoxide was prepared from sodium (0.506 g; 0.022 mole) and dry methanol (10 ml). This was reacted with dibenzoylmethane (4.93 g; 0.022 mole) and the sodio-derivative of the ligand thus obtained was reacted with anhydrous stannous chloride (1.89 g; 0.01 mole) in refluxing benzene with constant stirring for two hours. The product was processed like the salicylaldehyde derivative in 4.1.1. Yield 5 g (89 per cent).

Analysis: Found C 64.27, H 2.1, Sn 21.70 (gravimetry, by ignition) and 21.33 (volumetry); calculated for $(C_{15}H_{11}O_2)_2Sn$, C 63.75, H 3.89, Sn 20.98 per cent.

Orange yellow substance, m.p. 135° , insoluble in benzene and hexane. Decomposes in moist air; reacts with bromine and iodine and reduces ferric ions to ferrous quantitatively.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1600s, 1562s, 1520s, 1486s, 1383s, 1307s, 1289s, 1227s, 1186m, 1156m, 1130w, 1075m, 1058m, 1022m, 1001w, 975w, 943m, 939m, 845w, 819w, 780m, 746s, 730s, 714m, 685m.

4.1.6 Reaction with 8-hydroxyquinoline-

Sodio-derivative of 8-hydroxyquinoline was prepared from the ligand (3.19 g; 0.022 mole) and sodium methoxide obtained from sodium (0.506 g; 0.022 mole) and methanol. The sodio-derivative was then refluxed with anhydrous stannous chloride (1.89 g; 0.01 mole) in benzene (50 ml) with constant stirring for two hours.

The mixture was centrifuged and the benzene solution was concentrated. A yellow solid separated which was washed with hexane and kept at 60° under reduced pressure for drying. Yield 3 g (78 per cent).

Analysis: Found C 52.79, H 2.68, Sn 29.11 (gravimetry, by ignition) and 28.89 (volumetry); calculated for $(C_9H_8ON)_2Sn$, C 53.11, H 2.46, Sn 29.18 per cent.

Yellow non-hygroscopic powder, decomposes at 235°, insoluble in benzene and hexane; reacts with bromine and iodine and reduces ferric ions to ferrous quantitatively.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1613m, 1575s, 1493, 1460s, 1429w, 1379s, 1299s, 1274s, 1227m, 1170w, 1105s, 1058w, 1031w, 866w, 820m, 803m, 784m, 758m, 741s, 730s.

Attempts to prepare compounds of the type $[LSn(II)Cl]$ from one mole of sodio-derivative of the ligand and one mole of stannous chloride failed. The reaction always gave the chlorine-free big-chelated tin(II) compound.

4.2 Reactions of bis-chelated tin(II) compounds

4.2.1 Bromine addition reactions-

A solution of pure bromine (10 g) in dry methylene chloride (100 ml) was used for these studies.

4.2.1a With bis-salicylaldehyde tin(II)-

The compound (1.44 g; 0.004 mole) was suspended in methylene chloride (25 ml), stirred and cooled in ice. To the suspension, bromine (0.64 g; 0.008 mole) in the same solvent was added drop by drop. The colour of bromine disappeared instantaneously. When the addition was over, stirring was continued for 30 minutes. The product, which was only slightly soluble in methylene chloride, was filtered, washed with cold hexane and kept at 60° under reduced pressure for drying. Yield 1.6 g (78 per cent).

Analysis: Found Br 30.89, Sn 22.58; calculated for $(C_7H_5O_2)_2SnBr_2$, Br 30.70, Sn 22.81 per cent.

Deep yellow solid soluble in alcohol, slightly soluble in methylene chloride and benzene and insoluble in hexane, m.p. 260°.

4.2.1b With bis-methylsalicylate tin(II)-

Freshly prepared bis-methylsalicylate tin(II) (1.64 g; 0.004 mole) was reacted with bromine (0.64 g; 0.008 mole) in the same manner as in 4.2.1a. The product was soluble in methylene chloride and the solution was concentrated to crystallization.

Yield 1.9 g (82 per cent). It was ^{re-}crystallized from methylene chloride for analysis.

Analysis: Found Br 27.73, Sn 19.98; calculated for $(C_8H_7O_3)_2SnBr_2$, Br 27.53, Sn 20.45 per cent.

Orange solid, soluble in benzene and insoluble in hexane; decomposes on heating. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 576; calculated 581.

4.2.1c With bis-acetylacetonato tin(II)-

The substance (1.27 g; 0.004 mole) was dissolved in methylene chloride (25 ml) and bromine (0.64 g; 0.008 mole) in methylene chloride was added as in 4.2.1a. The clear yellow solution was concentrated to crystallization. The grey powder obtained was washed with hexane and dried at 60° under reduced pressure. Yield 1.4 g (83 per cent).

Analysis: Found Br 33.04, Sn 24.50; calculated for $(C_8H_7O_2)_2SnBr_2$, Br 33.54, Sn 24.91 per cent.

Grey powder, soluble in benzene and methylene chloride, insoluble in hexane, m.p. 181°. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 486; calculated 477.

4.2.1d With bis-benzoylacetonato tin(II)-

To a solution of bis-benzoylacetonato tin(II) (1.76 g; 0.004 mole) in methylene chloride (25 ml) was added bromine (0.64 g; 0.008 mole) in the same solvent with cooling and stirring. The dibromo derivative separated as a light yellow powder on concentrating the methylene chloride solution. Yield 1.8 g (75 per cent).

Analysis: Found Br 26.72, Sn 20.01; calculated for $(C_{10}H_9O_2)_2SnBr_2$, Br 26.61, Sn 19.76 per cent.

Pale yellow powder, soluble in benzene and methylene chloride and insoluble in hexane melts with decomposition at 189-190°. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 600; calculated 601.

4.2.1e With bis-dibenzoylmethano tin(II)-

The substance (2.26 g; 0.004 mole) was dissolved in methylene chloride (25 ml), cooled and treated with bromine (0.64 g; 0.008 mole) and processed similar to the method used for the methyl salicylate compound as in 4.2.2a. The yield of bis-dibenzoylmethano dibromo tin was 2 g (69 per cent).

Analysis: Found Br 22.22, Sn 16.32; calculated for $(C_{15}H_{11}O_2)_2SnBr_2$, Br 22.05, Sn 16.39 per cent.

Yellow solid melts with decomposition between 265-270° soluble in benzene and methylene chloride and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 715; calculated 725.

4.2.1f With bis-8-hydroxyquinoline tin(II)-

Bromine (0.64 g; 0.008 mole) in methylene chloride was slowly added to a solution of bis-8-hydroxyquinoline tin(II) (1.624 g; 0.004 mole) in the same solvent (25 ml) with cooling and stirring. An orange precipitate of the dibromide immediately separated. It was filtered, washed with hexane and dried at 60° under reduced pressure. Yield 1.8 g (79 per cent).

Analysis: Found Br 28.39, Sn 21.11; calculated for
 $(C_9H_6ON)_2SnBr_2$, Br 28.21, Sn 20.95 per cent.

Bright yellow powder, slightly soluble in benzene and stable to the action of cold water melts with decomposition above 250° .

4.2.2 Iodine addition reactions-

A solution of resublimed iodine (5 g) in dry methylene chloride (100 ml) was used for these studies.

4.2.2a With bis-salicylaldehyde tin(II)-

A suspension of bis-salicylaldehyde tin(II) (1.44 g; 0.004 mole) in methylene chloride (25 ml) was cooled and stirred and a solution of iodine (0.253 g; 0.008 mole) in the same solvent was added. Decolorization of iodine took place and a brown substance separated. This was filtered and washed with hexane and dried at 60° under reduced pressure. Yield 2 g (81 per cent).

Analysis: Found I 41.57, Sn 19.11; calculated for
 $(C_7H_5O_2)_2SnI_2$, I 41.30, Sn 19.32 per cent.

Reddish brown hygroscopic powder insoluble in benzene and hexane; melts with decomposition above 250° .

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 3344m, 1661m, 1613s, 1538w, 1340w, 1274m, 1205w, 1149m,
 1029w, 893w, 888w, 760m, 722w.

4.2.2b With bis-8-hydroxyquinolino tin(II)-

A solution of the substance (1.624 g; 0.004 mole) in methylene chloride (25 ml) was cooled and stirred and reacted with iodine (0.253 g; 0.008 mole) in the same solvent. Decolorization of iodine took place and a brown compound separated. This was filtered, washed with hexane and dried at 60° under reduced pressure. Yield 2 g (76 per cent).

Analysis: Found I 39.11, Sn 18.09; calculated for $(C_9H_6ON)_2SnI_2$; I 38.43, Sn 17.98 per cent.

Brown powder, insoluble in benzene and hexane; melts with decomposition above 250°.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 1600w, 1575w, 1502s, 1316s, 1264m, 1229m, 1212w, 1172w, 1143w, 1105s, 1034w, 970w, 890w, 826m, 806w, 786w, 734s.

Reactions of iodine with the other bis-chelated tin(II) compounds reported in 4.1 were also carried out and similar diiodo tin(IV) compounds were isolated. Their properties were found similar to those prepared from bis-salicylaldehyde tin(II) and bis-8-hydroxyquinolino tin(II).

4.2.3 Reactions with hydrogen sulphide-

Purified and dry hydrogen sulphide gas was slowly bubbled through a cooled solution (or a suspension) of the chelated tin(II) compound in dry methylene chloride. The tin compound

decomposed immediately and a dark brown precipitate was seen. This was separated by filtration and identified as stannous sulphide. The free ligand was isolated from the filtrate in each case.

4.2.4 Reactions with ferric ions-

A known amount of tin(II) chelate was treated with an excess of standard ferric alum solution containing dilute hydrochloric acid. The mixture was kept at the boiling point for ten minutes, after which it was cooled and the ferrous ion formed was estimated by titration with standard potassium dichromate using potassium ferricyanide as external indicator. The reduction was found quantitative. The procedure was used for the volumetric estimation of tin(II) in the tin(II) chelates prepared.

5. Thienyltin(IV) Compounds

Thienyl tin(IV) compounds

A. Discussion and Results

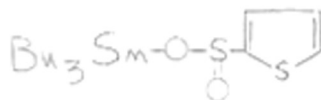
Studies in this section have indicated that tin(IV) κ -thienyl derivatives, about which little was known before, resemble the phenyltin compounds in chemical and physical properties. Tetra- κ -thienyltin and tetraphenyltin were both prepared from the corresponding Grignard reagents by reaction with anhydrous stannic chloride. They form needle shaped crystals, with melting points 153 and 225° respectively. κ -Thienyl triphenyltin and di- κ -thienyl dibutyl^{tin} were prepared from κ -thienyl Grignard reagent and the corresponding organotin chlorides. Compounds thus prepared are listed in Table 14. They are soluble in benzene and are stable enough for chromatographic purification on alumina (Grade I) using benzene as elutant. The butyltin compounds are liquids, but phenyltin derivatives are solids with sharp melting points. They are all monomeric in boiling benzene.

Among the κ -thienyltin derivatives reported above, κ -thienyl tributyltin and di- κ -thienyl dibutyltin reacted with SO₂ to give mono insertion products. The reactions took place in sulphur dioxide at -20°. The SO₂ insertion product of κ -thienyl tributyltin was a sticky solid while that of di- κ -thienyl dibutyltin was a solid melting at 148°. The compounds were stable at room temperature and the absorbed SO₂ was not given out under reduced pressure. SO₂ was lost on warming with dilute HCl or on treatment with aqueous iodine.

IR spectra

In thienyltin compounds, the tin is bonded to the α -carbon atom of the thiophene moiety. There is a close similarity between their spectra and that of α -iodo thiophene. Absorption bands in the region 820-850, 940-960 and 1040-1080 cm^{-1} , characteristic of 2-substituted thiophenes³²⁸, are found in all the compounds. In the mixed *n*-butyl and phenyl compounds of thienyltin, the characteristic bands due to both the ligands are clearly seen (1460, 1370, 2850, 2960 for *n*-butyl; 700 and 730-735 cm^{-1} for phenyl). Monomeric nature of the new compounds suggests a tetrahedral coordination around the tin atom.

The alkyl α -thienyltins react with one molecule of sulphur dioxide like the other unsymmetrical organotin reported by Kitching to form SO_2 insertion compounds. Their spectra also show the characteristic IR absorption bands in the region 900-1000 cm^{-1} . Their proposed structure, shown below, is therefore similar to that proposed by Kitching for similar insertion compounds (Section III 3).



Mass spectra

Mass spectra of organotin compounds have been little studied, largely on account of the polyisotopic nature of the metal which results in overlapping patterns except under high resolution. It is generally found that organotin compounds suffer much greater fragmentation in the mass spectrometer than the corresponding germanium and silicon derivatives because of the lower bond dissociation energies for tin compounds.³²⁹ The several naturally occurring isotopes of tin cause each ion fragment to appear as a cluster of peaks in the mass spectrum. This makes an unqualified interpretation difficult, and particularly so when two fragments differ only by one or two units of mass. All m/e values in the discussion presented here are based on the ¹²⁰Sn isotope only. Nothing has so far been reported about the behaviour of α -thienyltin(IV) compounds in the mass spectrometer. We have found that, contrary to the usual behaviour of organotin compounds which do not show large molecular ions in their mass spectra,^{330,331} these very stable derivatives show significant molecular ion peaks, and exhibit well-defined fragmentation pattern and cleavage sequences.

Mass spectral data on some tetraorganotins (symmetrical and unsymmetrical) reported in literature^{are} reproduced in Table 15 for comparison with those for a few thiophene derivatives prepared by us. Peak intensities due to molecular ions from tetra-n-butyltin, tetraphenyltin and trimethyl phenyltin are not high, indicating the instability of these compounds to electron impact. Comparatively, the α -thienyltin derivatives show

considerably greater intensities of the molecular ions. It is reasonable to suppose that this greater stability stems from the metal-carbon bond in which the carbon atom is a member of the thiophene ring system. A more detailed discussion of the three thienyltin compounds examined in the mass spectrometer has been made in the following paragraphs.

Tetra- \leftarrow -thienyltin

It will be seen in Table 15 that tetrabutyl- and tetraphenyl-tins have negligible intensities for their molecular ion peaks, but that for the thiophene counterpart is exceptionally strong (base peak). Several fragments observed in the mass spectra of tetrabutyl- and tetraphenyl-tins are absent in the spectrum of this compound, and no hydrogen transfer rearranged fragment is observed. Only four simple fragments are seen, which may be assumed to have formed by stepwise elimination of the thienyl groups as follows:



No fragmentation is observed after RSn^+ .

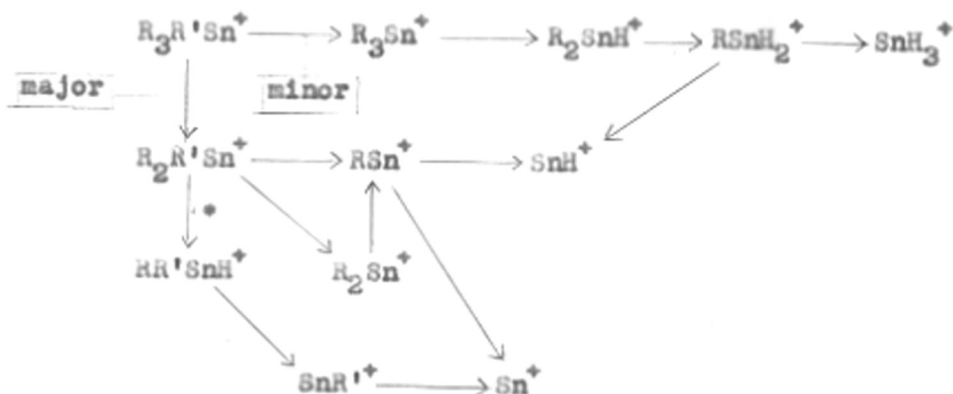
Tri-*n*-butyl \leftarrow -thienyltin

Compared to that of tetrabutyltin, the fairly large intensity of the molecular ion peak (34%) observed for this compound is indicative of the stability imparted to the molecule by the presence of the thiophene ring. Similar to trimethyl phenyltin, the base peak in this case is also due to a fragment containing both the ligands viz. $(C_4H_9)_2(C_4H_3S)Sn^+$.

This indicates that a butyl group is the first one to be lost from the molecular ion. A few (five) hydrogen transfer rearranged fragments are observed in this case, but it will be noted that the intensity of the fragment CH_3Sn^+ , which was 3% in tetrabutyltin, has been reduced to a negligible value (0.5%). A metastable peak is seen at m/e 215 which points to the loss of a neutral C_4H_8 molecule by the following process:



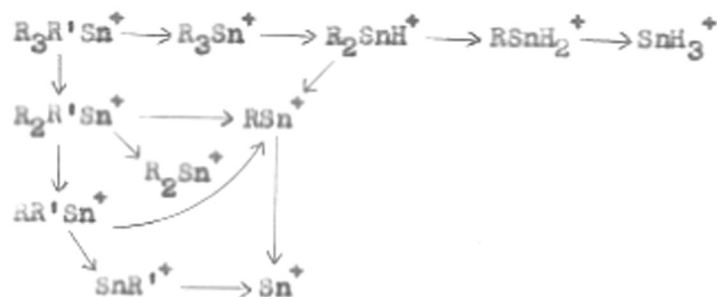
From the above observations, a plausible fragmentation pattern showing the fate of the molecular ion ($R = n$ -butyl, $R' = \leftarrow$ -thienyl) is suggested below:-



(* = metastable intermediate)

Triphenyl α -thienyl tin

The molecular ion intensity which was only 0.2% in tetraphenyltin has increased to 17% in this case, where one of the phenyl groups has been replaced by α -thienyl. Two peaks of nearly equal intensities, $(C_6H_5)_3Sn^+$ and $(C_4H_3S)Sn^+$, represent the base peak. In comparison with tetraphenyltin the hydrogen transfer rearranged fragments are less in number and intensity; the rest of the fragmentation pattern is nearly the same for both the compounds. The following fragmentation scheme of the molecular ion ($R = \text{phenyl}$, $R' = \alpha\text{-thienyl}$) can be suggested:



Fragmentation of the molecular ion by elimination of a ligand radical appears to be common to all the compounds. Elimination of either ligand may occur in compounds having two different ligands. Further elimination of ligand radicals follows, giving rise to smaller fragments containing tin.

The spectra of the tin compounds were recorded on a CBC 21-110B mass spectrometer in this Laboratory by direct inlet system under the following experimental conditions: electron energy: 70 eV; pressure: $1-2 \times 10^{-7}$ mm of mercury; ionization current: 20 μ amps; source temperature: 130° for tetra- α -thienyltin, 90° for tri- n -butyl- α -thienyltin and 180° for triphenyl α -thienyltin.

Table 14

Grignard reaction product of tin halide (A)
with α -thienyl magnesium iodide (B)

Tin halide (A)	Molar ratio A : B	Products isolated	Mol. wt. Found(calc.)	m. p. °C
Stannic chloride	1:5	$(C_4H_3S)_4Sn$	450(451)	153
Diphenyltin dichloride	1:2.5	$(C_4H_3S)_2Sn(C_6H_5)_2$	440(439)	178
Triphenyltin chloride	1:1.25	$(C_4H_3S)Sn(C_6H_5)_3$	442(433)	202
Dibutyltin dichloride	1:2.5	$(C_4H_3S)_2Sn(C_4H_9)_2$	388(399)	viscous liquid
Tributyltin chloride	1:1.25	$(C_4H_3S)Sn(C_4H_9)_3$	378(373)	b. p. 150°/1mm.

Table 15

Relative intensities of principal tin-containing fragments
in the calculated mono-isotopic spectra of tetraorganotins

	A	B	C	D	E	F
M^+	0.1	0.2	1.4	100	34	17
R_3Sn^+	58	100	2.3	55	50	47
$R_2R'Sn^+$	-	-	100	-	100	12
R_2SnH^+	80	2	-	-	10	14
$RR'SnH^+$	-	-	-	-	65	-
R_2Sn^+	1	42	1	2	10	87
$RR'Sn^+$	-	-	5.3	-	-	13
$RSnH_2^+$	100	1	-	-	10	60
RSn^+	21	57	7	20	60	100
$R'Sn^+$	-	-	33.2	-	65	98
CH_3Sn^+	3	-	-	-	0.5	-
SnH_3^+	14	-	-	-	5	29
SnH^+	43	-	-	-	28	-
Sn^+	9	71	12.9	-	31	75

A = tetrabutyltin, R = R' = butyl (ref.330)

B = tetraphenyltin, R = R' = phenyl (ref.330)

C = trimethyl phenyltin, R = methyl, R' = phenyl (ref.331)

D = tetra \leftarrow -thienyltin, R = R' = \leftarrow -thienyl

E = tri-n-butyl \leftarrow -thienyltin, R = n-butyl, R' = \leftarrow -thienyl

F = triphenyl \leftarrow -thienyltin, R = phenyl, R' = \leftarrow -thienyl

B Experimental Data

6.1 4-Thienyl tin(IV) derivatives

6.1.1 Preparation of 4-iodothiophene-

The procedure given by Wirth, Königstein and Kern³³² was followed. Freshly distilled thiophene (10.6 g; 0.126 mole), glacial acetic acid (40 ml), water (15 ml), carbon tetrachloride (10 ml), concentrated sulphuric acid (0.7 ml), iodine (10.2 g; 0.08 g atom) and iodic acid (4.1 g; 0.02 mole) were mixed and stirred vigorously at 40° till all the iodine dissolved (about 2 hrs.). The mixture was then poured into water containing sodium bisulphite and extracted with carbon tetrachloride. The organic layer was concentrated and chromatographed through a 50 cm. column of alumina (Grade I) using hexane as elutant. The hexane solution on fractionation gave 4-iodothiophene, boiling point 60-61° at 5 mm. (lit. 73-78 at 18 mm.). Yield 17 g (80 per cent; lit. yield 75 per cent).

Colourless liquid, turns red on keeping, miscible with organic solvents in all proportions. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 210; calculated 210.

Infrared absorption maxima (liquid film) are given below (in cm^{-1}): 3077m, 1786w, 1709w, 1639w, 1587w, 1504m, 1399s, 1333s, 1220s, 1080s, 1045s, 897w, 840s, 823s, 741s, 700s br.

5.1.2 Preparation of the Grignard compound-

α -Iodothiophene (2.1 g; 0.01 mole) was diluted with absolute ether and added dropwise to a stirred suspension of magnesium turnings (0.3 g; 0.0125 mole) in the same solvent in an atmosphere of dry nitrogen. Vigorous reaction took place and the reagent was ready for use within 30 minutes. The ether solution was used as such in the subsequent reactions.

5.1.3 Reaction with stannic chloride-

Anhydrous stannic chloride (2.61 g; 0.01 mole) was diluted with absolute ether (50 ml) with cooling and stirring. To the stannic chloride etherate thus formed was added drop by drop the clear ether solution of α -thienyl magnesium iodide prepared from α -iodothiophene (10.5 g; 0.05 mole) and magnesium (1.5 g; 0.0625 mole). The reaction was completed by refluxing for an hour after which ether was removed by distillation and benzene (50 ml) added. The mixture was then treated with a saturated aqueous solution of ammonium chloride (10 ml), and from the benzene layer a grey product was obtained on removing the solvent. This crude product when chromatographed through an alumina column using benzene as elutant, gave colourless needle shaped crystals, m.p. 153°. Yield 4 g (89 per cent).

Analysis: Found C 42.45, H 2.74, Sn 26.33; calculated for $(C_4H_3S)_4Sn$, C 42.60, H 2.66, Sn 26.32 per cent.

The crystals were soluble in benzene as well as hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 450; calculated 451.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 3077s, 2900s, 2850sh, 2174w, 1802w, 1724w, 1667w, 1626w, 1550w, 1493m,
 1389s, 1316m, 1242w, 1212s, 1078s, 1050m, 957s, 909m, 848s, 836s,
 746s, 714s.

5.1.4 Reaction with di-n-butyltin dichloride

Di-n-butyltin dichloride (3.04 g; 0.01 mole) was dissolved in ether (50 ml) and reacted with an ether solution of ϵ -thienyl magnesium iodide prepared from ϵ -iodothiophene (5.25 g; 0.025 mole) and magnesium (0.75 g; 0.0313 mole) as in 5.1.2. The product obtained after chromatography through alumina column was a viscous liquid. Yield 3 g (75 per cent).

Analysis: Found S 16.87, Sn 29.53; calculated for $(\text{C}_4\text{H}_3\text{S})_2\text{Sn}(\text{C}_4\text{H}_9)_2$, S 16.04, Sn 29.75 per cent.

The viscous liquid became solid on strong cooling in ice and salt, and decomposed when attempted to distil. It is soluble in benzene as well as hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 388; calculated 399.

Infrared absorption maxima (liquid film) are given below (in cm^{-1}):
 3077m, 2900s, 2850sh, 1852w, 1709w, 1587w, 1493m, 1460s, 1408m,
 1389s, 1370m, 1333w, 1325m, 1290m, 1250w, 1212s, 1176m, 1149w,
 1075s, 1047m, 1020w, 1000w, 962sh, 943s, 877m, 866m, 848s, 828s,
 746s, 704s br.

5.1.5 Reaction with tri-n-butyltin chloride-

An ether solution of the α -thienyl magnesium iodide, prepared from α -iodothiophene (2.6 g; 0.0125 mole) and magnesium (0.38 g; 0.0157 mole) was reacted with a solution of tri-n-butyltin chloride (3.25 g; 0.01 mole) in ether (50 ml) as in 5.1.3. A brown liquid obtained after removal of the solvent was chromatographed through alumina, and the colourless product obtained was distilled under reduced pressure. Yield 3.2 g (86 per cent).

Analysis: Found S 8.58, Sn 31.48; calculated for $(C_4H_3S)Sn(C_4H_9)_3$; S 8.58, Sn 31.83 per cent.

Colourless liquid, b.p. 150° at 1 mm, soluble in benzene and hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 378; calculated 373.

Infrared absorption maxima (liquid film) are given below (in cm^{-1}): 3077m, 2900s, 2850sh, 1493w, 1460s, 1408w, 1370s, 1333w, 1290m, 1250w, 1205s, 1176m, 1149w, 1075s, 1042m, 1020w, 1000w, 962m, 943s, 870s br, 848s, 826m, 746m br, 694s.

5.1.6 Reaction with diphenyltin dichloride-

Diphenyltin dichloride (3.44 g; 0.01 mole) was dissolved in ether (50 ml) and reacted with an ether solution of α -thienyl magnesium iodide prepared from α -iodothiophene (5.25 g; 0.025 mole) and magnesium (0.75 g; 0.0313 mole) as in 5.1.2. The dark product obtained was chromatographed through alumina and the benzene solution concentrated to give colourless crystals. Yield 3.8 g (86 per cent).

Analysis: Found C 56.38, H 4.13, Sn 26.96; calculated for $(C_4H_3S)_2Sn(C_6H_5)_2$, C 54.70, H 3.65, Sn 27.04 per cent.

White crystalline solid, m.p. 178° , soluble in benzene and hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 440; calculated 439.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 3070m, 2900s, 2850sh, 2381w, 1676w, 1481m, 1460s, 1429s, 1389s, 1370m, 1299w, 1266w, 1212s, 1176w, 1156w, 1075s, 1058w, 1026m, 1000s, 980w, 956s, 911w, 848s, 836s, 746s, 733s, 714s,br, 710s, 699s.

5.1.7 Reaction with triphenyltin chloride-

An ether solution of α -thienyl magnesium iodide, prepared from α -iodothiophene (2.6 g; 0.0125 mole) and magnesium (0.38 g; 0.0157 mole) was reacted with a solution of triphenyltin chloride (3.85 g; 0.01 mole) in ether (50 ml) as in 5.1.2. The grey solid obtained after removing benzene was chromatographed through alumina and the benzene solution concentrated to give colourless crystals. Yield 3.5 g (81 per cent).

Analysis: Found C 61.19, H 4.30, Sn 27.58; calculated for $(C_4H_3S)Sn(C_6H_5)_3$, C 61.01, H 4.16, Sn 27.42 per cent.

White crystals, m.p. 202° , soluble in benzene and hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4-1.2% w/w) found 442; calculated 433.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
3077s, 2900s, 2850sh, 1961w, 1887w, 1818w, 1767w, 1724w, 1633w,
1587w, 1481s, 1460s, 1429s, 1389s, 1379s, 1333m, 1299m, 1258m,
1212s, 1183m, 1156m, 1075s, 1064m, 1026s, 1000s, 990s, 980s,
980m, 952s, 917m, 868w, 848s, 836s, 746s, 736s, 720s, 710s, 700s.

6. Chelated Titano-stannoxanes

Chelated titano-stannoxanesA. Discussion and Results

Investigation in the field of titano-stannoxanes was stimulated by an observation of P.V.C. stabilizing property in some compounds having the Sn-O-Ti grouping. It is known that alkoxy groups in alkyl titanates are replaceable with chelating ligands, long chain and polyhydroxy alcohols, phenols etc. A similar reaction took place when an organotin oxide or hydroxide was made to react with chelated alkoxy titanium(IV) compounds.

The chelated titanium(IV) alkoxides were prepared from tetraalkoxy titanium(IV) by reacting with the chelating ligands in benzene. The reactions between organotin oxide/hydroxide and the chelated titanium alkoxides were carried out by refluxing in toluene. The ether/alcohol liberated in the reaction was identified qualitatively. The reaction product was isolated from the toluene filtrate and purified by precipitation with petroleum ether. Only the alkoxy groups were replaced; and the chelating ligand remained attached to the titanium.

The products were yellow to orange solids, soluble in benzene, stable in dry air, and monomeric in boiling benzene. Table 16 describes the alkoxy titanium chelates prepared; the new Ti-O-Sn compounds are listed in Table 17.

Table 18 shows the carbonyl absorption bands of the chelated chloro-, alkoxy- and stannoxy-titanium compounds. In salicylaldehyde trichlorotitanium and big-salicylaldehyde-dichloro-titanium, the carbonyl absorption band at 1661 cm^{-1} of the free ligand is replaced by an absorption near 1600 cm^{-1} indicating the coordination of the carbonyl group with the metal. The hydroxyl stretching frequency in the parent ligand is absent in the complexes. These chloro-titanium compounds are not sufficiently soluble for molecular weight determination.

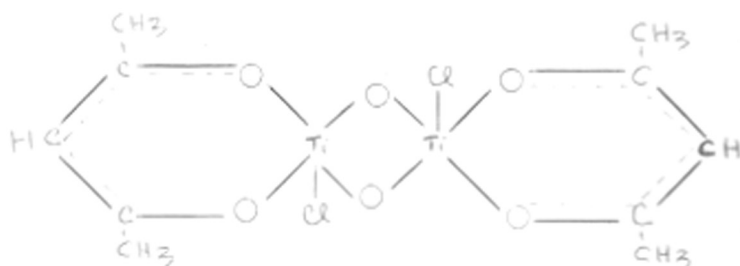
In big-chelated dibutoxy titanium compounds, the carbonyl frequency is not very different from that of the free ligand, indicating that the coordination in these complexes is not as strong as in the corresponding chloro-titanium chelates. This difference probably arises from the relatively larger electron density on the metal in the metal-OR bond than in the metal-Cl bond. Molecular weight determination indicated these alkoxy compounds to be monomers in boiling benzene. Similar compounds are described in literature as examples of hexa-coordinated titanium.

The IR spectra of compounds formed by reacting triphenyltin hydroxide or dibutyltin oxide and chelated alkoxy titaniums show some interesting features. For example, the spectrum shows that in the case of the salicylaldehyde titanoxo organostannes, the carbonyl group is more strongly coordinated to titanium than in the simple titanium compound, big-salicylaldehyde titanium dibutoxide. Among big-

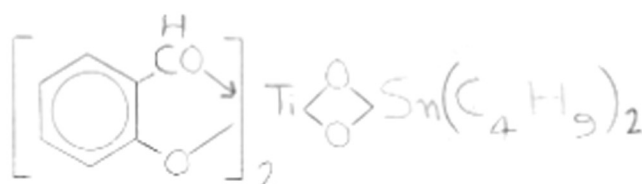
salicylaldehyde titanoxo derivatives of dibutyltin, dioctyltin and triphenyltin, this effect on the carbonyl frequency is the least in the dioctyltin derivative. The observed larger spectral shift of the carbonyl frequency in chelated titanium compounds containing Ti-O-Sn bond is attributable to the replacement of the alkoxy groups attached to titanium with the more electronegative alkyl stannoxy or aryl stannoxy groups.

The IR spectra of compounds containing Ti-O-Sn group consistently show a broad peak at ca. 800 cm^{-1} . Appearance of broad bands in the region of 800 cm^{-1} ³⁰⁸ and between 800 and 900 cm^{-1} ³³³ are reported for Ti-O-M polymeric structures where M is a metal including titanium. The broad peak around 800 cm^{-1} observed in these new compounds may thus be attributed to an inner vibration of the Ti-O-Sn group.

The new dibutyl stannoxy titanium chelates $\text{Bu}_2\text{SnO}_2\text{TiL}_2$ (LH = salicylaldehyde, methyl salicylate, dibenzoylmethane) may be postulated to contain Ti-O-Sn groups in analogy with the Ti-O-Ti grouping reported by Collis³⁰⁹ in the case of the acetyl acetone titanium complex shown below, both in the solid state and in solution:



Since all these titano-stannoxanes contain titanium atom linked to tin through oxygen, and are monomeric in solution, their possible structures, at least in solution, will be similar to Collis's compound. The following structure containing octahedral titanium may be assigned, for example, to the product formed by the reaction between big-salicylaldehyde dibutoxytitanium and dibutyltin oxide.



The other group of new titano-stannoxanes, which are obtained by reacting chelated titanium alkoxides with triphenyltin hydroxide, bears a similarity with tetraakis-(triphenyl stannoxy) titanium, $(\text{Ph}_3\text{SnO})_4\text{Ti}$, reported by ³³⁴ Cohen, in which one or two triphenyl stannoxy groups have been replaced by chelating ligands.

Table 16

Reactions of chelating ligands with alkyl titanates

Alkyl titanate	Ligand	Molar ratio	Product*	Mol. wt. Found (calc.)	m.p. °C
A	B	A:B			
n-Butyl titanate	Salicylaldehyde	1:2.2	$(C_7H_5O_2)_2Ti(OC_4H_9)_2$	444(436)	58
"	Methyl salicylate	1:2.2	$(C_8H_7O_3)_2Ti(OC_4H_9)_2$	500(496)	viscous liquid
"	Dibenzoylmethane	1:2.2	$(C_{15}H_{11}O_2)_2Ti(OC_4H_9)_2$	650(640)	85
n-Propyl titanate	Salicylaldehyde	1.1:1	$(C_7H_5O_2)TiO(OC_3H_7)_3$	500(244)	200 (d)
"	Methyl salicylate	1.1:1	$(C_8H_7O_3)Ti(OC_3H_7)_3$	380(376)	viscous liquid

* Based on analysis and molecular weight.

Table 17

Reaction products of organotin(IV) compounds with
alkoxytitanium(IV) chelates

Titanium compound A	Tin compound B	Molar ratio A:B	Product*	Mol. wt.	
				Found	(calc.)
1. Bis-salicylaldehyde di- <i>n</i> -butoxytitanium	dibutyltin oxide	1:2.2	(C ₇ H ₅ O ₂) ₂ Ti(O ₂ SnC ₄ H ₉) ₂	564(565)	250 (d)
2. Bis-methylsalicylato-di- <i>n</i> -butoxytitanium	"	1:2.2	(C ₈ H ₇ O ₃) ₂ Ti(O ₂ SnC ₄ H ₉) ₂	639(615)	240
3. Bis-dibenzoylmethano-di- <i>n</i> -butoxytitanium	"	1:2.2	(C ₁₆ H ₁₁ O ₂) ₂ Ti(O ₂ SnC ₄ H ₉) ₂	758(759)	78
4. Salicylaldehyde- <i>n</i> -propoxy oxotitanium	"	1:1.1	[(C ₇ H ₅ O ₂)TiO] ₂ (O ₂ SnC ₄ H ₉) ₂	**	250 (d)
5. Bis-salicylaldehyde di- <i>n</i> -butoxytitanium	Dioctyltin oxide	1:2.2	(C ₇ H ₅ O ₂) ₂ Ti(O ₂ SnC ₁₆ H ₃₄) ₂	632(667)	60
6. Bis-methylsalicylato di- <i>n</i> -butoxytitanium	"	1:2.2	(C ₈ H ₇ O ₃) ₂ Ti(O ₂ SnC ₁₆ H ₃₄) ₂	748(727)	viscous liquid
7. Bis-dibenzoylmethano di- <i>n</i> -butoxytitanium	"	1:2.2	(C ₁₆ H ₁₁ O ₂) ₂ Ti(O ₂ SnC ₁₆ H ₃₄) ₂	891(871)	66
8. Methylsalicylato-tri- <i>n</i> -propoxy titanium	Triphenyltin hydroxide	1:3.3	(C ₈ H ₇ O ₃) ₂ Ti(OSnC ₁₈ H ₁₅) ₃	1317(1296)	160

Titanium compound A	Tin compound B	Molar ratio A:B	Product*	Mol. wt. found(calc.)	m.p. °C
9. Bis-salicylaldehyde di- <i>n</i> -butoxytitanium	Triphenyltin hydroxide	1:2.2	(C ₇ H ₅ O ₂) ₂ Ti(OSnC ₁₈ H ₁₅) ₂	1040(1021)	250 (d)
10. Bis-methylsalicylate-di- <i>n</i> -butoxytitanium	**	1:2.2	(C ₉ H ₇ O ₃) ₂ Ti(OSnC ₁₈ H ₁₅) ₂	1089(1080)	250 (d)
11. Bis-dibenzoylmethane di- <i>n</i> -butoxytitanium	**	1:2.2	(C ₁₆ H ₁₁ O ₂) ₂ Ti(OSnC ₁₈ H ₁₅) ₂	1224(1226)	130
12. Salicylaldehyde- <i>n</i> -propoxy oxotitanium	**	1:1.1	(C ₇ H ₅ O ₂)TiO(OSnC ₁₈ H ₁₅)	**	150

** No appreciable elevation of boiling point was observed.

* All are new compounds.

Table 18

Absorption frequencies* in chelated chloro-, alkoxy-, and stannoxy-titanium compounds

Compound	Frequencies in the range 1500-1750 cm^{-1}
(Sal)TiCl ₃	1555(s), 1600(s)
(Sal) ₂ TiCl ₂	1555(s), 1600(s)
(Mesal) ₂ TiCl ₂	1553(m), 1592(s), 1613(s), 1631(s)
(Dbm) ₂ TiCl ₂	1500(s), 1540(s), 1590(s)
(Sal) ₂ Ti(OBu ⁿ) ₂	1587(m), 1626(s), 1667(w)
(Mesal) ₂ Ti(OBu ⁿ) ₂	1550(m), 1626(s), 1653(s)
(Dbm) ₂ Ti(OBu ⁿ) ₂	1515(s), 1538(s), 1587(s), 1667(w)
(Sal)TiO(OPr ⁿ)	1562(s), 1639(s)
(Sal) ₂ TiO ₂ SnBu ₂	1511(w), 1562(m), 1608(s), 1634(m)
(Mesal) ₂ TiO ₂ SnBu ₂	1511(s), 1540(m), 1582(s), 1608(s)
(Dbm) ₂ TiO ₂ SnBu ₂	1520(s), 1550(s), 1600(s)
(Sal) ₂ TiO ₂ Sn(Oct) ₂	1538(s), 1613(s), 1626(s), 1653(s)
(Sal) ₂ Ti(OSnPh ₃) ₂	1531(w), 1600(s), 1623(s)
(Mesal) ₂ Ti(OSnPh ₃) ₂	1522(m), 1580(m), 1610(s), 1647(s)
(Dbm) ₂ Ti(OSnPh ₃) ₂	1520(s), 1538(s), 1600(s)
(Sal)TiO(OSnPh ₃)	1553(s), 1631(s)

* Free ligands

SalH - (salicylaldehyde) 1595(s), 1616(s), 1642(sh), 1661(s)

MesalH - (methyl salicylate) 1600(s), 1626(s), 1689(s)

DbmH - (dibenzoylmethane) 1520(s), 1550(sh), 1570(s), 1600(s), 1681(s).

B Experimental Data6.1 Preparation of titanium(IV) alkoxides and chelated alkoxy-titanium(IV) compoundsTitanium tetrachloride

The crude sample, prepared by the chlorination of upgraded Indian ilmenite, was purified by refluxing it over bright copper turnings and distilling twice to obtain a clear, colourless liquid, b.p. 135-136°.

6.1.1 Tetra-n-propoxy titanium-

n-Propanol (30 g; 0.5 mole) and titanium tetrachloride (19 g; 0.1 mole), each diluted with benzene (50 ml), were mixed at 0° and then refluxed for four hours, after which dry ammonia gas was passed in at a slow rate for one hour. Ammonium chloride thus formed was filtered off and the filtrate fractionally distilled under reduced pressure. Tetra-n-propoxy titanium distilled at 140° at 1 mm/pressure (lit. 130° at 0.2 mm pressure).

Yield 17 g (60 per cent of theory). It is a colourless liquid, miscible with benzene and hexane in all proportions. It is easily hydrolysed on exposure to moist air.

6.1.2 Tetra-n-butoxy titanium-

This was prepared like the preceding ester using n-butanol (37 g; 0.5 mole) and titanium tetrachloride (19 g; 0.1 mole). The product distilled at 178° at 8 mm (lit. 179-180° at 8 mm).

Yield 20 g (58 per cent). It is a pale yellow liquid, miscible with benzene and hexane in all proportions, and is hydrolysed in moist air.

6.1.3 Bis-salicylaldehyde di-n-butoxy titanium-

Benzene solutions of tetra n-butoxy titanium (3.4 g; 0.01 mole) and salicylaldehyde (2.68 g; 0.022 mole) were mixed together and refluxed for two hours. The clear orange solution was evaporated under reduced pressure, and the red powdery residue, after washing with hexane, was kept at 60° under reduced pressure for drying. Yield 3 g (69 per cent).

Analysis: Found Ti 11.18; calculated for $(C_7H_5O_2)_2Ti(OC_4H_9)_2$, Ti 11.11 per cent.

Red powder, soluble in benzene, slightly soluble in hexane and carbon tetrachloride, m.p. 58°. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 444; calculated 436.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1667w, 1626s, 1587m, 1460s, 1389sh, 1379s, 1307s, 1282m, 1250w, 1205m, 1190w, 1149m, 1124w, 1031w, 909m, 885w, 825br, 760br.

6.1.4 Bis-methylsalicylate di-n-butoxy titanium-

benzene solutions of methyl salicylate (3.34 g; 0.022 mole) and tetra-n-butoxy titanium (3.4 g; 0.01 mole) were mixed and refluxed for two hours. The clear yellow solution thus obtained was evaporated under reduced pressure, and the orange coloured mass thus obtained was washed with hexane and kept at 60°

under reduced pressure for drying. Yield 3.2 g (65 per cent).

Analysis: Found Ti 9.41; calculated for $(C_8H_7O_3)_2Ti(OC_4H_9)_2$, Ti 9.68 per cent.

Orange-red viscous liquid, soluble in benzene, and slightly soluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 500; calculated 496.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1663s, 1626s, 1560m, 1481sh, 1471s, 1460s, 1449s, 1399m, 1370m, 1325s, 1299s, 1260s, 1220s, 1198m, 1163s, 1143m, 1093s, 1031w, 971br, 886br, 768br, 699br.

6.1.5 Bis-dibenzoylmethane di-n-butoxy titanium-

Dibenzoyl methane (4.93 g; 0.022 mole) and tetra *n*-butoxy titanium (3.4 g; 0.01 mole) were reacted and the product isolated in a manner similar to 6.1.3. The yield was 6 g (78 per cent).

Analysis: Found Ti 7.39; calculated for $(C_{15}H_{11}O_2)_2Ti(OC_4H_9)_2$, Ti 7.50 per cent.

Orange-red powder, m.p. 85° , soluble in benzene and slightly soluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 650; calculated 640.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1667w, 1587s, 1538s, 1516s, 1475s, 1460m, 1439s, 1370s, 1307s, 1290s, 1227s, 1176w, 1156w, 1143w, 1117m, 1075s, 1036m, 1020m, 1000w, 966m, 943m, 930w, 870w, 810br, 790w, 752s, 725s, 690s.

6.1.6 Methylsalicylate tri-n-propoxy titanium-

Tetra-n-propoxy titanium (3.12 g; 0.011 mole) and methyl salicylate (1.52 g; 0.01 mole) were refluxed in benzene for two hours and the product isolated similarly as in 6.1.3.

Yield 2.5 g (53 per cent).

Analysis: Found Ti 12.68; calculated for $(C_8H_7O_3)_3Ti(OC_3H_7)_3$, Ti 12.76 per cent.

Yellow viscous liquid, soluble in benzene, fairly soluble in hexane but insoluble in carbon tetrachloride. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 380; calculated 376.

6.1.7 Salicylaldehyde monopropoxy oxotitanium-

Freshly distilled tetra-n-propoxy titanium (3.12 g; 0.011 mole) was dissolved in benzene (10 ml), and salicylaldehyde (1.22 g; 0.01 mole) in benzene added drop by drop. The mixture was refluxed for an hour, after which the solvent (and other low-boiling products) were removed under reduced pressure. The viscous red residue, when kept at 80-90° at 1 mm pressure for about 15 minutes, became a red porous mass. This was washed with hexane and then dried under reduced pressure at 60°. Yield 2.3 g (94 per cent).

Analysis: Found C 48.92, H 5.43, Ti 19.83; calculated for $(C_7H_5O_2)_2TiO(OC_3H_7)$, C 49.18, H 4.92, Ti 19.67 per cent.

Red powder, stable up to 200°, soluble in benzene and alcohol, but insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 500; calculated (for dimer) 488.

6.2 Reactions of di-n-butyltin oxide with chelated alkoxytitanium compounds

6.2.1 Reaction with bis-salicylaldehyde di-n-butoxy titanium-

Dibutyltin oxide (2.74 g; 0.011 mole) was mixed with bis-salicylaldehyde di-n-butoxy titanium (4.36 g; 0.01 mole) in toluene (50 ml) and the mixture refluxed for 4-5 hours. The toluene solution was then cooled, filtered and the clear filtrate evaporated under reduced pressure. The crude product was purified by dissolving the residue in a small quantity of benzene and precipitating with hexane. The compound was finally washed with hexane and dried at 60° under reduced pressure. Yield 4.5 g (80 per cent).

Analysis: Found C 48.07, H 5.83, Sn 20.04, Ti 8.39; calculated for $(C_7H_5O_2)_2TiO_2Sn(C_4H_9)_2$, C 47.60, H 5.05, Sn 21.40, Ti 8.63 per cent.

Orange-red solid, non-hygroscopic, melts with decomposition at 250°, soluble in benzene, insoluble in hexane and carbon tetrachloride. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 554; calculated 555.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1634m, 1608s, 1562m, 1511w, 1481s, 1460s, 1377s, 1263s, 1147m, 1111m, 1075m, 1020m, 965w, 929sh, 889br, 793br, 756s.

6.2.2 Reaction with bis-methylsalicylate di-n-butoxy titanium-

Dibutyltin oxide (2.74 g; 0.011 mole) was reacted with bis-methylsalicylate di-n-butoxy titanium (4.96 g; 0.01 mole) in toluene as in the preceding experiment, and the product isolated similarly. The yield was 4.3 g (70 per cent).

Analysis: Found C 47.87, H 5.26, Sn 18.94, Ti 7.52; calculated for $(C_8H_7O_3)_2TiO_2Sn(C_4H_9)_2$, C 46.86, H 5.21, Sn 19.32, Ti 7.79 per cent.

Orange solid, m.p. 240° , soluble in benzene, insoluble in hexane and carbon tetrachloride. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 639; calculated 615.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1608s, 1582s, 1540m, 1511s, 1460s, 1418s, 1399s, 1378s, 1346s, 1319m, 1245s, 1163w, 1147s, 1103w, 1034m, 957w, 901s, 852s, 809br, 763s, 703m, 682s.

6.2.3 Reaction with bis-dibenzoylmethano di-n-butoxy titanium-

Bis-dibenzoylmethano di-n-butoxy titanium (3.4 g; 0.01 mole) was dissolved in toluene and reacted with dibutyltin oxide (2.74 g; 0.011 mole) by refluxing for 4-6 hours. The product was isolated as in 6.2.1. Yield 5.7 g (75 per cent).

Analysis: Found C 60.03, H 6.42, Sn 15.39, Ti 6.13; calculated for $(C_{15}H_{11}O_2)_2TiO_2Sn(C_4H_9)_2$, C 60.12, H 6.27, Sn 15.65, Ti 6.31 per cent.

Yellow-red solid, m.p. 78° , soluble in benzene, insoluble in hexane and carbon tetrachloride. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 758; calculated 759.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1600s, 1550s, 1520s, 1479s, 1447s, 1376s, 1315s, 1227m, 1183w, 1160w, 1126w, 1074m, 1031m, 1003w, 975w, 949w, 933w, 866br, 816m, 790m, 756s, 723s, 686s.

6.2.4 Reaction with salicylaldehyde *n*-propoxy oxotitanium-

The titanium compound (2.44 g; 0.01 mole) was reacted with dibutyltin oxide (1.37 g; 0.0055 mole) in boiling toluene and the product isolated in a similar way as in 6.2.1. Yield 2.4 g (68 per cent).

Analysis: Found C 44.70, H 5.74, Sn 18.90, Ti 15.26; calculated for $[(\text{C}_7\text{H}_5\text{O}_2)\text{TiO}]_2\text{OSn}(\text{C}_4\text{H}_9)_2$, C 41.61, H 4.41, Sn 18.71, Ti 15.10 per cent.

Orange solid, decomposes without melting above 250° , soluble in benzene, insoluble in hexane and carbon tetrachloride. It did not show any appreciable elevation of boiling point in benzene in the concentration range of 0.4 - 1.2% w/w).

6.3 Reactions of di-n-octyltin oxide with chelated alkoxy titanium compounds

6.3.1 Reaction with bis-salicylaldehyde di-n-butoxy titanium-

Diocetyl tin oxide (3.97 g; 0.011 mole) was mixed with bis-salicylaldehyde di-n-butoxy titanium (4.36 g; 0.01 mole) in toluene (50 ml) and refluxed for 4-5 hours. The toluene solution was allowed to cool and processed in a manner similar to 6.2.1. The product (a sticky solid) weighed 4 g (60 per cent).

Analysis: Found Sn 17.31, Ti 6.73; calculated for $(C_7H_5O_2)_2TiO_2Sn(C_8H_{17})_2$; Sn 17.80, Ti 7.2 per cent.

Red sticky solid, becomes liquid at 60° , soluble in benzene and carbon tetrachloride, but slightly soluble in hexane.

Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 632; calculated 667.

Infrared absorption maxima (in CCl_4) are given below (in cm^{-1}): 2900s, 1663m, 1626s, 1613s, 1538s, 1481s, 1471s, 1399s, 1379sh, 1351w, 1316s, 1282s br, 1235w, 1206s, 1176w, 1149s, 1130m, 1111s, 1067w, 1031s, 930s, 909s, 889s, 859m, 823s br, 714m.

6.3.2 Reaction with bis-methylsalicylate di-n-butoxy titanium-

Diocetyl tin oxide (3.97 g; 0.011 mole) was reacted with bis-methylsalicylate di-n-butoxy titanium (4.96 g; 0.01 mole) in toluene as in 6.2.1. The product isolated was a thick yellow liquid, yield 5 g (68 per cent).

Analysis: Found Sn 16.22, Ti 6.61; calculated for $(C_8H_7O_3)_2TiO_2Sn(C_8H_{17})_2$; Sn 16.34, Ti 6.61 per cent.

Viscous yellow liquid, soluble in benzene and carbon tetrachloride and slightly soluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 748; calculated 727.

6.3.3 Reaction with bis-dibenzoylmethano di-n-butoxy titanium-

This substance (6.4 g; 0.01 mole) was dissolved in toluene and reacted with dioctyltin oxide (3.97 g; 0.011 mole) by refluxing 4-6 hours. The product was isolated as in 6.2.1. Yield 6 g (69 per cent).

Analysis: Found Sn 13.43, Ti 6.32; calculated for $(C_{18}H_{11}O_2)_2TiO_2Sn(C_8H_{17})_2$; Sn 13.63, Ti 6.61 per cent.

Yellow sticky solid, becomes liquid at about 65° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 891; calculated 871.

6.4 Reactions of triphenyltin hydroxide with chelated alkoxy titanium compounds

6.4.1 Reaction with methylsalicylato tri-n-propoxy titanium-

Triphenyltin hydroxide (6.06 g; 0.0165 mole) was refluxed with methylsalicylato tri-n-propoxy titanium (1.88 g; 0.005 mole) in boiling toluene for 4-5 hours. Then the toluene solution was cooled, filtered and the clear filtrate evaporated under reduced pressure. The crude product was washed with hexane, dissolved in a small quantity of benzene and precipitated by adding hexane. The compound was finally washed with hexane and dried at 60° under reduced pressure. Yield 5 g (77 per cent).

Analysis: Found C 57.56, H 4.60, Sn 28.01, Ti 3.79; calculated for $(C_8H_7O_3)_2Ti[OSn(C_6H_5)_3]_3$, C 57.40, H 4.01, Sn 27.47, Ti 3.70 per cent.

Yellow solid, m.p. 160°, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 1317; calculated 1296.

6.4.2 Reaction with bis-salicylaldehyde di-n-butoxy titanium-

Triphenyltin hydroxide (4.04 g; 0.011 mole) was reacted with bis-salicylaldehyde di-n-butoxy titanium (2.18 g; 0.005 mole) in boiling toluene and product isolated in a similar way as in 6.3.1. The yield of the product was 4 g (78 per cent).

Analysis: Found C 56.4, H 4.74, Sn 23.56, Ti 4.75; calculated for $(C_7H_5O_2)_2Ti[OSn(C_6H_5)_3]_2$, C 58.78, H 3.92, Sn 23.25, Ti 4.69 per cent.

Red solid, melts with decomposition at 265° ; soluble in benzene, insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 1040; calculated 1021.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1623s, 1600s, 1531w, 1481s, 1449s, 1429s, 1376s, 1304m, 1268s, 1073m, 1100s, 1075w, 1026s, 1000s, 930w, 909w, 890w, 804s, 759s, 733s, 699s.

6.4.3 Reaction with bis-methylsalicylato di-n-butoxy titanium-

A toluene solution of bis-methylsalicylato di-n-butoxy titanium (2.48 g; 0.005 mole) was reacted with triphenyltin hydroxide (4.04 g; 0.011 mole) in a similar way as in 6.3.1. The yield of the product isolated was 3.8 g (70 per cent).

Analysis: Found Sn 21.17, Ti 4.25; calculated for $(C_8H_7O_3)_2Ti[OSn(C_6H_5)_3]_2$, Sn 21.98, Ti 4.43 per cent.

Yellow solid, decomposes without melting above 250° , soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 1089; calculated 1080.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2900s, 1647s, 1610s, 1580m, 1522m, 1470s, 1437s, 1379s, 1319s,
 1250s, 1188w, 1163m, 1149m, 1126w, 1095m, 1081m, 1036m, 1029m,
 1000m, 920m, 897m, 870m, 852m, 813br, 765s, 736s, 700s.

6.4.4 Reaction with bis-dibenzoylmethano di-n-butoxy titanium-

This compound (3.2 g; 0.006 mole) and triphenyltin hydroxide (4.04 g; 0.011 mole) were mixed and reacted in boiling toluene as in 6.3.1. The product was isolated and purified similarly. Yield 4 g (66 per cent).

Analysis: Found Sn 18.97, Ti 3.62; calculated for $(\text{C}_{15}\text{H}_{11}\text{O}_2)_2\text{Ti}[\text{OSn}(\text{C}_6\text{H}_5)_3]_2$, Sn 19.37, Ti 3.91 per cent.

Yellow-red solid, m.p. 129-130°, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 1224; calculated 1225.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2851s, 1600s, 1550s, 1520s, 1479s, 1447s, 1429s, 1379s, 1316s,
 1252m, 1163m, 1185w, 1160w, 1074s, 1026m, 1000w, 943w, 830m,
 794m, 769br, 732s, 698s.

6.4.5 Reaction with salicylaldehyde n-propoxy oxotitanium-

Triphenyltin hydroxide (4.04 g; 0.011 mole) and salicylaldehyde n-propoxy oxotitanium (2.44 g; 0.01 mole) were mixed and reacted in toluene as in 6.3.1. The product, isolated similarly, was 4.5 g (80 per cent).

Analysis: Found C 53.69, H 5.32, Sn 21.00, Ti 8.67; calculated for $(C_7H_8O_2)TiO[OSn(C_6H_5)_3]$, C 54.48, H 3.63, Sn 21.56, Ti 8.69 per cent.

Orange solid, m.p. 149-150°, soluble in benzene and insoluble in hexane. The substance did not show appreciable elevation of boiling point in benzene in the concentration range of 0.4 - 1.2% w/w).

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1631s, 1553s, 1484s, 1481s, 1460s, 1431s, 1399w, 1383m, 1313s, 1269s, 1238w, 1211w, 1196w, 1166m, 1124w, 1100m, 1081s, 1031s, 1005m, 976w, 909m, 813br, 763s, 735s, 706s.

Reactions of dibutyltin oxide, dioctyltin oxide and triphenyltin hydroxide with big-acetylacetonone dibutoxy titanium gave viscous products of indefinite composition.

7. Chelated Oxotitanium(IV) Mono-esters and
other Derivatives

Chelated oxotitanium(IV) mono esters and other derivativesA Discussion and Results

The only mono chelate of oxotitanium(IV) reported in the literature³⁰⁹ is that of acetylacetonone. Salicylaldehyde chelates of titanium being comparable in stability to those of acetylacetonone, it could be expected that salicylaldehyde might give a stable oxotitanium derivative. Salicylaldehyde oxotitanium mono-alkoxides have been prepared by us in good yields by careful thermal decomposition of salicylaldehyde trialkoxy titanium compounds at about 80°C under reduced pressure. The salicylaldehyde trialkoxy titaniums, in their turn, were obtained by two different methods, (a) by the esterification of salicylaldehyde trichloro-titanium with an excess of alcohol (in presence of ammonia), and (b) by one alkoxy substitution of tetraalkoxy titanium with salicylaldehyde. The thermal decomposition could be carried out without isolating the triester. Salicylaldehyde oxotitanium mono-alkoxides (C₂-C₄) prepared by the method (a) were yellow, non-hygroscopic substances, fairly soluble in benzene; those obtained by method (b) were red, hygroscopic solids, very soluble in benzene. They showed identical IR spectra, but from the molecular weight determination by ebullioscopy in benzene it was apparent that the former compounds were more polymeric (tetramer) than the latter ones (dimer). (Table 19)

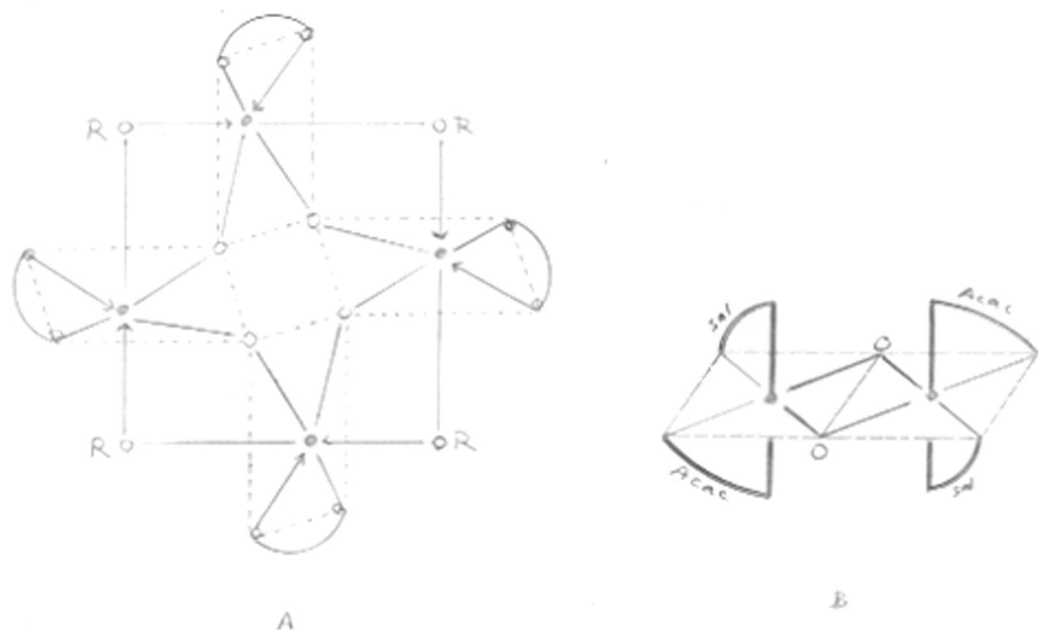
Thionyl chloride converted both the products back to salicylaldehyde trichloro-titanium. They formed ammonia and pyridine adducts like other organoxy titanium compounds. ^{299,335} An interesting and useful property observed in these new compounds was the reactivity of the lone alkoxy group. It was easily replaced by ligands such as phenols, diketones, diketoesters, salicylaldehyde, methyl salicylate and 8-hydroxyquinoline. All the alkoxy-substituted products were yellow to red non-hygroscopic solids, decomposing without melting above 200°. Some of them were soluble in benzene, but all dissolved in pyridine. The products obtained by reaction with phenol, cyclohexanol, acetylacetone, benzoylacetone, dibenzoylmethane and ethylacetoacetate were soluble in benzene and were found to be dimeric in 0.1 - 0.25% concentration in the boiling solvent (benzene). The compounds are listed in Table 20.

IR Spectra

The IR carbonyl absorption frequencies of chelated oxotitanium compounds are shown in Table 21. The hydrogen-bonded carbonyl frequency at 1661 cm^{-1} in free salicylaldehyde ligand shows considerable spectral shift in ^{the} salicylaldehyde alkoxy oxotitanium compounds, indicating strong coordination of the carbonyl group of the ligand with titanium. The lone salicylaldehyde group in salicylaldehyde butoxy oxotitanium (carbonyl band at 1613 cm^{-1}) seems more strongly coordinated than in bis-salicylaldehyde dibutoxy titanium (carbonyl band at 1667 cm^{-1}). (Table 18)

In the mixed oxotitanium chelates formed by the replacement of alkoxy group of salicylaldehyde alkoxy oxotitanium by a different chelating ligand, the carbonyl shifts indicate that the second carbonyl group is not often as strongly coordinated with titanium. In the case of phenols, superimposition of some of the carbonyl bands with those of the aromatic bands in the region 1600 cm^{-1} is probable.

The molecular structure of these compounds is interesting because of the three possible structures, namely, a monomeric molecule with $\text{Ti}=\text{O}$, a dimer with oxygen bridges, and a polymer with $-\text{Ti}-\text{O}-\text{Ti}-\text{O}$ chains. Broad bands are observed in the region $800-900\text{ cm}^{-1}$ in the IR spectra of these compounds. Their IR spectra do not show any absorption peak corresponding to $\text{Ti}=\text{O}$ which is reported to occur around 1000 cm^{-1} .^{308, 309} On the other hand, their spectra are similar to those of the compounds with $\text{Ti}-\text{O}-\text{Ti}$ bonds such as titanyl sulphate ($820-920\text{ cm}^{-1}$), potassium titanyl oxalate ($800-900\text{ cm}^{-1}$) and $[\text{TiO}(\text{acac})_2]_2$ (829 cm^{-1}).²⁸⁶ Of the compounds prepared by us, those which were soluble in benzene were found to be dimeric. Thus evidences seem to indicate that the alkoxy oxotitanium chelates and their alkoxy substituted products probably have a dimeric structure with oxygen bridges. We propose to assign structure A for salicylaldehyde monoalkoxy oxotitanium tetramer and structure B for dioxo-di[salicylaldehyde acetylacetonato titanium] dimer.



The alkoxy substitution products obtained from salicylaldehyde mono-propoxy oxotitanium and cyclohexanol, catechol and resorcinol also indicate expected features. Strong chelation between the carbonyl group of salicylaldehyde and titanium is evident from the carbonyl spectral shift. In the cyclohexanol derivative, the OH band of the parent ligand is absent while in catechol and resorcinol derivatives bands at 3226 cm^{-1} and 3390 cm^{-1} respectively (OH stretching vibration) are clearly seen indicating that only one OH of the dihydric phenols has reacted.

Table 19

Salicylaldehyde oxotitanium mono alkoxides

Reactants		Molar ratio A:B	Products	Mol. wt. Found(calc)
A	B			
Salicylaldehyde trichloro-titanium	ethanol	1:4	$(C_7H_5O_2)TiO(OC_2H_5)$	
" "	n-propanol	1:4	$(C_7H_5O_2)TiO(OC_3H_7)$	954(244)
" "	n-butanol	1:4	$(C_7H_5O_2)TiO(OC_4H_9)$	
Salicylaldehyde	ethyl titanate	1:1.1	$(C_7H_5O_2)TiO(OC_2H_5)$	466(230)
" "	n-propyl titanate	1:1.1	$(C_7H_5O_2)TiO(OC_3H_7)$	500(244)
" "	n-butyl titanate	1:1.1	$(C_7H_5O_2)TiO(OC_4H_9)$	560(258)

Table 20

Reaction products of salicylaldehyde η -propoxy
oxotitanium (Sal)TiO(OPr)

Reactant A	Molar ratio A:(Sal)TiO(OPr)	Product	Mol. wt. Found(calc.)
Thionyl chloride	16:1	(Sal)TiCl ₃	
Ammonia	excess of A	(Sal)TiO(OPr)2NH ₃	
Pyridine	10:1	(Sal)TiO(OPr)C ₅ H ₅ N	
Phenol	1.1:1	(Sal)TiO(C ₆ H ₅ O)	567(278)
Catechol	1.1:1 and 1:2	(Sal)TiO(C ₆ H ₅ O ₂)	
Resorcinol	1.1:1 and 1:2	(Sal)TiO(C ₆ H ₅ O ₂)	
Cyclohexanol	1.1:1 and 1:2	(Sal)TiO(C ₆ H ₁₁ O)	578(284)
Cyclohexane-1,4-diol	1.1:1 and 1:2	(Sal)TiO(C ₈ H ₁₁ O ₂)	
Acetylacetone	1.1:1	(Sal)TiO(C ₈ H ₇ O ₂)	560(284)
Benzoylacetone	1.1:1	(Sal)TiO(C ₁₀ H ₉ O ₂)	700(346)
Dibenzoylmethane	1.1:1	(Sal)TiO(C ₁₅ H ₁₁ O ₂)	812(408)
Ethylacetoacetate	1.1:1	(Sal)TiO(C ₈ H ₉ O ₃)	628(314)
Benzoyl ethylacetate	1.1:1	(Sal)TiO(C ₁₁ H ₁₁ O ₃)	735(376)
Salicylaldehyde	1.1:1	(Sal) ₂ TiO	
Methyl salicylate	1.1:1	(Sal)TiO(C ₈ H ₇ O ₃)	
Acetoacetanilide	1.1:1	(Sal)TiO(C ₁₀ H ₁₀ O ₂ N)	
8-Hydroxyquinoline	1.1:1	(Sal)TiO(C ₉ H ₆ ON)	

Table 21

IR spectra of chelated oxotitanium compounds

Compound	Peaks in the range 1500-1750 cm^{-1}
Salicylaldehyde	1575(s), 1616(s), 1642(sh), 1661(s)
(Sal)TiO(OEt)	1555(m), 1634(s)
(Sal)TiO(OPr)	1550(w), 1587(s), 1626(s)
(Sal)TiO(Obu)	1538(sh), 1582(s), 1613(s)
(Sal) ₂ TiO	1550(s), 1621(s)
Methyl salicylate	1600(s), 1626(s), 1689(s)
(Sal)(Mesal)TiO	1555(s), 1621(s), 1634(s)
Acetylacetone	1613(s), 1704(s), 1727(m)
(Sal)(Acac)TiO	1536(s) 1587(s)
Benzoylacetone	1513(m), 1527(s), 1562(s), 1600(s)
(Sal)(Ba)TiO	1511(s), 1550(s), 1587(s), 1613(s)
Dibenzoylmethane	1520(s), 1550(sh), 1570(s), 1600(s), 1681(s)
(Sal)(Dbm)TiO	1515(s), 1550(s), 1587(s), 1626(s)
Ethylacetoacetate	1524(m), 1540(m), 1640(s), 1735(s)
(Sal)(Eaa)TiO	1524(s), 1600(s), 1626(s), 1709(s)
Benzoylethylacetate	1572(m), 1587(m), 1626(s), 1695(s), 1739(s)
(Sal)(Bea)TiO	1522(s), 1575(s), 1626(s), 1686(s), 1739(s)
Acetoacetanilide	1538(m), 1600(s), 1661(s), 1724(s)
(Sal)(Aaa)TiO	1538(s), 1587(s), 1600(m)
8-Hydroxyquinoline	1504(s), 1587(s)
(Sal)(8HQ)TiO	1562(s), 1639(m)
Phenol	1600(s)
(Sal)(PhO)TiO	1575(m), 1531(s), 1562(s), 1587(s)

Table 21 (continued)

Compound	Peaks in the range 1500-1750 cm^{-1}
Catechol	1608(s), 1623(s)
(Sal)(Catech)TiO	1646(s), 1600(s), 1626(s)
Resorcinol	1627(m), 1650(w), 1608(s)
(Sal)(Resor)TiO	1660(s), 1600(s), 1613(s)

B Experimental Data

7.1 Preparation of salicylaldehyde alkoxy oxotitaniums from chelated chlorotitaniums

7.1.1 Preparation of salicylaldehyde trichloro-titanium-

salicylaldehyde (2.44 g; 0.02 mole) in benzene (10 ml) was added dropwise to titanium tetrachloride (5.7 g; 0.03 mole) in benzene (20 ml) at 0° and the mixture refluxed till hydrogen chloride was no longer evolved (about four hours).

The brown solid separated was filtered, washed with benzene and dried at 80° at 1 mm pressure. Yield 4 g (73 per cent).

Analysis: Found C 30.30, H 1.84, Cl 37.99, Ti 17.42; calculated for $(C_7H_5O_2)TiCl_3$, C 30.51, H 1.82, Cl 38.64, Ti 17.43 per cent.

Chocolate powder, hygroscopic, absorbs moisture on exposure and turns yellow. Sparingly soluble in benzene and hexane, but soluble in alcohol.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1600s, 1555s, 1397m, 1333w, 1269m, 1242m, 1220m, 1156m, 1124w, 1031w, 909s, 810m, 766s.

7.1.2 Esterification of salicylaldehyde trichloro-titanium with n-propanol-

salicylaldehyde trichloro-titanium (2.75 g; 0.01 mole) was dissolved in dry n-propanol (2.4 g; 0.04 mole) and diluted with benzene (25 ml). Through the cooled solution, dry ammonia gas

was slowly bubbled for 30 minutes. Ammonium chloride formed was filtered off and the benzene solution concentrated under reduced pressure. The viscous red residue thus obtained, became a yellow porous mass. This was washed with hexane and dried under reduced pressure, yield 2.2 g (90 per cent).

Analysis: Found C 49.67, H 5.54, Ti 19.67; calculated for $(C_7H_5O_2)_4TiO(OC_3H_7)$, C 49.18, H 4.92, Ti 19.67 per cent.

Yellow powder, decomposes on heating, fairly soluble in benzene, more soluble in alcohol and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 954; calculated (for tetramer) 976.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1626s, 1687m, 1550w, 1460s, 1449s, 1399m, 1379s, 1325s, 1250s, 1156sh, 1099s, 1081s, 1036s, 1010s, 965m br, 921s br, 893s, 866br, 758s.

7.1.3 Esterification of salicylaldehyde trichloro-titanium with ethyl alcohol-

Salicylaldehyde trichlorotitanium (2.75 g; 0.01 mole) and dry ethanol (1.84 g; 0.04 mole) were mixed and reacted in presence of ammonia as in 7.1.2, and product isolated. Yield 2 g (86 per cent).

Analysis: Found Ti 20.78; calculated for $(C_7H_5O_2)_4TiO(OC_2H_5)$, Ti 20.86 per cent.

Yellow powder, sparingly soluble in benzene and hexane but soluble in alcohol.

7.1.4 Esterification of salicylaldehyde trichlorotitanium with n-butanol-

n-Butanol (2.96 g; 0.04 mole) and salicylaldehyde trichlorotitanium (2.76 g; 0.01 mole) were mixed and reacted in presence of ammonia as in 7.1.2. The red viscous mass was kept at 120-130° at 0.5 mm. pressure for 30 minutes and the yellow porous mass obtained was washed with hexane and dried at 60° under reduced pressure. Yield 2.3 g (89 per cent).

Analysis: Found Ti 19.10; calculated for $(C_7H_6O_2)_4TiO(OC_4H_9)$ Ti 19.04 per cent.

Yellow powder, decomposes on heating without melting, slightly soluble in benzene, but soluble in alcohol.

7.2 Alternative preparation of salicylaldehyde alkoxy oxotitaniums from titanium alkoxides

- 7.2.1 Reaction between tetra-n-propoxy titanium and salicylaldehyde-
 Freshly distilled tetra-n-propoxy titanium (3.12 g; 0.011 mole) was diluted with benzene (10 ml). Salicylaldehyde (1.22 g; 0.01 mole) in benzene was added drop by drop and the mixture refluxed for an hour, after which the solvent and other low-boiling products were removed under reduced pressure. The viscous red residue thus obtained when kept at 30-90° at 1 mm pressure for about 15 minutes became a red porous mass. This was washed with hexane and dried under reduced pressure at 60°. Yield 2.3 g (94 per cent).

Analysis: Found C 48.92, H 5.43, Ti 19.34; calculated for $(C_7H_5O_2)_2TiO(OC_3H_7)$, C 49.18, H 4.92, Ti 19.67 per cent.

Red hygroscopic powder, stable up to 200° , soluble in benzene and alcohol and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 500; calculated (for monomer) 244.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1626s, 1587s, 1550w, 1449s, 1460s, 1399s, 1379s, 1325s, 1250s, 1156s, 1099s, 1081s, 1036s, 1000s, 957s br, 885s, 866s br, 758s.

7.2.2 Reaction between tetra-ethoxy titanium and salicylaldehyde-

Tetra-ethoxy titanium (2.51 g; 0.011 mole) and salicylaldehyde (1.22 g; 0.01 mole) were mixed in benzene, reacted and product isolated as in the preceding experiment. Yield 2.1 g (91 per cent).

Analysis: Found Ti 20.95; calculated for $(C_7H_5O_2)_2TiO(OC_2H_5)$ Ti 20.86 per cent.

Red hygroscopic solid, decomposes on heating without melting, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 465; calculated (for dimer) 460.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1634s, 1555m, 1479s, 1449s, 1408m, 1379m, 1311s, 1280m, 1232m, 1207v, 1149m, 1121m, 1036w, 980w, 948sh, 906s, 820sbr, 763s br, 720m.

7.2.3 Reaction between tetra-n-butoxy titanium and salicylaldehyde-
Salicylaldehyde (1.22 g; 0.01 mole) and tetra-n-butoxy titanium (3.74 g; 0.011 mole) were mixed in benzene and reacted in a manner similar to 7.2.1. The red viscous product obtained after removing solvent and other volatile products when kept at 120-130° at 0.5 mm pressure for 30 minutes became a red porous mass. This was washed with hexane and dried under reduced pressure at 60°. Yield 2.3 g (89 per cent).

Analysis: Found Ti 18.90; calculated for $(C_7H_6O_2)Ti_2(O_2C_4H_9)_4$, Ti 19.04 per cent.

Red hygroscopic powder, decomposes on heating without melting, soluble in benzene and insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 560; calculated (for dimer) 516.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1613s, 1582m, 1538w, 1460s, 1439s, 1370m, 1316m, 1241s, 1152m, 1106sh, 1092s, 1033s, 966m, 921br, 900sh, 750br.

7.3 Reactions of salicylaldehyde n-propoxy oxotitanium with various reagents*

7.3.1 Reaction with thionyl chloride-

Salicylaldehyde n-propoxy oxotitanium (2.44 g; 0.01 mole) was dissolved in benzene (50 ml) and cooled to 0°. To this solution freshly distilled thionyl chloride (10 ml) in benzene (10 ml)

* In the reactions described under 7.3, the propoxy oxotitanium compound was always prepared by the alternative procedure of alkoxy substitution (7.2).

was added drop by drop with constant stirring. When the addition was over, the mixture was refluxed for 30 minutes. The chocolate precipitate which separated was filtered, washed with benzene and dried under reduced pressure at 60°. Yield 2.5 g (90 per cent).

Analysis: Found Cl 39.06; Ti 17.51; calculated for $(C_7H_5O_2)TiCl_3$, Cl 38.64, Ti 17.43 per cent.

Chocolate powder, identical with the product in 7.1.1.

7.3.2 Reaction with ammonia-

Ammonia from a cylinder was dried by passing it at a medium rate through a tower filled with sodium hydroxide pellets. The dried gas was bubbled through a suspension of salicylaldehyde *n*-propoxy oxotitanium (2.44 g; 0.01 mole) in dry ether (50 ml) at 0° for 15 minutes. The solid product obtained was filtered, washed with ether and dried at room temperature under reduced pressure. Yield 2.7 g (95 per cent).

Analysis: Found Ti 17.32, NH₃ 12.86; calculated for $(C_7H_5O_2)TiO(C_3H_7O).2NH_3$. Ti 17.27, NH₃ 12.23 per cent.

Yellow powder, non-melting, insoluble both in benzene and hexane. On heating, it decomposes without melting above 200°.

7.3.3 Reaction with pyridine-

Salicylaldehyde *n*-propoxy oxotitanium (2.44 g; 0.01 mole) was dissolved in freshly dried and distilled pyridine (10 ml). The excess of pyridine was removed by heating the clear solution to 80° under reduced pressure. The dry residue was washed with hexane. Yield 2.8 g (87 per cent).

Analysis: Found C 54.31, H 5.78, Ti 15.31; calculated for $(C_7H_5O_2)TiO(C_3H_7O).C_6H_5N$, C 55.73, H 5.26, Ti 14.86 per cent.

7.3.4 Reaction with phenol-

Freshly distilled phenol (1.04 g; 0.011 mole) was dissolved in benzene (10 ml) and was reacted with salicylaldehyde *n*-propoxy oxotitanium (2.44 g; 0.01 mole) in the same solvent (50 ml) by gently refluxing for 3-4 hrs. The product was soluble in benzene and was isolated from the filtrate by concentrating it and precipitating with hexane. Yield 2 g (72 per cent).

Analysis: Found C 55.26, H 4.41, Ti 16.92; calculated for $(C_7H_5O_2)TiO(C_6H_5O)$, C 56.11, H 3.60, Ti 17.27 per cent.

Orange solid, soluble in benzene and slightly soluble in hexane. On heating, it decomposes without melting. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 567; calculated (for monomer) 278.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2899s, 1667w, 1587s, 1562s, 1531s, 1515m, 1493w, 1460sh, 1439s, 1397m, 1359s, 1316w, 1250s, br, 1202s, 1143s, 1111m, 1055w, 1026m, 1010m, 990m, 969m, 936w, 909sh, 885s, 857s, 813m, br, 776m, 749s, 685s.

7.3.5 Reaction with catechol-

Catechol (1.21 g; 0.011 mole) was dissolved in benzene (10 ml) and reacted with salicylaldehyde *n*-propoxy oxotitanium (2.44 g; 0.01 mole) in the same solvent (50 ml) by stirring and refluxing for 3-4 hrs. A red solid separated which was filtered, washed with benzene and dried at 80° under reduced pressure. Yield 2 g (68 per cent).

Analysis: Found C 54.16, H 4.50, Ti 16.09; calculated for $(C_7H_5O_2)_2TiO(C_6H_5O_2)$, C 53.07, H 3.40, Ti 16.32 per cent.

Red solid, insoluble in benzene and hexane. On heating, it decomposes without melting.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 3226s, 2941s, 1626s, 1600s, 1553m, 1546s, 1493m, 1481s, 1460s, 1449s, 1408m, 1370s, 1268sh, 1242s, 1198m, 1145m, 1111w, 1098m, 1015m, 971w br, 881s br, 803s br, 778w, 740s br.

7.3.6 Reaction with resorcinol-

Resorcinol (1.21 g; 0.011 mole) and salicylaldehyde *n*-propoxy oxotitanium (2.44 g; 0.01 mole) were reacted in benzene and product isolated as in 7.3.5. Yield 2.5 g (85 per cent).

Analysis: Found C 53.91, H 4.31, Ti 16.12; calculated for $(C_7H_5O_2)_2TiO(C_6H_5O_2)$, C 53.07, H 3.40, Ti 16.32 per cent.

Orange solid, insoluble in benzene and hexane. On heating, it decomposes without melting.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 3390s, 2941s, 1613s, 1600s, 1550s, 1460s, 1399w, 1370s, 1290s,
 1250m, 1227w, 1170s, 1143s, 1117sh, 1070w, 1036w, 1014w, 975s,
 901s, 844s br, 760s br, 722br, 685s br.

The same product was obtained by reacting resorcinol and salicylaldehyde η -propoxy oxotitanium in the molar ratio 1:2.

7.3.7 Reaction with cyclohexanol-

Cyclohexanol (1.1 g; 0.011 mole) was reacted with salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) in benzene and product isolated as in 7.3.4. Yield 2.1 g (76 per cent).

Analysis: Found C 54.27, H 6.12, Ti 16.01; calculated for $(\text{C}_7\text{H}_6\text{O}_2)\text{Ti}(\text{C}_6\text{H}_{11}\text{O})$, C 54.93, H 5.63, Ti 16.90 per cent.

Yellow hygroscopic solid, readily soluble in benzene, slightly soluble in hexane. Decomposes on heating without melting.

Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 578; calculated (for dimer) 568.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
 2950s, 1626s, 1596s, 1575sh, 1550s, 1460s, 1449s, 1361m, 1333m,
 1370m, 1302s, 1258s, 1230s, 1198m br, 1147s, 1111m br, 1013m br,
 985m, 969m, 934w, 893s, 782s.

7.3.8 Reaction with cyclohexane-1,4-diol-

Salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) was dissolved in benzene and reacted with cyclohexane-1,4-diol (1.28 g; 0.011 mole) in the solvent as in 7.3.5.

Yield 2.4 g (80 per cent).

Analysis: Found C 52.13, H 6.17, Ti 16.09; calculated for $(C_7H_6O_2)_2TiO(C_6H_{11}O_2)$, C 52.00, H 5.33, Ti 16.00 per cent.

Yellow solid, insoluble in benzene and hexane.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 3448s, 2950s, 1626m, 1600m, 1481sh, 1460s, 1449s, 1370m, 1250s, 1070s, 1010m, 990w, 957m, 930w br, 898m br, 755s, 719w.

The same product was obtained by reacting cyclohexane -1,4-diol and salicylaldehyde η -propoxy oxotitanium in the molar ratio 1:2.

7.3.9 Reaction with acetylacetone-

Acetylacetone (1.1 g; 0.011 mole) diluted with benzene (10 ml) and salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) in the same solvent (50 ml) were mixed, stirred, gently refluxed for 3-4 hrs. and filtered. The product was isolated from the filtrate by concentrating the latter and precipitating with hexane. Yield 1.6 g (57 per cent).

Analysis: Found C 51.23, H 5.11, Ti 17.00; calculated for $(C_7H_6O_2)_2TiO(C_5H_7O_2)$, C 50.71, H 4.23, Ti 16.90 per cent.

Orange solid, soluble in benzene, slightly soluble in hexane. On heating, it decomposes without melting. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 560; calculated (for dimer) 568.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2950s, 1587s, 1536s, 1460s, 1370m, 1266s, 1105w, 1026m, 934m, 900m, 755s, 722m br.

7.3.10 Reaction with benzoylacetone-

Benzoylacetone (1.78 g; 0.011 mole) and salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) were mixed in benzene, reacted, and the product isolated as in 7.3.9. Yield 3 g (87 per cent).

Analysis: Found C 60.08, H 5.19, Ti 13.97; calculated for $(\text{C}_7\text{H}_5\text{O}_2)_2\text{Ti}(\text{C}_{10}\text{H}_9\text{O}_2)$, C 59.96, H 4.05, Ti 13.87 per cent.

Yellow powder, soluble in benzene and insoluble in hexane. Decomposes on heating without melting. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 700; calculated (for dimer) 692.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2900s, 1613s, 1587s, 1550s, 1511s, 1460s, 1481s, 1449s, 1370m, 1289br, 1205w, 1176w, 1143w, 1105m, 1070m, 1026w, 954w, 966w, 897w, 847m, 806m br, 757s br, 711m, 673m.

7.3.11 Reaction with dibenzoylmethane-

Dibenzoylmethane (2.46 g; 0.011 mole) and salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) were mixed in benzene, reacted and product isolated as in 7.3.9. Yield 3.5 g (88 per cent).

Analysis: Found C 66.64, H 5.01, Ti 11.70; calculated for $(C_7H_6O_2)_2TiO(C_{15}H_{11}O_2)$, C 64.71, H 3.92, Ti 11.76 per cent.

Yellow light solid. On heating, it decomposes without melting. Soluble in benzene, but insoluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 812; calculated (for dimer) 816.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1724w, 1653w, 1626s, 1587s, 1550s, 1515s, 1460s, 1443s, 1370m, 1311m, 1220m, 1176w, 1111w, 1066m, 1025w, 1000w, 971w, 942w, 910w, 808m br, 752s br, 716s, 682m.

7.3.12 Reaction with ethylacetoacetate-

Freshly distilled ethyl acetoacetate (1.43 g; 0.011 mole) and salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) were mixed and reacted as in 7.3.9. The product, being very soluble in benzene, was obtained by removing the solvent under reduced pressure and washing with hexane. Yield 2.2 g (67 per cent).

Analysis: Found C 51.11, H 5.40, Ti 15.26; calculated for $(C_7H_6O_2)_2TiO(C_8H_9O_3)$, C 49.68, H 4.46, Ti 15.29 per cent.

Red crystalline solid, decomposing at 170° without melting. It is soluble in benzene and carbon tetrachloride, but only slightly soluble in hexane. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 628; calculated (for dimer) 628.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2941s, 1709m, 1626s, 1600s, 1524s, 1460s, 1477sh, 1449s, 1414w, 1370m, 1274s, 1176m, 1155s, 1096m, 1058m, 1012m, 978m, 900m, br, 862m br, 797m, 756s.

7.3.13 Reaction with benzoylethylacetate-

Salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) was reacted with freshly distilled benzoylethylacetate (2.11 g; 0.011 mole) as in 7.3.9. Yield 3 g (80 per cent).

Analysis: Found Ti 12.94; calculated for $(\text{C}_7\text{H}_5\text{O}_2)_2\text{Ti}(\text{C}_{11}\text{H}_{11}\text{O}_3)$ Ti 12.76 per cent.

Red solid, soluble in benzene and carbon tetrachloride but insoluble in hexane. Decomposes on heating without melting. Molecular weight (ebullioscopy in benzene in the concentration range of 0.4 - 1.2% w/w) found 736; calculated (for dimer) 752.

Infrared absorption maxima (in CCl_4) are given below (in cm^{-1}): 2941w, 1739w, 1686w, 1626s, 1575s, 1522s, 1484s, 1449s, 1414m, 1379m, 1361m, 1290s, 1263s, 1198s, 1149m, 1111s, 1081w, 1042s, 1027s, 1000w, 921m br, 795-755s br, 697m.

7.3.14 Reaction with salicylaldehyde-

Salicylaldehyde (1.34 g; 0.011 mole) was diluted with benzene (10 ml) and a solution of salicylaldehyde η -propoxy oxotitanium (2.44 g;

0.01 mole) in the same solvent (50 ml) added to it. The mixture was stirred and refluxed gently for 3-4 hours. An orange product separated which was filtered, washed with benzene and dried at 80° under reduced pressure. Yield 2.5 g (83 per cent).

Analysis: Found C 56.10, H 4.51, Ti 15.58; calculated for $(C_7H_5O_2)_2TiO$, C 54.91, H 3.27, Ti 15.69 per cent.

Orange powder, insoluble in benzene and soluble in alcohol. On heating, it decomposes without melting above 200° .

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2899s, 1621s, 1550m, 1527w, 1511w, 1460s, 1449s, 1395w, 1370m,
1299s, 1271s, 1235m, 1205m, 1149m, 1114m, 1079w, 1029m, 1018w,
976w, 966w, 935w, 905m, 893m, 832br, 787sh, 757s, 732br

7.3.16 Reaction with methyl salicylate-

Methyl salicylate (1.67 g; 0.011 mole) and salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) were reacted in benzene as in 7.3.14. The yellow product which separated was washed with benzene and dried at 80° under reduced pressure. Yield 2.9 g (86 per cent).

Analysis: Found C 51.66, H 4.21, Ti 14.44; calculated for $(C_7H_5O_2)TiO(C_8H_7O_3)$, C 53.58, H 3.57, Ti 14.29 per cent.

Yellow hygroscopic powder, slightly soluble in benzene and insoluble in hexane. Decomposes on heating without melting.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}):
2900s, 1621s, 1555s, 1490sh, 1460s, 1453s, 1414s, 1370m, 1351s,
1333s, 1323s, 1280s, 1250s, 1205m, 1149m, 1130sh, 1099m, 1036m,
976m, 966w, 948w, 893s, 840s, 763s br, 707br.

7.3.16 Reaction with acetoacetanilide-

Acetoacetanilide (1.98 g; 0.011 mole) and salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) were reacted and product isolated as in 7.3.14. Yield 3 g (83 per cent).

Analysis: Found C 56.72, H 4.97, Ti 13.18; calculated for $(C_7H_5O_2)TiO(C_{10}H_{10}O_2N)$, C 56.50, H 4.16, Ti 13.29 per cent.

Yellow solid, insoluble in benzene, carbon tetrachloride and hexane. Decomposes on heating without melting.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2899s, 2353w, 1695w, 1600sh, 1587s, 1538s, 1488s, 1460s, 1471s, 1443s, 1399m, 1370m, 1307s, 1299m, 1250s, 1179m, 1156w, 1100w br, 1047m, 1030w, 995w, 974s, 895m, 755s, 741m, 730m, 692s br.

7.3.17 Reaction with 8-hydroxyguinoline-

The ligand (1.6 g; 0.011 mole) was reacted with salicylaldehyde η -propoxy oxotitanium (2.44 g; 0.01 mole) and product isolated as in 7.3.14. Yield 2.8 g (85 per cent).

Analysis: Found Ti 14.36; calculated for $(C_7H_5O_2)TiO(C_9H_6O_2N)$ Ti 14.59 per cent.

Red solid, insoluble in benzene and hexane. On heating it decomposes without melting.

Infrared absorption maxima (in Nujol) are given below (in cm^{-1}): 2857s, 1639w, 1562s, 1481s, 1460s, 1449s, 1370m, 1312s, 1250s, 1168w, 1103s, 1026w, 897s br, 823s, 806s, 784s, 743s, 720sh.

REFERENCES

: : R E F E R E N C E S : :

1. Sidgwick, N.V., Ann. Reports, 1933, 30, 120.
2. Van der Kerk, G.J.M., Chimia, 1962, 16, 10.
3. Van der Kerk, G.J.M., Rec. Trav. Chim., 1962, 81, 202.
4. Nelson, W.H. and Martin, D.F., J. Inorg. Nucl. Chem., 1965, 27, 89.
5. Neumann, W.P., Angew. Chem., 1963, 75, 225.
6. Neumann, W.P. and König, K., Annalen, 1964, 677, 1, 12.
7. Johnson, W.A., 'Tin and its uses', 1962, 5.
8. Seyferth, D. and Stone, F.G.A., J. Amer. Chem. Soc., 1967, 79, 515.
9. Netherlands Pat. No. 6,607,716. Chem. Abstr., 1966, 64, 17640.
10. French Pat. No. 1,449,872. Chem. Abstr., 1967, 66, 95200.
11. Maire, J.C., Ann. Chim. Paris, 1961, 6, 969.
12. Baborn, C., Hornfeld, H.L. and Walton, D.R.M., J. Organometallic Chem., 1967, 10, 429.
13. Jaura, K.L. et al., Ind. J. Chem., 1966, 4, 329.
14. Jaura, K.L. et al., Ind. J. Chem., 1967, 5, 211.
15. Kubinchik, G.F. and Haulkin, Z.M., Zh. Obshch. Khim., 1966, 36, 261, 748, 1301.
16. Pollard, F.H., Nickless, G. and Nolan, D.N., Chem. and Ind., 1965, 1027.
17. Kazankova, M.A. et al., Zh. Obshch. Khim., 1967, 37, 1710.
18. Tamborski, C., Soloski, S.J. and Dec, S.M., J. Organometallic Chem., 1966, 4, 446.
19. Gilman, H. and Zuech, S.A., J. Amer. Chem. Soc., 1960, 82, 2522.
20. Kupchik, E.J. and Perciaccante, V.A., J. Organometallic Chem., 1967, 10, 181.
21. Kuivila, H.G. and Beumel, O.F., J. Amer. Chem. Soc., 1968, 90, 3250.
22. Kupchik, E.J. et al., J. Organometallic Chem., 1967, 10, 269.

23. Leavitt, P.C. et al., *J. Amer. Chem. Soc.*, 1960, 82, 5099.
24. Atwell, W.H. and Keyenberg, D.R., *J. Org. Chem.*, 1967, 32, 885.
25. U. S. Pat. No. 3,234,239. *Chem. Abstr.*, 1966, 64, 11261.
26. Cohen, S.C. and Massey, A.G., *J. Organometallic Chem.*, 1967, 10, 471.
27. Neumann, W.P., *Angew. Chem. Intern. Edn. Eng.*, 1963, 2, 165.
28. Horder, J.R. and Luppert, M.F., *J. Chem. Soc. (A)*, 1968, 1167.
29. Neumann, W.P. and Schneider, B., *Annalen.*, 1967, 707, 7.
30. French Pat. No. 1,467,849. *Chem. Abstr.*, 1968, 68, 49769.
31. U. S. Pat. No. 3,247,795. *Chem. Abstr.*, 1966, 64, 14220.
32. Foldesi, I. and Gomorg, P., *Chem. Abstr.*, 1965, 63, 16377.
33. Seyforth, D. et al., *J. Organometallic Chem.*, 1960, 6, 573.
34. Nguyen, D.H. et al. *Chem. Abstr.*, 1968, 62, 19274.
35. Burdon, J., Coe, P.L. and Fulton, M. C. *J. Chem. Soc.*, 1965, 2094.
36. Seyforth, D. and Andrews, S.B., *J. Organometallic Chem.*, 1969, 18, 21.
37. Van der Kerk, G.J.M. and Luijten, J.G.A.,
'Investigations in the Field of Organotin Chemistry'
Tin Research Institute, Greenford, 1955.
38. Srivastava, T.N. and Bhattacharya, S.N.
Z. Anorg. Allgem. Chem., 1966, 344, 102.
39. Peddle, G.J.D., *J. Organometallic Chem.*, 1968, 14, 139.
40. Stegmann, H.B. and Scheffler, K., *Tetrahedron Letters*, 1964, 3387.
41. German Pat. No. 1,212,086. *Chem. Abstr.*, 1966, 64, 19675.
42. U. S. Pat. No. 3,372,097. *Chem. Abstr.*, 1968, 68, 101279.
43. Van der Kerk, G.J.M., Luijten, J.G.A. and Noltes, J.G.,
Chem. and Ind., 1956, 352.
44. Neumann, W.P., Niermann, H. and Sommer, R., *Annalen.*, 1962, 662, 27.
45. Ohara, M. and Okawara, R., *J. Organometallic Chem.*, 1965, 3, 484.
46. Japanese Pat. No. 6737. *Chem. Abstr.*, 1966, 65, 5496.
47. Moedritzer, K., *Organometallic Chem. Rev.*, 1966, 1, 179.

48. Belgian Pat. No. 638,642. Chem. Abstr., 1966, 62, 11455.
49. Kuivila, H.G., "Advances in Organometallic Chemistry", Academic Press, 1964, 1, 47.
50. Van der Kerk, G.J.M. et al., Chem. and Ind., 1966, 352.
51. Van der Kerk, G.J.M. and Moltes, J.G., J. Applied Chem., 1959, 9, 106.
52. Nesmeyanov, A.N. et al., Izv. Akad. Nauk SSSR., Ser. Khim., 1967, 1141.
53. Kraihanzel, C.S. and Losee, M.L., J. Organometallic Chem., 1967, 10, 427.
54. Nesmeyanov, A.N., Borisov, A.E., Dokl. Akad. Nauk. SSSR., 1967, 174, 96.
55. Nesmeyanov, A.N. and Borisov, A.E. Izv. Akad. Nauk., SSR. Ser. Khim., 1967, 226.
56. Kuivila, H.G. et al., J. Amer. Chem. Soc., 1962, 84, 3684.
57. Seyferth, D. et al., J. Org. Chem., 1963, 28, 703.
58. Polish Pat. No. 51771. Chem. Abstr., 1968, 68, 49776.
59. Greene, F.D. and Lovry, M.L., J. Org. Chem., 1967, 32, 882.
60. Gilman, H., Ingham, A.K. and Rosenberg, S.D., Chem. Reviews., 1960, 60, 479.
61. Gielen, M. and Nasielski, J., J. Organometallic. Chem., 1963, 1, 173.
62. Gielen, M., Boue, S. and Nasielski, J., J. Organometallic Chem., 1967, 9, 443.
63. Gielen, M. and Nasielski, J., J. Organometallic Chem., 1967, 7, 273.
64. Gielen, M., Boue, S. and Nasielski, J., Tetrahedron Letters, 1968, 1047.
65. Gielen, M., Nasielski, J. and Topart, J., Rec. Trav. Chim., 1968, 87, 1051.
66. Faleschim, S. and Tagliavini, G., Chem. Abstr., 1968, 68, 95053.
67. Gielen, M., Boue, S., Nasielski, J., Austin, J. and Limbourg, M., J. Organometallic Chem., 1968, 15, 267.
68. Kuivila, H.G. and Verdone, J.A., Tetrahedron Letters, 1964, 119.

69. Van der Berghe, E. A. and Van der Kelen, G. P.,
J. Organometallic Chem., 1966, 6, 5-2.
70. Netherlands Pat. No. 6,513,659. Chem. Abstr., 1966, 66, 7218.
71. U. S. Pat. No. 3,297,732. Chem. Abstr., 1967, 66, 115807.
72. German Pat. No. 1,222,503. Chem. Abstr., 1966, 66, 13763.
73. British Pat. No. 1,070,942. Chem. Abstr., 1967, 67, 43925.
74. Matsuda, S. et al., Chem. Abstr., 1968, 68, 37373.
75. Moedritzer, K. "Advances in Organometallic Chemistry",
Academic Press, New York, 1968, 6, 171.
76. Moedritzer, K., Organometallic Chem. Rev., 1966, 1, 179.
77. Neumann, W. P. and Burkhardt, G., Annalen., 1963, 663, 11.
78. Grant, D. and Van Wazer, J. R., J. Organometallic Chem.,
1966, 4, 229.
79. Frankland, E., Annalen., 1849, 71, 171.
80. Sisido, K., Kozima, S. and Hanada, T., J. Organometallic Chem.,
1967, 2, 99.
81. French Pat. No. 1,456,268. Chem. Abstr., 1967, 66, 115806.
82. Nosek, J., Collection Czech. Chem. Commun.,
1964, 29, 3173.
83. Oakes, V. and Hutton, R. L., J. Organometallic Chem.,
1966, 6, 133.
84. Netherlands Pat. No. 6,506,444. Chem. Abstr., 1966, 64, 11251.
85. Sisido, K., Kozima, S. and Tuzi, T., J. Organometallic Chem.,
1967, 2, 109.
86. Netherlands Pat. No. 6,614,326. Chem. Abstr., 1967, 67, 100247.
87. British Pat. No. 1,064,178. Chem. Abstr., 1967, 67, 43924.
88. Matsuda, S., et al., Chem. Abstr., 1966, 65, 18612.
89. Matsuda, S., et al., Chem. Abstr., 1968, 68, 39756.
90. Matsuda, S., et al., Chem. Abstr., 1968, 68, 77384.
91. Matsuda, S., et al., Chem. Abstr., 1968, 68, 13109.
92. Matsuda, S., et al., Chem. Abstr., 1968, 68, 59672.
93. Matsuda, S., et al., Chem. Abstr., 1966, 65, 5482.

94. Matsuda, S., et al., Chem. Abstr., 1968, 62, 87127.
95. Matsuda, S., et al., Chem. Abstr., 1968, 62, 87363.
96. Matsuda, S., et al., Chem. Abstr., 1968, 68, 13108.
97. Pentiman, A.F., et al., J. Organometallic Chem., 1966, 6, 645.
98. U. S. Pat. No. 3,397,131. Chem. Abstr., 1968, 62, 776503.
99. Ross, A., et al., J. Organometallic Chem., 1964, 41, 1239.
100. Poller, R.C., "Chemistry of Organo Tin Compounds", Logos Press Ltd., London 1970, 69.
101. Davies, A.G., Harrison, P.G. and Palan, P.R., J. Organometallic Chem., 1967, 10, 33.
102. Davies, A.G. and Harrison, P.G., J. Organometallic Chem., 1967, 2, 13.
103. Brown, M.P., Okawara, R. and Rochow, G.J., Spectrochim. Acta., 1960, 16, 595.
104. Shostakovskii, M.F., et al., Zh. Obshch. Khim., 1966, 36, 751.
105. Atavin, A.S. et al., Zh. Obshch. Khim., 1966, 36, 1806.
106. Rubinchik, G.F. and Manulkin, Z.M., Chem. Abstr., 1968, 62, 77394.
107. Mehrotra, R.C. and Bachlas, B.P., J. Organometallic Chem. 1970, 22, 121.
108. Brilkina, T.G. et al., Zh. Obshch. Khim., 1966, 36, 2202.
109. Japanese Pat. No. 6172. Chem. Abstr., 1966, 65, 8490.
110. Davies, A.G., Palan, P.R. and Vasishtha, S.C., Chem. and Ind., 1967, 229.
111. Japanese Pat. No. 12415. Chem. Abstr., 1968, 68, 49777.
112. French Pat. No. 1,406,428. Chem. Abstr., 1966, 63, 14904.
113. Alleston, D.L. and Davies, A.G., J. Chem. Soc., 1962, 2040.
114. Emeleus, H.J. and Zuckerman, J.J., J. Organometallic Chem., 1964, 1, 328.
115. Van der Kerk, G.J.M. et al., "Advances in Organometallic Chemistry", Academic Press., 1965, 2, 397.
116. Jones, K. and Lappert, M.F., Organometallic Chem. Rev., 1966, 1, 67.

117. Jones, K. and Lappert, M.F., *J. Chem. Soc.*, 1965, 1944.
118. Wright, C.M. and Muetterties, E.L., *Inorg. Syn.*, 1967, 10, 137.
119. Van der Kerk, G.J.M. and Luijten, J.G.A., *Rec. Trav. Chim.*, 1963, 82, 1181.
120. Sisido, K. and Kozima, S., *J. Org. Chem.*, 1962, 27, 4051.
121. Scherer, O.J. and Horrig, P., *J. Organometallic Chem.*, 1967, 8, 466.
122. Scherer, O.J., and Schmidt, M., *Chem. Abstr.*, 1966, 66, 10606.
123. Scherer, O.J. and Schmidt, M., *J. Organometallic Chem.*, 1966, 3, 156.
124. Scherer, O.J. and Biller, D., *Z. Naturforsch.*, 1967, B 20, 1079.
125. Scherer, O.J. and Biller, D., *Angew. Chem. Intern. Ed. Engl.*, 1967, 6, 446.
126. George, T.A., Jones, K. and Lappert, M.F., *J. Chem. Soc.*, 1966, 2157.
127. Jones, K. and Lappert, M.F., *J. Organometallic Chem.*, 1966, 3, 295.
128. George, T.A. and Lappert, M.F., *Chem. Comm.*, 1966, 463.
129. Scherer, O.J., *Organometallic Chem. Rev.*, Section A 1968, 3, 281.
130. Van der Kerk, G.J.M. et al., "Investigations in the Field of Organotin Chemistry", Tin Research Institute, 1965, 97.
131. Davies, A.G. et al., *J. Chem. Soc.*, (C), 1966, 1311.
132. Noltes, J.G., *Rec. Trav. Chim.*, 1966, 84, 799.
133. Noltes, J.G. and Janssen, M.J., *J. Organometallic Chem.*, 1964, 1, 346.
134. Abel, E.W. and Armitag, D.A., "Advances in Organometallic Chemistry", Academic Press, 1967, 5, 1.
135. Abel, E.W. and Brady, D.B., *J. Chem. Soc.*, 1965, 1192.
136. Davidson, W.E. et al., *J. Organometallic Chem.*, 1966, 2, 285.
137. Wieber, M. and Schmidt, M.J., *J. Organometallic Chem.*, 1964, 1, 336.
138. Wieber, M. and Schmidt, M.J., *J. Organometallic Chem.*, 1964, 2, 129.

139. Pang, M. and Becker, E.I., *J. Org. Chem.*, 1964, 29, 1948.
140. Reichle, W.T., *Inorg. Chem.*, 1962, 1, 650.
141. Poller, R.C. and Spillman, J.A., *J. Organometallic Chem.*, 1966, 9, 668.
142. Abel, E.W. et al., *J. Organometallic Chem.*, 1966, 9, 260.
143. Weiss, R.W., "Organometallic Compounds", Springer-Verlag, 1967.
144. Jen-Hsicho et al., *Chem. Abstr.*, 1966, 65, 13753.
145. *Compt. Rend.*, 1966, 262, 480.
146. Japanese Pat. No. 3632, *Chem. Abstr.*, 1966, 65, 2298.
147. Japanese Pat. No. 8856, *Chem. Abstr.*, 1966, 65, 12240.
148. Japanese Pat. No. 7941, *Chem. Abstr.*, 1968, 62, 87186.
149. U. S. Pat. No. 3,257,194. *Chem. Abstr.*, 1966, 65, 12240.
150. Vertiy Smith, H. "Development of the Organotin Stabilizers", Tin Research Institute, Greenford, 1960.
151. Mufti, A.S. and Poller, R.C., *J. Chem. Soc.(C)*. 1967, 1362, 1767.
152. Netherlands Pat. No. 6,604,233. *Chem. Abstr.*, 1967, 66, 76166.
153. International Tin Research Council, Annual Report, 1969, 29.
154. Gielen, M. and Sprecher, N., *Organometallic Chem. Rev.*, 1966, 1, 455.
155. Beatlie, I.R., *Quart. Rev.*, 1963, 17, 382.
156. Paul, R.C., Singal, H.R. and Chadha, S.L., *J. Inorg. Nucl. Chem.*, 1970, 32, 3205; 1970, 32, 2141.
157. Goldshlein, I.P. et al., *Dokl. Akad. Nauk. SSSR.*, 1961, 136, 1079.
158. Wardell, J.L., *J. Organometallic Chem.*, 1967, 9, 89; 1967, 10, 53.
159. Nelson, W.H. and Martin, D.F., *J. Organometallic Chem.*, 1965, 4, 67.
160. Bonati, F., *Organometallic Chem. Rev.*, 1966, 1, 379.
161. Mullins, M.A. and Curran, C., *Inorg. Chem.*, 1968, 7, 2584.
162. Nelson, W.H. et al., *Inorg. Synth.*, 1967, 9, 52.
163. Mehrotra, R.C. and Gupta, V.G., *J. Organometallic Chem.*, 1965, 4, 237.

164. Ueeda, R. et al., *J. Organometallic Chem.*, 1966, 5, 194.
165. Komura, M. et al., *Inorg. Chim. Acta.*, 1968, 2, 321.
166. Muetterties, E.L. and Wright, C.M., *J. Amer. Chem. Soc.*, 1964, 86, 5132.
167. Mehrotra, R.C. and Bachlas, B.P., *J. Organometallic Chem.*, 1970, 22, 129.
168. Srivastava, T.N. and Saxena, K.L., *Ind. J. Chem.*, 1971, 9, 601.
169. Paul, R.C. et al., *Indian J. Chem.*, 1969, 7, 822.
170. Davies, A.G. and Symes, W.R., *J. Chem. Soc. (C)*, 1967, 1009.
171. Clark, H.C. and Tsai, T.S., *Inorg. Chem.*, 1966, 5, 1407.
172. Clark, H.C., Sotton, J.D. and Tsai, T.S., *Inorg. Chem.*, 1966, 5, 1582.
173. Bibler, J.P. and Wojcicki, A., *J. Amer. Chem. Soc.*, 1966, 88, 4862.
174. Coffield, T.H. et al., *J. Org. Chem.*, 1967, 22, 598.
175. Edmondson, R.C. and Newland, M.J., *Chem. Commun.*, 1968, 1219.
176. Lindner, E. et al., *J. Organometallic Chem.*, 1970, 24, 119, 131.
177. Kitching, W. and Fong, C.W., *Organometallic Chem. Rev.*, A 5, 1970, 281.
178. Lappert, M.F. and Prokai, B., *Adv. Organometallic Chem.*, 1967, 5, 225.
179. Lindner, E. and Kunze, U., *J. Organometallic Chem.*, 1970, 23, C53.
180. Lindner, E. and Kunze, U., *Z. Naturforsch B*, 1971, 26, 164.
181. Kitching, W. and Fong, C. W., *J. Organometallic Chem.*, 1970, 22, 95.
182. Kitching, W., et al., *J. Amer. Chem. Soc.*, 1969, 91, 767.
183. Kitching, W. et al., *J. Organometallic Chem.*, 1969, 20, 253.
184. Kitching, W. et al., *J. Organometallic Chem.*, 1970, 21, 365.
185. Kitching, W. et al., *J. Organometallic Chem.*, 1970, 25, C20.
186. Palazzi, A., *J. Organometallic Chem.*, 1970, 25, 249.

187. Graziani, M., Res, R and Carturan, G., J. Organometallic Chem., 1971, 22, C19.
188. Deacon, G.B. et al., J. Organometallic Chem., 1971, 26, C10.
189. Deacon, G.B. et al., Australian J. Chem., 1971, 24, 1599.
190. Harrison, P.G., Organometallic Chem. Rev., Section A, 1969, 4, 379.
191. Okawara, R. and Sugita, K., J. Amer. Chem. Soc., 1961, 83, 4480.
192. Okawara, R., White, D.G., Fujitani, K. and Sato, H., J. Amer. Chem. Soc., 1961, 83, 1342.
193. Schmidbauer, H. and Hussek, H., J. Organometallic Chem., 1964, 1, 244.
194. Andrianov, K.A. and Zhdanov, A.A., Bull. Acad. Sc. USSR. Eng., 1958, 756.
195. Ruidisch, I and Schmidt, M., J. Organometallic Chem., 1963, 2, 328.
196. Thies, C. and Kinsinger, J.B., Inorg. Chem., 1964, 3, 561.
197. Davies, A.G., Harrison, P.G. and Silk, T.A.G., Chem. and Ind., 1968, 949.
198. Kochkin, D.A., et al., Zh.Obshch Khim., 1963, 33, 1946.
199. Andrianov, K.A. et al., Chem. Abstr., 1957, 51, 3487.
200. Delman, A.D., et al., J. Polymer Sci., Pt.A-1, 1966, 4, 2307.
201. Cohen, H.J., J. Org. Chem., 1960, 25, 164.
202. Cohen, H.J., J. Organometallic Chem., 1967, 2, 177.
203. British Pat. No. 928,496 (1963). Chem. Abstr., 1963, 52, 11683.
204. Gilman, H., et al., "Advances in Organometallic Chemistry", Academic Press., 1966, 4, 1.
205. Mackay, K.M. and Watt, R., Organometallic Chem. Rev., A 1969, 4, 137.
206. Kraus, C.A. and Neal, A.M., J. Amer. Chem. Soc., 1929, 51, 2403.
207. Gilman, H. and Cartledge, F.A., J. Organometallic Chem., 1966, 5, 48.
208. Neumann, W.P. et al., Tetrahedron Letters, 1964, 3875.

209. Neumann, W.P. and Schneider, B., *Angew Chem.*, 1964, 76, 891.
210. Neumann, W.P., et al., *Annalen*, 1966, 692, 1.
211. Saville, B., *Angew Chem. Intern. Ed. Engl.*, 1967, 6, 928.
212. Neumann, W.P. et al., *Annalen.*, 1966, 694, 9.
213. Razuvaev, G.A., et al., *Organometallic Chem. Rev., Sec.A.* 1968, 3, 233.
214. Watt, G.W., *Chem. Rev.*, 1960, 46, 317.
215. Tamborski, C., et al., *J. Org. Chem.*, 1963, 28, 181, 237.
216. Gilman, H. and Rosenberg, S.D., *J. Amer. Chem. Soc.*, 1963, 75, 2607.
217. Tamborski, C. and Soloski, E.J., *J. Amer. Chem. Soc.*, 1961, 83, 3734.
218. Van der Kerk, G.J.M., et al., *Chem. Comm.*, 1966, 914.
219. Eaborn, C. et al., *Chem. Comm.*, 1968, 1051.
220. Schumann, H. and Ronecker, S., *Z. Naturforsch.*, 1967, B22, 542.
221. Van der Kerk, G.J.M. and Willemsen, L.C., *J. Organometallic Chem.* 1964, 2, 260.
222. Creemers, H.M.J.C. et al., *J. Organometallic Chem.*, 1968, 15, 125.
223. Creemers, H.M.J.C. and Noltes, J.G., *J. Organometallic Chem.*, 1967, 7, 237.
224. Coutts, R.S.P. and Wailles, P.G., *Chem. Commun.*, 1968, 260.
225. Kingston, B.M. and Lappert, M.F., *Inorg. Nucl. Chem. Letters.*, 1968, 4, 371.
226. Fowles, G.W.A. et al., *J. Chem. Soc.*, 1964, 1389, 3026.
227. Schumann, H. et al., *Chem. Ber.*, 1966, 99, 2057.
228. Schumann, H. et al., *J. Organometallic Chem.*, 1967, 8, 105.
229. Razuvaev, G.A., et al., *J. Organometallic Chem.*, 1966, 6, 474.
230. Schumann, H., Thom K.F. and Schmidt, M., *J. Organometallic Chem.* 1964, 2, 361.
231. Breitschaft, S. and Basolo, F., *J. Amer. Chem. Soc.*, 1966, 88, 2702.
232. Patil, H.R.A. and Graham, W.A.G., *Inorg. Chem.*, 1966, 5, 1401.

233. Lappert, M.F. et al., *Inorg. Nucl. Chem. Letters*, 1968, 1, 366.
234. Nesmeyanov, A.N. et al., *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1967, 1396.
235. Nesmeyanov, A.N. et al., *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1966, 1292.
236. Maxfield, P.L., *Inorg. Nucl. Chem. Letters*, 1970, 6, 707.
237. Travers, M.F., *J. Chem. Soc.*, (A) 1970, 3303.
238. Patmore, D.J. and Graham, W.A.G., *Inorg. Chem.*, 1966, 5, 2222.
239. Ibekwe, S.D. and Newlands, M.J., *Chem. Commun.*, 1966, 114.
240. Farbwerke Hoechst, A.G., *British Pat. No. 841,151*.
Chem. Abstr., 1960, 54, 26007.
241. Knowles, D.G., *Plastics Technol.*, 1960, 6, 35, 42.
242. Caldwell, J.R., *U.S. Pat. No. 2,720,507*. *Chem. Abstr.*, 1956,
50, 2206.
243. Horn, C.F. and Vineyard, H., *British Pat. No. 899,896*.
Chem. Abstr., 1962, 52, 11391.
244. Yngve, V., *U.S. Pat. No. 2,307,092*. *Chem. Abstr.*, 1943, 37, 3532.
245. Quattlebaum, W.M. and Hoffsinger, C.A., *U. S. Pat.*
No. 2,307,157. *Chem. Abstr.*, 1943, 37, 3533.
246. Mack, G.P., Parker, E., *U. S. Pat. No. 2,938,013*.
Chem. Abstr., 1960, 54, 20334.
247. *Tin and Its Uses.*, 1966, 67, 3.
248. Luijten, J.G.A. and Van der Kerk, G.J.M.,
'Investigations in the field of Organotin Chemistry',
Tin Research Institute, Greenford, 1966.
249. Van der Kerk, G.J.M. and Luijten, J.G.A., *J. Appl. Chem.*,
1954, 4, 314.
250. Van der Kerk, G.J.M. et al., *Chimica.*, 1962, 16, 36.
251. Luijten, J.G.A. and Van der Kerk, G.J.M., *J. Appl. Chem.*,
1961, 11, 35.
252. Noltes, J.G., Luijten, J.G.A. and Van der Kerk, G.J.M.,
J. Appl. Chem., 1961, 11, 38.
253. Zedler, R.J., 'Tin and its uses', 1961, 53, 7.
254. Hartel, K., *Angew. Chem.*, 1958, 70, 136.
255. Holmes, T.D. and Storey, I.F., *Plant Pathology*, 1962, 11, 139.

256. Tin and its uses, 1960, 50, 9.
257. Hof, T. and Luijten, J.G.A., 'Tin and its uses', 1964, 64, 5.
258. Richardson, B.A., 'Tin and its uses', 1964, 64, 5.
259. Melnikov, N.N., Ivanova, N.N., Russian Pat. No. 125325, Chem. Abstr., 1960, 54, 12372.
260. Ingham, R.K., Rosenberg, S.D. and Gilman, H., Chem. Rev., 1960, 60, 459.
261. Zavaglia, E.A., Mosher, W.A. and Billmeyer, F.W., Chem. Abstr., 1966, 63, 3054.
262. Belgian Pat. No. 645,019. Chem. Abstr., 1966, 63, 10142.
263. British Pat. No. 1,018,035. Chem. Abstr., 1966, 64, 12933.
264. U. S. Pat. No. 3,274,134. Chem. Abstr., 1967, 66, 3916.
265. Netherlands Pat. No. 6,609,502. Chem. Abstr., 1968, 68, 88279.
266. German Pat. No. 1,249,833. Chem. Abstr., 1967, 67, 100703.
267. Ross, A., Ann. N.Y. Acad. Sci., 1966, 125, 107.
268. Anand, L.C., Deshpande, A.B. and Kapur, S.L., Indian J. Chem., 1967, 5, 186.
269. Netherlands Patent No. 6,500,606. Chem. Abstr., 1966, 64, 5276.
270. Leznov, N.S. et al., Chem. Abstr., 1966, 62, 2875.
271. British Pat. No. 1,033,903. Chem. Abstr., 1966, 65, 10757.
272. German Pat. No. 36,060. Chem. Abstr., 1966, 63, 15066.
273. Netherlands Pat. No. 6,407,761. Chem. Abstr., 1966, 63, 10132.
274. Netherlands Pat. No. 6,516,388. Chem. Abstr., 1966, 65, 15613.
275. British Pat. No. 1,020,501. Chem. Abstr., 1966, 64, 19949.
276. British Pat. No. 1,041,851. Chem. Abstr., 1966, 65, 20337.
277. French Pat. No. 1,424,599. Chem. Abstr., 1966, 65, 13928.
278. French Pat. No. 1,506,186. Chem. Abstr., 1968, 62, 106878.
279. Netherlands Pat. No. 6,612,421. Chem. Abstr., 1967, 67, 44618.
280. Netherlands Pat. No. 6,516,388. Chem. Abstr., 1966, 65, 15613.
281. French Pat. No. 1,357,974. Chem. Abstr., 1966, 62, 7943.
282. French Pat. No. 1,364,456. Chem. Abstr., 1965, 62, 6632.

283. Czech. Pat. No. 125,310. Chem. Abstr., 1968, 62, 67906.
284. U. S. Pat. No. 3,397,969. Chem. Abstr., 1968, 62, 79047.
285. Netherlands Pat. No. 6,413,376. Chem. Abstr., 1966, 64, 420.
286. Yamamoto, A. and Kambara, S., J. Amer. Chem. Soc., 1957, 79, 4344.
287. Rust, J.B. and Takimoto, H.H., J. Org. Chem., 1961, 26, 2467.
and
288. Puri, D.M. / Mehrotra, R.C., J. Indian Chem. Soc., 1962, 39, 499.
289. Ishino, T. and Minami, S., Chem. Abstr., 1959, 53, 962.
290. Puri, D.M. and Mehrotra, R.C., J. Less Common Metals, 1961, 3, 247.
291. Varma, I.D. and Mehrotra, R.C., *ibid.*, 1961, 3, 321.
292. Yamamoto, A. and Kambara, S., J. Inorg. Nucl. Chem., 1961, 21, 58.
293. Dilthey, W., Ann. Phys. Lpz., 1906, 314, 300.
294. Rosenheim, A., Ber., 1903, 36, 1883.
295. Pande, K.C. and Mehrotra, R.C., Chem. and Ind., 1958, 1198.
296. Lutschinsky, G.P., Z. anorg. Chem., 1936, 225, 321.
297. Lutschinsky, G.P., J. Gen. Chem., Moscow. 1937, 7, 2045.
298. Cox, M., Lewis, J. and Nyholm, R.S., J. Chem. Soc., 1964, 6113.
299. Gopinathan, C. and Gupta, J., Indian J. Chem., 1965, 3, 231.
300. Gopinathan, C. and Gupta, J., Indian J. Chem., 1966, 4, 374, 375.
301. Bradley, D.C. and Holloway, C.E., J. Chem. Soc., (A), 1969, 282.
302. Fay, R.C. and Lowry, R.N., Inorg. Chem., 1970, 9, 2048.
303. Fraser, M.J. et al., J. Chem. Soc., (A) 1969, 2133.
304. Bradley, D.C., Gaze, R. ^{and} Wardlaw, W., J. Chem. Soc., 1955, 721.
305. Bradley, D.C., Gaze, R. and Wardlaw, W., J. Chem. Soc., 1967, 469.
306. Nesmeyanov, A.N., Friedlina, R.K. and Nogiva, O.V., Dokl. Akad. Nauk. SSSR., 1964, 95, 813.
Chem. Abstr., 1964, 48, 9254.
307. Nesmeyanov, A.N., Nogiva, O.V. and Dubovitskii, V.A., Izvest. Akad. Nauk. SSSR. Otdel. Khim. Nauk., 1961, 437.
Chem. Abstr., 1961, 55, 23312.

308. Beattie, I.R. and Fawcett, V., *J. Chem. Soc. (A)*, 1967, 1683.
309. Collis, R.E., *J. Chem. Soc. (A)*, 1969, 1895.
310. Babashinskaya, T.S. and Hocheshkov, K.A., *J. Gen. Chem. USSR*, 1938, 8, 1850. *Chem. Abstr.*, 1940, 1, 359.
311. U. S. Pat. No. 2,479,918 (1948).
312. Kijima, I., Asakawa, A., Katayama, M. and Kanisawa, H., *Kogyo Kagaku Zasshi.*, 1969, 72, 1353. (Translation through INSDOC, New Delhi).
313. Vogel, A.I., "A Text Book of Practical Organic Chemistry", Longmans, 1966, 284-288.
314. Wirth, H.O., Konigstein, O. and Kern, W., *Annalen*, 1960, 634, 102.
315. Bellamy, L.J., "Infrared Spectra of Complex Molecules", Methuen and Co., London, 1958, 146.
316. Rasmussen, R.S., et al., *J. Amer. Chem. Soc.*, 1949, 71, 1068.
317. Dictionary of Organic Compounds, Vol. II. Eyre and Spottiswoode, London, 1965, 902.
318. Greenwood, N.N., *J. Chem. Soc.*, 1960, 1130.
319. Hildebrand, J.H. and Carter, J.M., *J. Amer. Chem. Soc.*, 1932, 54, 3594.
320. Weissburger, A., "Technique of Organic Chemistry", Vol. 7, Organic Solvents. Interscience, New York, 2nd Edn. 1955.
321. Bellamy, L.J., "Infrared Spectra of Complex Molecules", Methuen and Co., London, 1958, 360.
322. Bellamy, L.J., in "Organic Sulphur Compounds", Vol. I, Pergamon Press, Oxford, 1961, 46.
323. Schroeter, L.C., "Sulphur dioxide", Pergamon Press, Oxford, 1966, 21.
324. Simon, A. and Knegsmann, H., *Z. Physik. Chem.*, 1956, 204, 369.
325. Byran, R.F. and Manning, A.R., *Chem. Commun.*, 1968, 1220.
326. Kitching, W., *Tetrahedron Letters*, 1966, 3689.
327. Kitching, W. and Kumar Das, V.G., *J. Organometallic Chem.*, 1967, 10, 59.
328. Katriitzky, A.R. and Ambler, A.P., "Physical Methods in Heterocyclic Chemistry", Vol. II. Academic Press, London, 1963, 201.

329. Neumann, W.P., "The Organic Chemistry of Tin", Interscience, London, 1967, 8.
330. Occolowits, J.L., Tetrahedron Letters, 1966, 6291.
331. Gielen, M. and Naskielski, J., Bull. Soc. Chim. Belges., 1968, 77, 5.
332. Wirth, H.O., Korigstein, O. and Kern, W., Annalen, 1960, 634, 102.
333. Cox, M., Lewis, J. and Nyholm, R.S., J. Chem. Soc., 1966, 2840.
334. Cohen, H.J., J. Org. Chem., 1960, 25, 154.
335. Gopinathan, C. and Gupta, J., Indian J. Chem., 1965, 3, 470.
336. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Edition. Wiley-Interscience, 1970, 89.
337. Nyholm, R.S., et al., Pure and Applied Chemistry, 1971, 22, 127.
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