

**STUDIES ON SOME ORGANOTIN ARYLOXY
ACETATES : SYNTHESIS OF POTENTIAL
HEPTA CO-ORDINATED TRIORGANOTIN
CARBOXYLATES.**

Thesis
Submitted for the Degree of Doctor of
Philosophy (Science)
of the
University of North Bengal



by
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TO THE MEMORI OF LATE MR. RAJIB ROY
DHAKA, BANGLADESH.

ACKNOWLEDGEMENT

The present work embodies results of research carried out by me at the Department of Chemistry, North Bengal University, West Bengal, India.

At the first opportunity I would like to express my most sincere gratitude and profound thanks to Mr. S. Majee, Reader in Chemistry, North Bengal University, for his guidance, active supervision and keen interest throughout the research programme.

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I do also cheerfully remember the valuable inspiration I received from my beloved Mr. Madhusaita Maitra.

(II)

Lastly, I would like to thank my colleagues, the Scientific Officer, Electro-Instrumentation Officer and all other well wishers.

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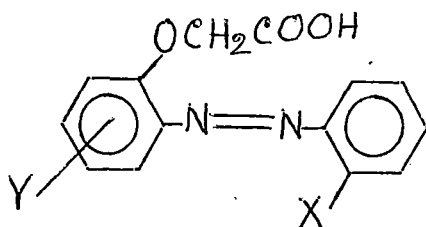
R E P E R A C E

The Lewis acidity or the acceptor strength of the tin atom in organotin compounds depends on the number of organic groups attached to the tin atom. The acceptor strength decreases in the sequence $\text{SnX}_4 \gg \text{R}_3\text{SnX}_3 \gg \text{R}_2\text{SnX}_2 \gg \text{RSnX} \gg \text{R}_4\text{Sn}$ ($X = \text{electronegative substituent}$). Thus, tetra organotin compounds hardly form any molecular complexes, the triorganotin compounds generally form 5 co-ordinate complexes; 6-co-ordination is more common with diorgano or mono organo tin compounds and even examples of 7 coordinate complexes are well known in the later case.

Although triorganotin compounds generally form 5-co-ordinate complexes, a number of 6-co-ordinate chelates using (aryloxo)benzoates as ligands have been recently prepared. Though a few potentially 7 co-ordinate addition complex of the type $\text{R}_3\text{SnX} \cdot \text{L}$ ($R = \text{Ph or Me}$; $X = \text{Cl or HCl}$; $L = 3\text{-[2-(1,10-phenanthrolyl)]-5,6-dimethyl-1,2,4-triazine}$ and $3\text{-[2-(1,10-phenanthrolyl)]-5,6-diphenyl-1,2,4-triazine}$) have been reported, example of 7 co-ordinate chelates of triorganotin derivative of the R_3SnL ($L = \text{tetradentate ligand}$) has been hitherto unknown.

(IV)

The rather low acceptor strength of the tin atom attached to three organic group disfavors formation 7-co-ordinated chelates unless of course, a sterically favourable environment is created with suitably designed ligand. The case with which 6-co-ordinated triorganotin chelates of O-(2-hydroxy benzene azo)benzoic acid were prepared in this laboratory, led us to believe that I would be a good tetradentate ligand for our purpose.

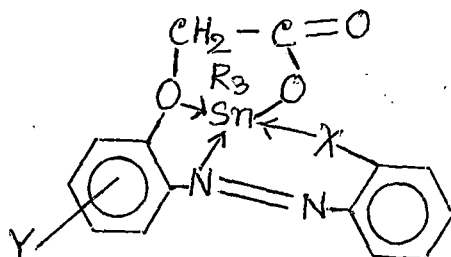


X = OH, F, Cl etc.

I

With appropriate choice of the diazo and coupling components such ligands could be synthesized without great difficulty. Esterification of the carboxyl group by triorganotinanyl group may then be expected to lead to the desired chelates (II) under favourable conditions.

(V)



II

The present thesis describes the results of our studies aimed at synthesizing hitherto unknown 7-co-ordinate triorganotin chelates.

The thesis is divided into four chapters. The first and second chapters provide the back ground material with a review of organotin chemistry in general and organotin complexes and carboxylates in particular.

Synthetic procedure, analytical data and infrared spectra are discussed in chapter III while the electronic absorption spectra are discussed in the last chapter where evidence in favour of 7-co-ordinate complex of type (II) are presented.

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CHAPTER - I

A SHORT HISTORY OF ORGANIZED CRIMINALITY

1A. Introduction

Organotin compounds are those which contain at least one tin-carbon bond. The first chemist to report an organotin compound seems to have been G. Frankland (1,2). But his work appears to remain unknown to most of his contemporaries as well as to later authors. The work of G. Lewis (3) in 1832 has usually been considered to represent the beginning of organotin chemistry. Apart from the compounds described by Lewis, many significant contributions were made in this field during the next few decades.

The vast majority of organotin compounds fall within the four classes:



R can be identical or different, substituted or unsubstituted, aliphatic or aromatic groups. X can be negative groups such as $-OR$, $-SR$, $-OOR$, $-OSnR_3$, $-NR_2$ or halogen or some other acid radicals or neutral ligands such as $-H$ or electropositive one such as Li or Ba . The three series of organotin hydrides R_3SnH , R_2SnH_2 , $RSnH_3$ have recently assumed considerable importance (4-7). The acceptor strength of the organotin compounds generally follows the sequence: $R_3SnH < R_2SnH_2 < RSnH_3$.

Stannyl metal compounds of the type R_2SnH_2 , R_2SnH_2 (3-9), Ph_3Sn or Ph_3 , Ph_3Sn or $Si(OC_2H_5)_3$, $R_3Sn-SnR_3$ (2), Hg_2 or $Hg-SnR_3$, $R_3Sn-Hg-SnR_3$, ⁹⁷ (4) Ph_3Sn or Sn or Ph_3 , Ph_3Sn or Sn or Ph_3 , are also known where R may be aliphatic or aromatic, R may be Li, Na or K.

The discovery of industrial applications of organotin compounds as stabilizers of polyvinyl chloride plastic, rubber antioxidants, Ziegler type catalysts in the polymerization of olefins, food preservatives, agricultural fungicides and as active ingredients in certain veterinary medicine (10) and also an increased general scientific interest produced or striking renaissance of organotin chemistry starting about 1943 and continuing to the present day.

1B. Bonding in organotin compounds

The electronic configuration of tin atom is:



the ground state being $3P$ state derived from $5p^2$ configuration (II). The tetra covalent state is derived from the sp^3 hybridization by promoting one of the $5s$ electrons to the $5p$ level. A large number of organotin compounds consist of tetravalent tin atom because of its much more frequent occurrence than the divalent atom. The metals of group IV A

form organometallic compounds which are more stable and less reactive than those of Gr. III or IV B metals. The increased stability may be partly due to sp^3 hybridisation. Thus, tetra-valent tin is unreactive towards air and water but Hg_2In and Hg_2Sb have a strong affinity towards these reagents. The significant increase in stabilities of R_4Sn compounds over R_3Sn types also show the effect of increased hybridisation on the stability. Metal-carbon bond strengths have been reviewed by Skinner (12) who observed that mean bond dissociation energies ($\bar{D}$) fall as the sub group is descended so that $\bar{D}(C-R) > \bar{D}(Si-R) > \bar{D}(Ge-R) > \bar{D}(Sn-R) > \bar{D}(Pb-R)$. The mean values of the bond dissociation energies are C-C: 87, C-H: 70, C-O: 60, C-Sn: 50, C-Pb: 31.37 kcal/mole. Moreover, these values are dependent on the nature of the alkyl group i.e. on the stabilisation of the corresponding alkyl radical by hyperconjugation etc.

The tin atom has covalent radius of $1.4A^0$ and is independent of the nature of the ligands. There is some sort of decrease in bond lengths only when strongly negative ligands are accumulated around the tin. The bonding of the tin would thus appear to be almost entirely covalent at least in crystalline solids, in the vapour and in non polar media. However, the electronegativity of tin being less than most of the common ligands, e.g., carbon, nitrogen, oxygen, halogen

and even hydrogen, the bonds are expected to be sufficiently polar in the sense δ^+ δ^- and dipole moments of various Sn-A bonds have also been estimated. The dipole moment of the alkyl tin bond, recently estimated as 0.45-0.6D (13-15) depends both in direction and magnitude on the nature of the alkyl group (16-17).

The electronegativities of Gr. IV elements have been investigated by several workers (20a-d). The results always vary in accordance with the method of measurement and the compounds selected. It is not surprising since the electronegativity, not being a uniquely defined parameter, depends on the method of measurement and the environment of the atom in question. In fact, one always works not with an electronegativity of tin, but with a value for tin in a particular combination and allowances will have to be made for the influence of all ligands.

Table - 1

Electronegativities of Gr IVB elements

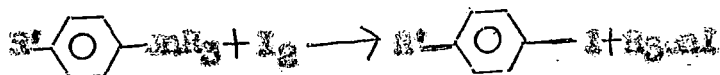
	Pauling	Anderson	Fineman Dalgault	Allred-Rochow
Ge	2.5	2.47	2.57	2.60
Si	1.8	1.74	1.80	1.80
Ge	1.8	2.31	2.02	2.00

Contd..

Table - 1 (Contd..)

	Pauling	Sanderson	Pinnau Painault	Allred-Rochow
Sn	1.8	2.02	2.47	1.03
Pb	1.8	—	—	2.45

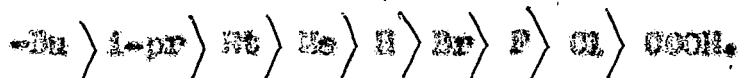
Closely related with this is the inductive effect which the tin atoms or stannyl groups exert on their surroundings. The bond polarisation $\overset{-\delta}{C} - \overset{+\delta}{Sn}$, which is there in principle, may be changed by substitution at C as well as at Sn. All data on organotin compounds (18-19) and semiempirical calculations of Majee and Gupta (50) emphasise this. According to Saborn et al (21), polarisation is increased by electron donor substituents R' in the p-position in a phenyl group, as demonstrated by the increase in the rate of cleavage of C-Sn bond by iodine according to the reaction (A). Thus, this reaction may be marked as electrophilic aromatic substitution.



(A)

The electron attracting groups R' diminish the rate by lowering the nucleophilicity of the ring carbon attached to tin.

The sequence of relative reaction rates is for R' = OMe



Electron donor properties increase in the series (R = Me): $MeR_3 < EtR_3 < nPrR_3$, as may be seen from the relative rates of acidolysis of $p-R_3H \text{ CH}_2 \text{ CH}_2 - SnR_3$. These are: $H = 31$ 1.00, Me 1.36, Et 3.41 (22). A similar sequence emerges from IR and NMR measurements (23) and also from IR studies on esters of the type $MeCOOR_3$ (R = O, Me, Et) (24).

A problem which often arises in the investigations to measure relative inductive effects is that there may be some π -character in a bond between tin and an element possessing p-electrons (25-27). Thus in a $sn-X$ bond where X is O ($3p^2$), S, Se, or halogen, it is possible that, opposing the inductive electron drift $Sn \xrightarrow{+\delta} X \xleftarrow{-\delta}$, there may be some overlap between an empty 5d orbital on Sn and a filled p-orbital on X causing a transfer of electron density in the opposite direction.

In spite of many disputes (27-30) it is widely accepted that there are significant ($p\pi \rightarrow d\pi$) contributions to the $sn-X$ bonds in compounds such as the planar trialkyl amine (31). There is some evidence that in phenyl tin compounds, interaction occurs between the electrons of the phenyl groups and

the 5d orbitals of tin. This conclusion is based on the interpretation of NMR (32-33), IR (34), UV (34) and dipole moments (35) of Ph_3Sn compounds and the acid strengths of the substituted benzoic acids $p\text{-Me}_3\text{SnC}_6\text{H}_4\text{COOH}$ ($M = \text{O, Si, Ge, Sn}$). It can not be assumed that other aromatic groups behave similarly since the pK_a values for a series of pyridine having Me_3M ($M = \text{O, Si, Ge, Sn}$). Substituents in the 2-position indicated the absence of $p\pi - d\pi$ bonding in the tin-pyridine link (36). Calculation based upon nuclear quadrupole resonance measurements indicated π -character in the $\text{Sn}-\text{I}$ bonds of diethyl tin diiodide whereas it was concluded from the dipole moments of organotin chlorides that the $\text{Sn}-\text{Cl}$ bond order is close to unity (35). There is evidence for $d\pi - d\pi$ interaction in the bonds formed between tin and certain transition metals (37, 38). On the other hand Majee and Gupta has shown in a series of papers (50) that most of the properties of organotin compounds may be interpreted without assuming any $d\pi - p\pi$ interaction. However, in a more recent article Majee demonstrated that the success of earlier Del Es calculations does not necessarily rule out such interactions (90).

10. Organotin Complexes

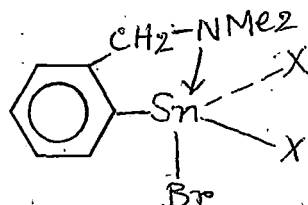
Organotin compounds can form various types of complexes with ligands. The structural aspect of these compounds

has been exhaustively reviewed by Ingham et al (8), Poller (39), Glöck and Sprecher (51) and more recently by Ho, Zuckerman (43), P.G. Harrison (33), Bulton (33), Koton (61), Poliansi (36).

The most interesting example is afforded by R_3SnX type compounds which form various type of adducts with Lewis bases (4). These compounds are generally penta co-ordinated (40-41). For $X = Cl, Br, I$, R_3SnX type are usually tetrahedral but for $X = ClO_4^-, F^-, SO_3^{2-}, BF_4^-, SO_3^-, AsF_6^-, OsO_4^-,$ the compounds are five co-ordinate about tin where the anions are probably either bridging or chelate type (43, 93). R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents, viz. 8-hydroxy quinoline (45,46,94), acetyl acetone (47,48), 1,10 phenanthroline (49,50) etc, which may be five, six or sometimes even eight co-ordinated compounds.

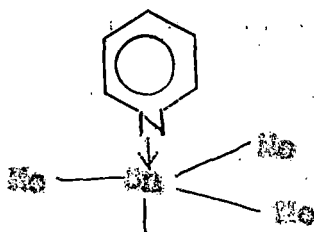
β -substituted salicylidineimine trialkyltin derivatives have been prepared by the reaction of the trialkyltin chloride or alkoxides with the corresponding Schiff (52) bases and β co-ordination is proposed for Sn in these complexes. Trimethyl tin derivative of sulphur containing Schiff bases are known (53). Several triorganotin dithiocarbonates of the formula $R_3Sn S_2C(OR)_2$ ($R = Ph, n-Bu, Et$, etc $= n-Pr, n-Bu, 2$ -phenyl, dibenzyl etc. - dithiocarbonates) have been reported by Brivastava (54). The quarternary phosphonium cations $[\geq PCH_2 Sn Me_3]^+$ is also known (55).

Recently a nitrate complex of organotin (IV) containing triphenyl phosphine oxide has been reported (56). The tri-organotin halides which contain potentially bidentate ligand the $\text{Me}_3\text{P}(\text{OR})_2$ group is reported. In view of the known tendency of triorganotin halides to form 1:1 complexes with Lewis bases, for novel triorganotin compounds, the trigonal bipyramidal structure I in which the tin atom is penta co-ordinate as a result of intramolecular Sn-1 bond formation.

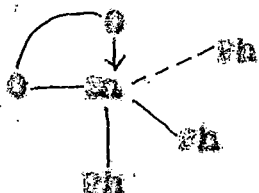


I

A well known example is the penta co-ordinated str. of 1:1 complex of trimethyl tin chloride with pyridine.

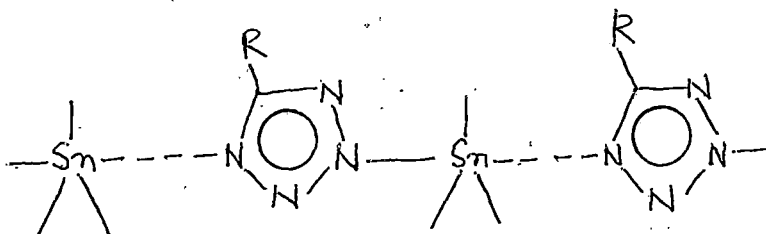


An X-ray study was reported for (1,3-diphenyl propane-1,3-dionato) triphenyl tin which established the occurrence of penta co-ordination as a result of intramolecular co-ordination with the ligand spanning axial-equatorial sets (37).



O-O = 1,3-diphenylpropane -1,3-dionato

The intermolecular associated form of 2-(tri-n-butyl stannyl) tetrazoles in benzene and chloroform is confirmed as a 1,3 structure (38).

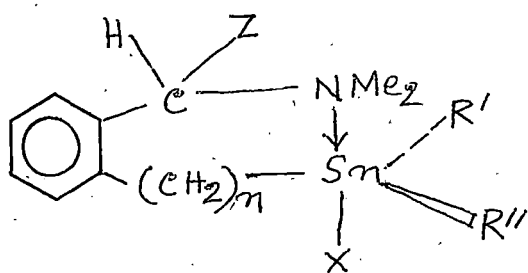


Nine n-substituted 4-(triphenyl stannyl) cyanamides have been reported and the tin in these complexes is shown to have a co-ordination no. 6 by means of IR and Mossbauer spectroscopy (39). The Mossbauer parameters of n-substituted 4-(triphenyl stannyl) cyanamides are given in Table 2.

Table - 2

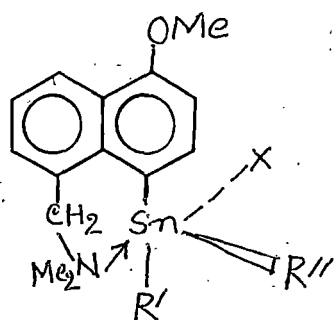
Compound	δ	ΔE	$\Delta E/\delta$
$\text{CH}_3\text{O}(\text{OO})(\text{CH})\text{SnPh}_3$	1.07	4.54	4.24
$\text{CH}_3\text{OO}(\text{O})(\text{CH})\text{SnPh}_3$	1.55	4.23	2.73
$\text{PhSO}_2(\text{CH})\text{SnPh}_3$	1.07	4.54	4.24
$\text{HCO}(\text{O})(\text{CH})\text{SnPh}_3$	1.55	4.23	2.73

A compound of the formula $[\text{Sn}^{\text{II}}(\text{SO}_2)[(\text{C}_6\text{H}_5)_3\text{Sn}^{\text{IV}}]]$ containing a $\text{Sn}^{\text{IV}} - \text{Sn}^{\text{II}}$ bond, has been reported. The environment of $\text{Sn}(\text{IV})$ is tetrahedral. The tin(II) atom is five coordinate by the Ph_3Sn moiety via tin and by four oxygen atoms from two adjacent nitro groups (OO). The synthesis and characterization of triorganotin compounds $\text{RR}'\text{R}''\text{Sn}$ in which one of the organic group (R) is a potentially bidentate ligand, has been reported.

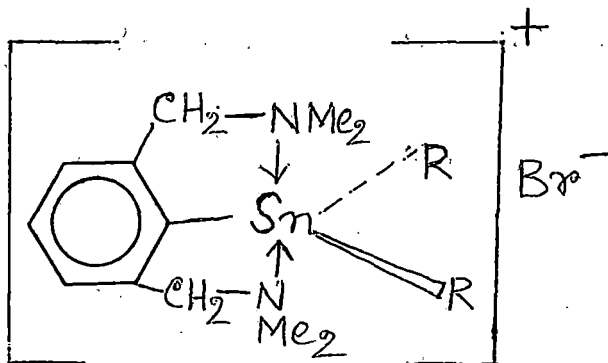


$Z = H \text{ or } Me ; n = 0 \text{ or } 1.$

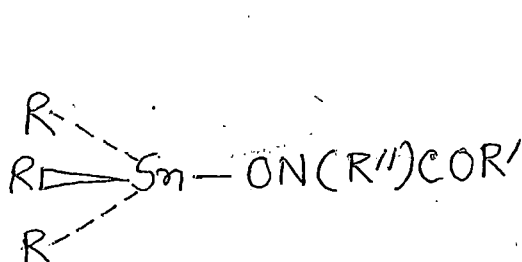
$R' \text{ and } R'' = Me \text{ and } Ph.$



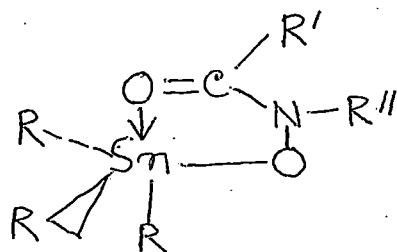
Preferential intramolecular co-ordination of the built-in ligand, $O(E) NMe_2$ with the tin atom which renders the tin atom 6 co-ordinate, appears to be a common structural feature of these compounds. 2,6-bis [dimethyl amino/methyl] phenyl group could act as a tetradentate ligand in triorganotin halides. The existence of penta co-ordinated catalytic species has also been investigated (61).



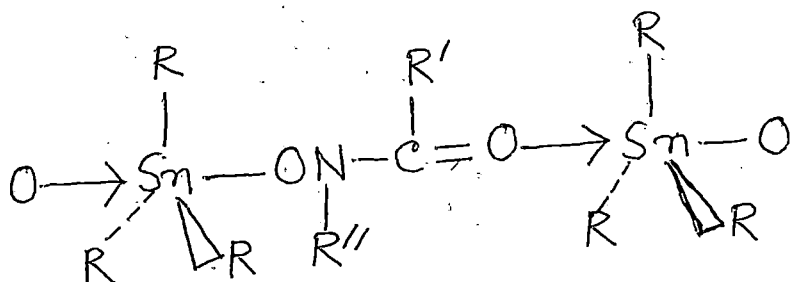
The first example of a compound containing organotin (II) and organotin (IV) in one molecule, $(\text{Me}_3\text{Sn}^{\text{IV}} \text{C}_6\text{H}_5)_2\text{Sn}^{\text{II}}$ has been reported recently (62). The triorganotin derivatives of *N*-acylhydroxyl amine, e.g. $\text{Me}_3\text{Sn} \left[\text{ON}(\text{Ph})\text{SO}_2\text{C}_6\text{H}_4\text{OH}_2 \right]$, $(\text{CH}_3)_3\text{Sn} \left[\text{ON}(\text{Ph})\text{CO}_2\text{Ph} \right]$, $\text{Me}_3\text{Sn} \left[\text{ON}(\text{Me})\text{SO}_2\text{Me} \right]$ have been prepared. The presence of a second donor site in the *N*-acylhydroxyl amine ligand permits its potential function as a unidentate or a chelating or a bidentate ligand; thus giving rise to the possible four co-ordinated structures (I) or the two 5-co-ordinated structures III and IV (63)



II

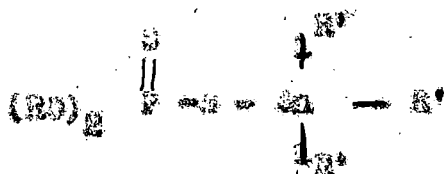


III

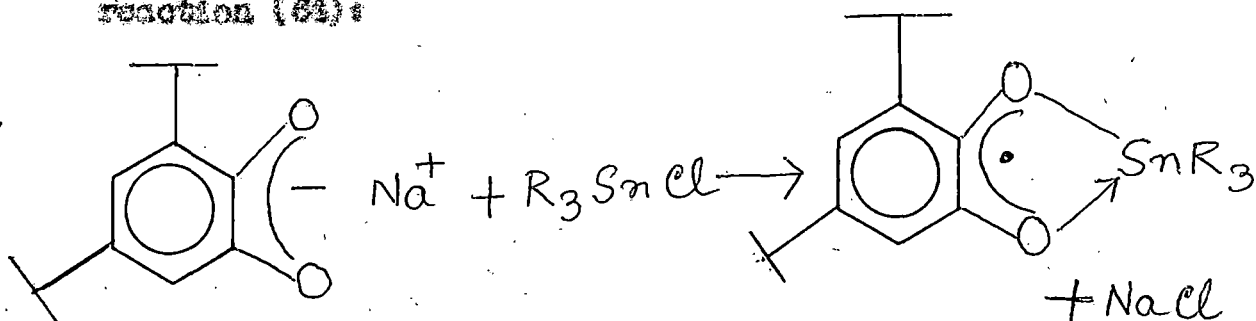


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Triorganotin dialkyl thiophosphates, $(RO)_2P(-S)SnR'_3$ ($R = Et, i-Pr, n-Pr$ or Ph and $R' = Me, Et, Bu$ or Ph) have been prepared (33). An ester type structure has been proposed for these compounds.



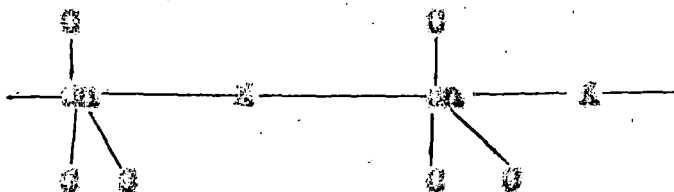
The initial ESR spectra observe for the reactions of O-quinones with R_3SnHCl are analogous to the signals of tin containing semiquinones formed according to the reaction (34):



R_3SnCl forms 1/1, 5-co-ordinate adducts with pyridine or 4-methyl pyridine and R_3SnSO_3 forms adducts with 1,10-phenanthroline (co-ordination no. of tin > 5). $\alpha, \beta, \gamma, \delta$ -

tetramethyl 1,2-diamino-ethane gave either 1/1 adducts or 5-co-ordinated 1/2 adducts depending upon the group R and concentration of H_2SO_4 (65). A molecular adduct of nitratophenyl tin with pyridine N-oxide, $[Sn(C_6H_5)_3(NO_3)(C_5H_5NO)]$ has been synthesized and characterized by IR and X-ray analysis (66). Moreover, a molecular adduct of nitratophenyl tin with triphenyl arsenic oxide $[Sn(C_6H_5)_3(NO_3)(C_6H_5)_3AsO]$ has been synthesized. The co-ordination about tin is bipyramidal with phenyl ring in the equatorial and oxygenated ligands in the axial positions (67).

The most general feature of the penta co-ordinated tin is a polymeric str. formed by the bridging of an anionic group to the tin atom from either side of the plane of the trialkyl tin group. This kind of structure is designated as type V.



Type V

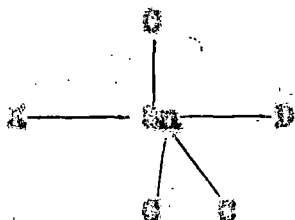
In compounds of str. type VI a donor molecule is co-ordinated to a triorganotin halide to give a trigonal bipyramidal arrangement. The best studied example is the

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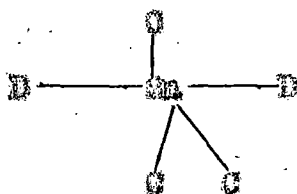
1:1 addition compounds $(\text{CH}_3)_3\text{SnI}$ and pyridine.



(D = donor molecule)

Type VI

In cases where the anionic groups have no co-ordinating sites e.g., $\text{B}(\text{C}_6\text{H}_5)_4^-$, two molecules of a mono-anionic Lewis base viz., water can occupy the co-ordination sphere, giving a planar SnO_2 arrangement with a penta co-ordinated tin atom (Type VII)



Type VII

This finding may well be applied to interpret the str. of 1:3 addition compounds of formula $\text{H}_3\text{SnI} \cdot 3\text{D}$ (3) as that containing a bipyranidial $\left[\text{H}_3\text{SnO}_2 \right]$ and I^- anion, and may preclude the existence of 6-co-ordinated tin atoms in such triorganotin complexes (4).

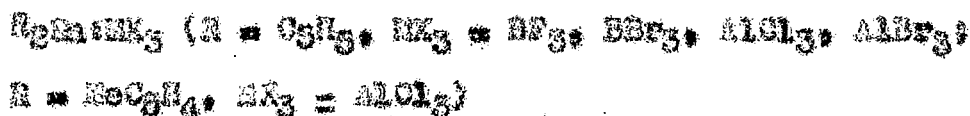
If the X group in R_3SnX belongs to a chelating ligand, intramolecular co-ordination can occur as shown in the structure (VIII).



Type VIII

In contrast to penta co-ordinate triorganotin compounds, examples of 6-coordinate triorganotin compounds are very few. Recently a number of 6-(6'-substituted aryl and) benzenes of triorganotin compounds have been synthesised (96). Spectral and other studies indicate these to 6-coordinated triorganotin group.

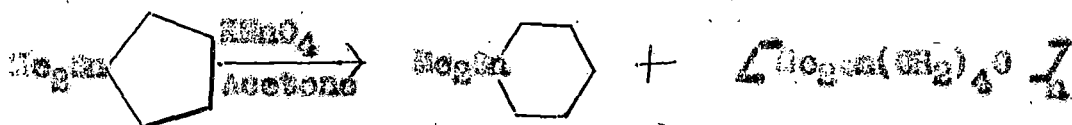
The reaction of dicyclopenta -diethyl tin and bis (methyl cyclo-pentadienyl) tin with some boron, aluminium trihalides give complexes of the composition $(\frac{2}{2})^{68}$:



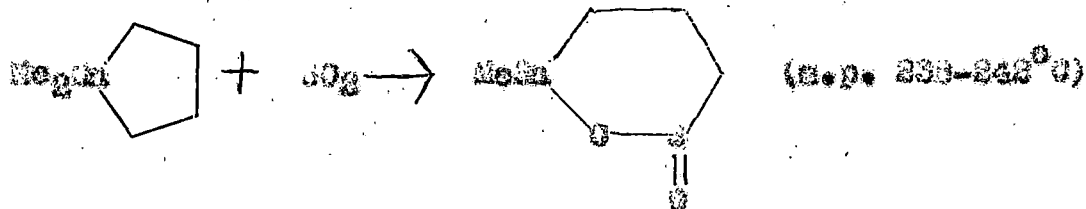
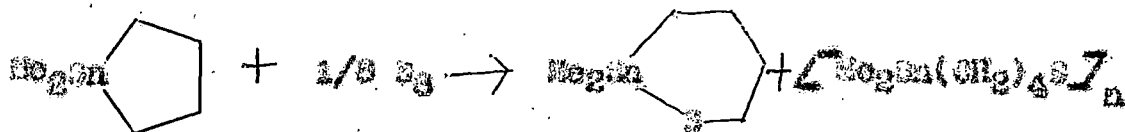
The addition of dicyclopentadienyl tin to THF solutions of the complexes $M(CO)_5$ THF ($M = Cr, Mo, W$) produces complexes $(\frac{2}{2})^{69}$: $R_2Sn : M(CO)_5$, where $R = C_5H_5$ $M = Cr, Mo, W$; $R = MeC_5H_4$, $M = Cr, W$. The evidence for Cis-Bis (2,4-

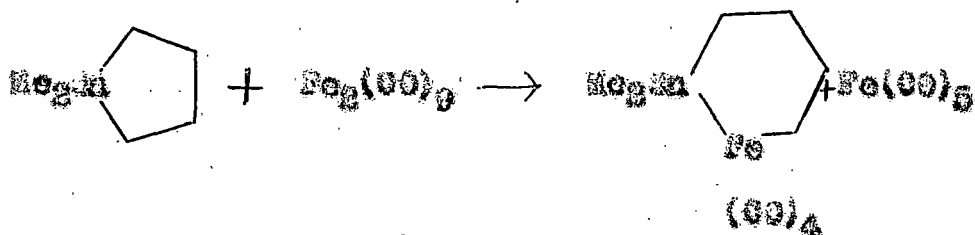
pentanedionate) dimethyl tin (IV) has been found in solution (70).

As a result of the enhanced reactivity of the endocyclic tin-carbon bond, 1,1, dimethyl-1-stannacyclopentane (DMSC-5) readily undergoes ring expansion reactions with a variety of substrates to produce new organotin heterocycles. A few examples given include ring expansion reactions with O_2 , SO_2 , SO_2 , SO_2 (71).



Reaction of DMSC-5 with sulphur at 200°C proceeds to give the monomeric ring expansion product.



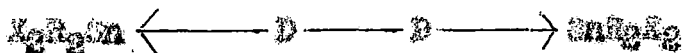


In case of diorganotin derivatives, both penta co-ordinated and hexa co-ordinated tin compounds have been reported. Penta co-ordinated tin is observed in dialkyl tin dihalides, carbonylates, dialkyl tin halide oxides and dimethyl (1,3- dimethyl triazono) tin halides (72) Type (IX)



Type IX

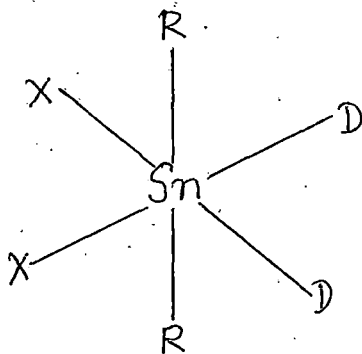
The 2:1 addition compound of $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{NCO})_2$ and bipyridine is another type of penta co-ordinated di-organotin structure A.



Type K

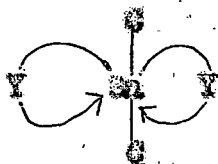
Infrared spectroscopic investigations have shown that the addition compounds of R_2SnX_2 (X a halogen) and monodentate

amines in 1:2 mole ratio or bidentate amines in 1:1 mole ratio are of the type XI.



Type XI

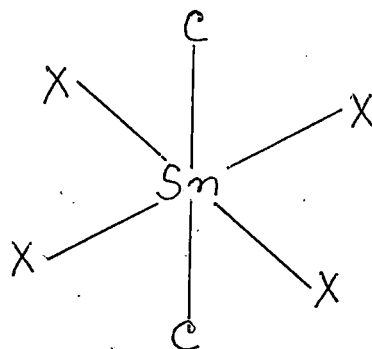
Many di-organotin bis(cholates) have been isolated (49,72,73,94) and found to contain hexa co-ordinated tin atom. Some representative compounds are acetyl acetonates, oxinates and carboxylates. The alkyl group in these compounds exists predominantly in the trans position (Type XII).



Type XII

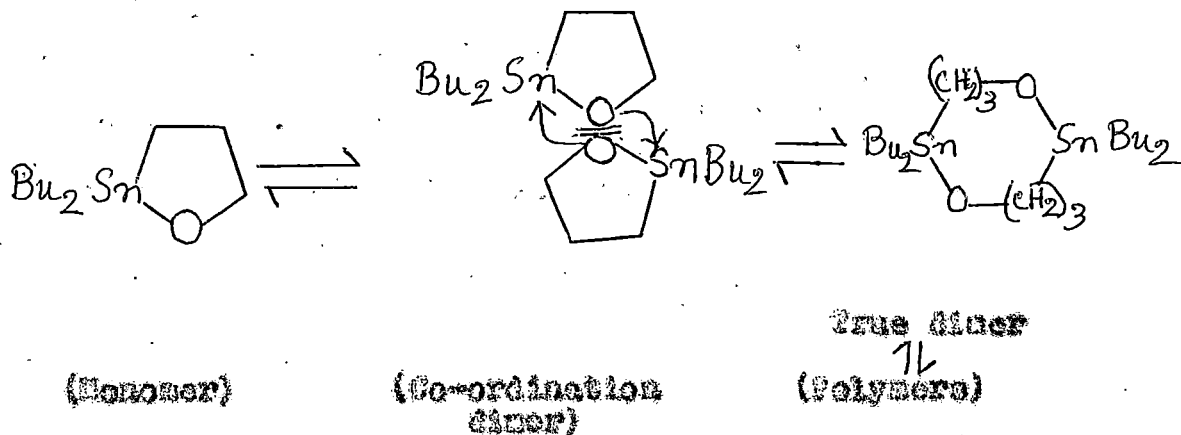
For diorganotin dioxinates such a conventional octahedral structure is however, far from correct as X-ray investigation of dimethyl tin dioxinate shows this molecule to be some what like a highly disturbed tetrahedron (91).

The most symmetric species is the $(CH_3)_2SnX_4^{-2}$ anion ($X = F, Cl, Br, I, S \equiv$) where the structure is represented by XIII. Tobias et al have shown that there are analogous species $[(CH_3)_2Sn(OH)_4]^{2-}$ as well as cationic hydrated species in aqueous solution of diethyl tin compounds (74, 75, 76).



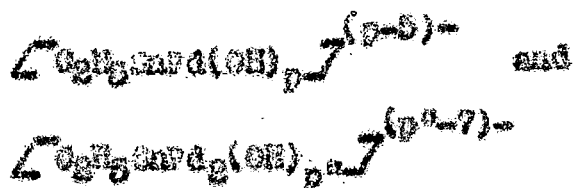
Type XIII

An analysis of IR spectra in the $1800-300\text{ cm}^{-1}$ of the compounds of the type $n\text{-Bu}_2\text{Sn} \text{---} CH_2 \text{---} CH \text{---} R^1CH^2 \text{---} O$ ($R^1 = R^2 = H$ or Me) allow us to distinguish between monomers, co-ordination dimers with large cycles or polymers (79).

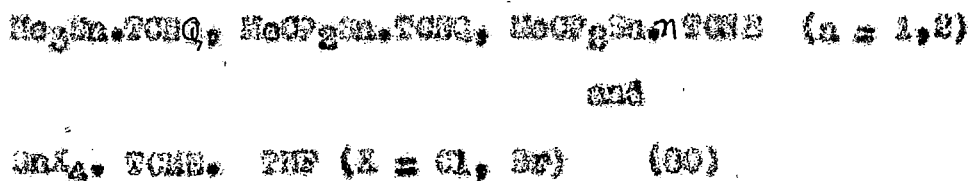


Reports on mono-organotin compounds indicate that some of these might have hexa co-ordinated and even hepta co-ordinated tin atoms. However, little work has been done on their detailed configurations. Mono-organotin halide bis acetyl acetonates (77) and bis oxinates (78) as well as the addition compounds of formula $RnSnX_2 \cdot 2D$ (79) are examples of 6-co-ordinated tin compounds.

In basic aqueous media the derivatives of ethyl tin (IV) and palladium (II) ions give two mono organotin complexes (81).



Recently organotin complexes of strong π -acids of the type



have been prepared (TCHQ = Tetracyano p-quinodimethane TCHC = tetracyano ethylene). From the detailed investigation, the complex $R_nSn \cdot TCHQ$ is best represented by the canonical

form $(H_3Sn)^+(SO_3O)^-$, and provides the first example of an isolable paramagnetic organotin complex.

III. 7-Coordinate Organotin Complexes

The mono-, di- and tri- organotin compounds generally exhibit a coordination number from 4-6. However, not many organotin compounds have been found to possess hepta co-ordinated tin, the geometry of which is expected to be pentagonal bipyramidal one. Phenyl tin tri-terephthalate has been reported (82) to be monomeric in methylene chloride, suggesting a seven co-ordination around the tin. Kawanishi et al (83) have concluded from UV, NMR and IR data that n-butyl tin tri-oxinate may have 7-coordinated tin atom. Riddick and Rees (84) from Raman^{sc} spectroscopy, determined the co-ordination number around tin in $BuSn(Ox)_3$ which is consistent with seven co-ordination, with three equivalent bidentate oxine groups. Anhydrous methyl tin triazotate crystallizes with three chelating azotate groups forming a pentagonal bipyramid about tin (85), Fig. XIV.

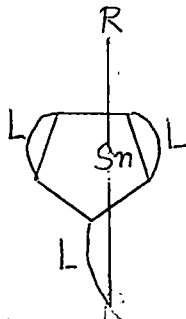


Fig. XIV

Tris(dimethyl sulphoxide) nitrate diphenyl-tin-nitrate has been characterised as a hepta co-ordinated organotin complex from IR and X-ray crystallography (66). The structure consists of monomeric hepta co-ordinated cation $\left[\text{Sn}(\text{C}_6\text{H}_5)_2\text{NO}_3 \left\{ (\text{CH}_3)_2\text{SO} \right\}_3 \right]^+$ and NO_3^- anion. Co-ordination around tin is pentagonal bipyramidal with the bidentate nitrate group and the three dimethyl sulphoxide molecules in the equatorial positions and the two phenyl ring at the apices.

The only example of a probable 7-co-ordinate triorgano-tin complex is provided by dimethyl di isothiocyanato (terpyridyl)-tin (IV), $\left[(\text{CH}_3)_2\text{Sn}(\text{SCN})_2(\text{C}_{10}\text{H}_8\text{N}_3)_3 \right]$, which contains two Sn-S bonds, has recently been shown to be 7-co-ordinate (67).

The scarcity of 7-co-ordinated triorganotin complexes are, understandable because of the very low Lewis acidity of the triorganotin atom attached to three carbon atoms. It is, however, possible to realise such complexes with suitable polydentate ligand where geometrical factors would favour such co-ordination. The present work will describe some examples of this type.

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CHAPTER - II

ORGANOTIN CARBOXYLATES

IIA. Introduction:

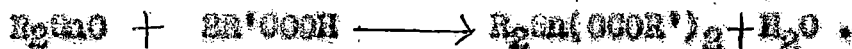
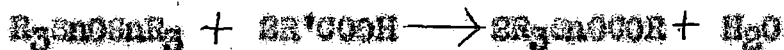
Organotin carboxylates comprise one of the most important class of interesting research in the field of compounds in organotin chemistry. Apart from the academic interests (theoretical and structural) organotin carboxylates are finding more and more industrial and agricultural applications.

The compounds containing $-OOCR$ groups bonded to tin which may be either monomeric or polymeric are of three general types viz., $R_3SnOOCR$, $R_2Sn(OOCR')_2$ and $Rn(OOCR')_3$ where R and R' may be same or different groups. Tin tetracarboxylates, $Sn(OOCR)_4$ are not organotin compounds in the rigid sense of the term, in spite of that they are sometimes included in the discussion of organotin carboxylates for the sake of comparison. A number of discussions with varying degree of details are available on these compounds (1-3) and as such only the more important aspects will be discussed here.

IIIB. Preparation:

A variety of methods have been applied for the preparation of organotin carboxylates. These are generally

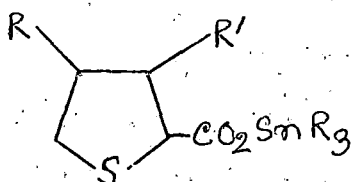
prepared by the reaction between organotin oxides and hydroxides and carboxylic acids or their anhydrides (74-81, 8,46).



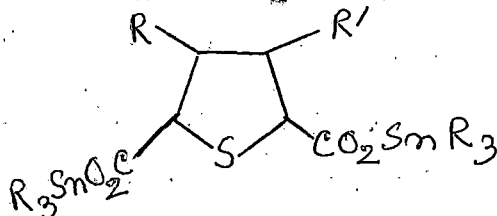
The water produced in these reactions is removed usually by azeotropic distillation or alternatively by refluxing at higher temperature (4).



Recently a number of their thiophene carboxylates (5) of the type I & II have been prepared from the thiophene carboxylic acids and R_3SnOH or $(R_3Sn)_2O$.



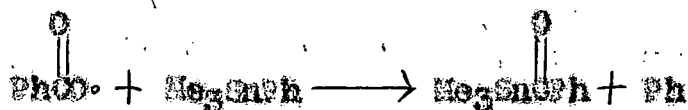
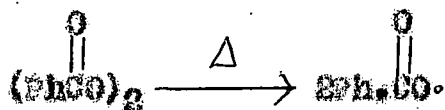
I



II

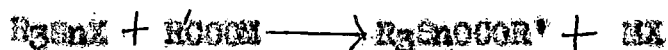
$R = Ph$; $R' = Bu, Me, Cyclo C_6H_{11}$ etc.

Triethyl tin benzoate has been prepared by the thermal decomposition of benzoyl peroxide in presence of triethylphenyl tin (6).



The triphenyl tin carboxylates $\text{Ph}_3\text{SnO}_2\text{OR}$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-MeOC}_6\text{F}_4$, $p\text{-EtOC}_6\text{H}_4$ or $o\text{-HO}_6\text{H}_4$), $p\text{-(Ph}_3\text{SnO}_2\text{O)}_2\text{C}_6\text{F}_4\cdot\text{H}_2\text{O}$ and $o\text{-(Ph}_3\text{SnO}_2\text{O)}_2\text{C}_6\text{F}_4\cdot\text{H}_2\text{O}$ have been prepared by the reaction of triphenyl tin hydroxide with the appropriate polyfluorocarboxylic acids in MeOH (7).

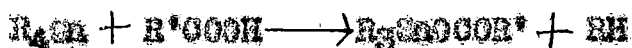
Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halides with the alkali metal or silver salts of carboxylic acids either by stirring the reactants in mixture of organic/aqueous medium at room temperature or by refluxing the mixture (8-11). This method represented as



$\text{R} = \text{Et}, \text{K}, \text{Hg}; \text{X} = \text{halogen}.$

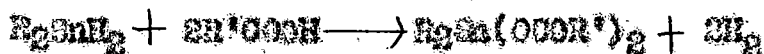
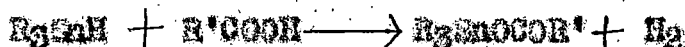
is generally used for its simplicity.

The ability of carboxylic acids to cleave M - C bonds is the basis of another method for the preparation of organotin carboxylates (12,13).



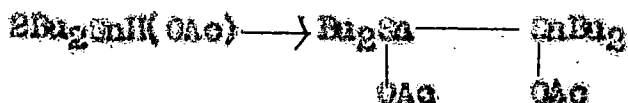
The cleavage of organic groups depends on the acid strength, nature of groups R and R' and also on the temperature (14-16). Vinyl groups are cleaved more rapidly than normal alkyl groups but less readily than phenyl groups. $Pb(CH_3COO)_2$ has also been used for acylation of R_3SnH , R_2SnH_2 , $R_3(Sn)_2$, R_4Sn and $(R_3Sn)_2O$ (17).

Organotin hydrides react with carboxylic acids resulting in the formation of carboxylates (35).

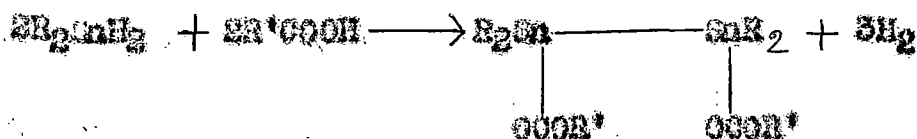


With di n-butyl tin dihydride, the intermediate hydride carboxylate decomposes to tetra-n-butyl 1,2, diacetate.

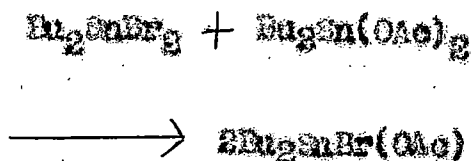




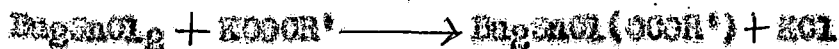
Similarly, 1,2 dicarboxylates have also been prepared (23-25).



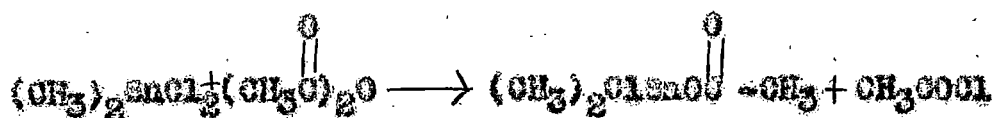
Halo carboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular mixture of the dihalide and the dicarboxylate in an inert solvent (18,19).



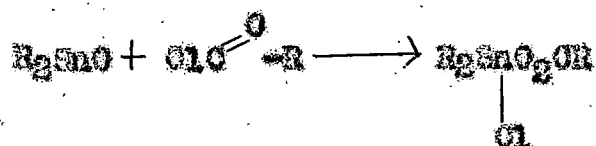
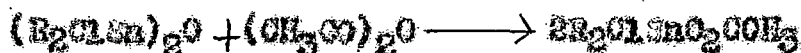
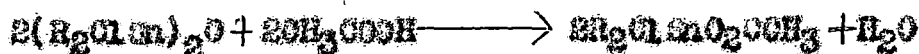
These compounds may also be synthesized by the reaction (20, 21).



(2) Dimethyl tin chloride acetate, has been prepared by Okamoto and Hoshino by the reaction of acetic anhydride on dimethyl tin dichloride.

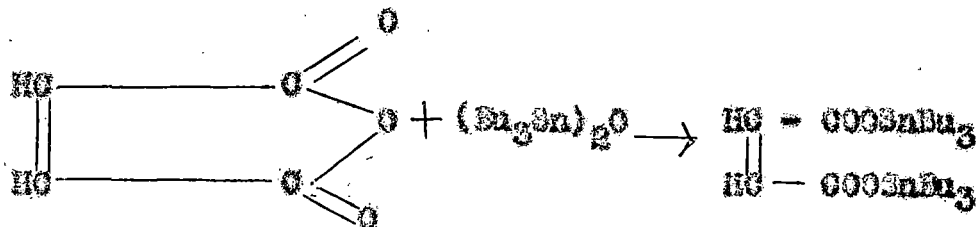


A number of dialkyl tin halide acetates have been prepared according to reactions (24):



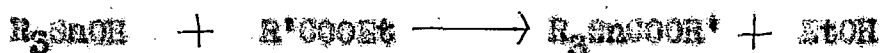
Thermodynamic data are reported 1/1 adducts of $\text{Ph}_2\text{Sn}(\text{OCOMe})_2$, $\text{Bu}_2\text{Sn}(\text{OCOMe})_2$ and $\text{Bu}_2\text{Sn}(\text{COOEt})_2$ with pyridine, 4-methylpyridine, HBu_3 , PBu_3 , $\text{H}, \text{H}, \text{H}', \text{H}'$ - Tetraethyl-1-2-diamino ethane and 1,10, phenanthroline have been reported (25).

Anhydride of an unsaturated acid (e.g., maleic anhydride) produces disubstituted organotin esters when reacted with hexabutyl distannoxane (23).



A novel method of preparation of trialkyl tin acetate by electrochemical method using R_3Sn ($R = Me, Et, Pr, Bu$) and $Hg(I)$, acetate have been described by Fogliavine et al (26).

Organotin carboxylates may also be prepared from carboxylates may also be prepared from carboxylic esters by the following reactions (26,27):



Tricarboxylate derivatives of the type $R_3Sn(COOR')_3$ are generally synthesized from the corresponding trichloride by the action of silver salts of carboxylic acids (28).

III. Physical properties of organotin carboxylates

The Sn-O bond in organotin carboxylates is essentially covalent but undergoes polar reactions depending on the solvents and the attacking groups. This is the reason for the higher solubility of the carboxylates with the small organic groups in alcohol, ether etc. than in water (29). Many of the carboxylates have low melting points indicating these to be covalent compounds.

The polymeric stannic acids are colourless, infusible, few of them are soluble in chloroform, carbon tetrachloride and reasonably stable to hydrolysis.

The physical properties of some representative carboxylates are given in Table I.

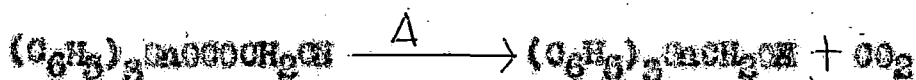
Table - 1

Compound	Type	B.P. (°C/mm)	M.P. (°C)
Trimethyl tin Acetate	$R_3SnOOCOR'$	—	196.5 - 197.5
Triphenyl tin formate	"	—	202 - 205
Tricyclohexyltin acetate	"	—	62 - 63
Tripropyl tin trifluoroacetate	"	88-90/1	—
Dibutyl tin diacetate	$R_2Sn(OCOR')_2$	142-146/10	—
Diphenyl tin diacetate	"	—	116 - 117
Diethyl chlorotin acetate	$R_2SnX(OCOR')$	—	94
Dibutyl bromotin acetate	"	—	67 - 68.5
Butyltin triacetate	$RSn(OCOR')_3$	117 - 119/1	—
Ethyltin Tribenzoate	"	171 - 173/1	—

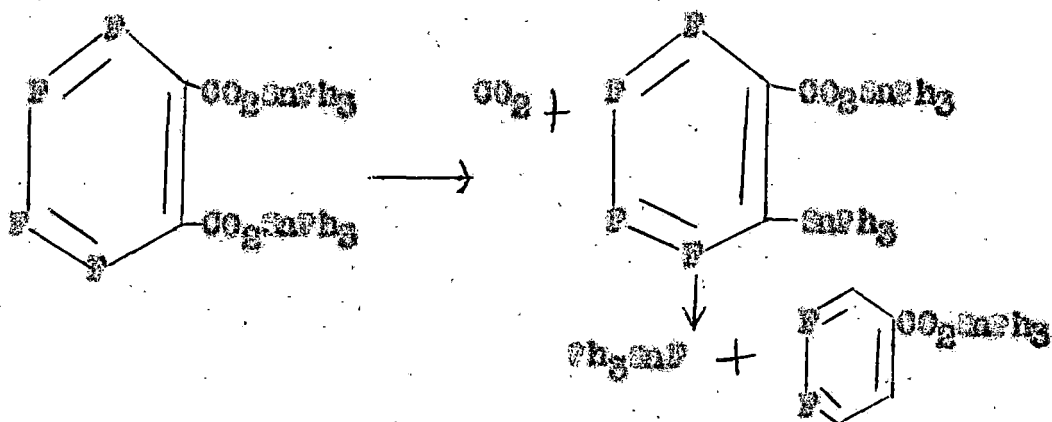
p-(Methylphenyl isopropyl stannyl) benzaldehyde has been prepared and resolved methyl carbazate in ethanol, $[\alpha]_D^{20} = 34.6^\circ$. Functional exchange with acetone of the less soluble diastereomer catalyzed by traces of p-toluenesulphonic acid yields the optically active aldehyde with $[\alpha]_D^{20} + 0.350$ (33).

III. Chemical properties of the organotin carboxylates

Decarboxylation and disproportionation reactions are the most interesting features of the organotin carboxylates. A cyanoethyl derivative is formed when triphenyl cyanoacetate is heated under vacuum (34).

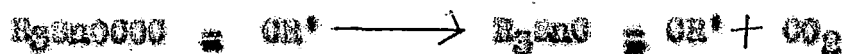


p-(Ph₃SnO₂C)₂C₆F₄ is readily decarboxylated to p-(Ph₃Sn)₂C₆F₄·Ph₃SnC₂OR (where R = p-CH₃OC₆F₄ or p-C₂H₅OC₆F₄) undergoes disproportionation reaction resulting in the formation of Ph₄Sn and Ph₂Sn(O₂OR)₂. Thermal decomposition of bis(triphenyltin) tetrafluorothalate give an insoluble high melting solid, Ph₃SnF.

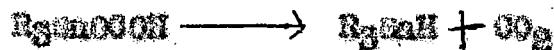


Thermal decomposition of $\text{Ph}_3\text{SnO}_2\text{C}_6\text{H}_3\text{F}_3$ in boiling pyridine give the corresponding polyfluorophenyl triphenyl tin Ph_3SnR (7).

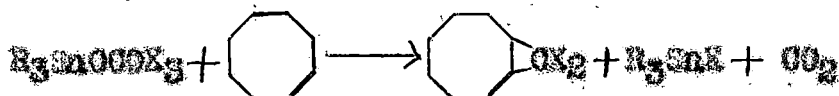
Trialkyl tin carboxylate of unsaturated acids gives tetrasubstituted organotin compounds after decarboxylation (36,37).



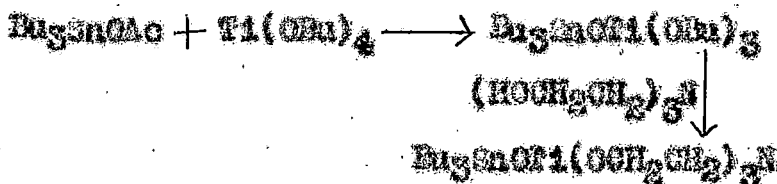
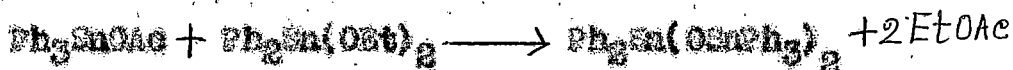
Thermal decomposition of triorganotin formate yields the corresponding hydride and this reaction is useful for the preparation of hydrides (38).



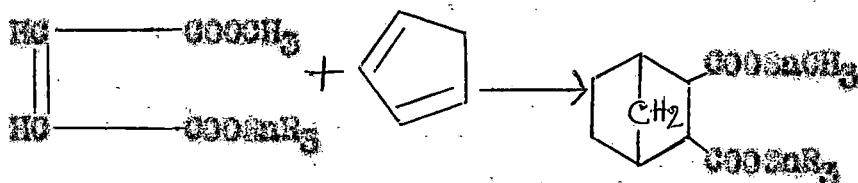
Seyferth et al (39) have used the reaction of triorganotin carboxylates of the halogen substituted carboxylic acids with cyclooctane as a carbene transfer reaction.



Action of alkoxy derivatives of metals and metalloids on organotin carboxylates produces metalloctanones (40, 41) as follows:

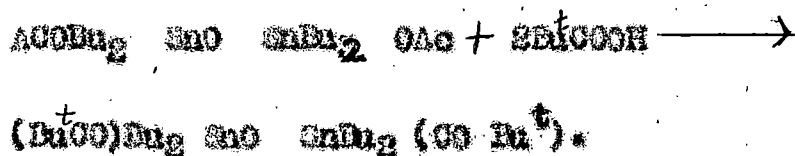


Diels - Alder reactions between organotin carboxylates and dienes are known (20)

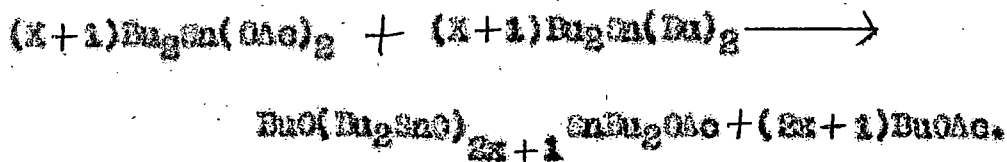


Diorganotin dicarboxylates undergoes redistribution with diorganotin dihalides, di-alkoxides and dihydrides to produce mixed carboxylates of the type $R_2SnX(OCOR')$, where $X = Cl, Br, I, OCH_3, H$ (56).

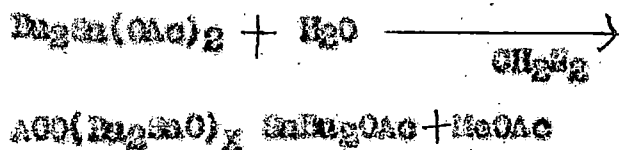
There are some evidences where carboxylate groups may be exchanged with other, carboxylate groups as follows (9, 42):



Oligomeric acetate is usually formed when a dialkyl tin diacetate and a dialkyl tin dialkoxide are heated at $180^\circ C$ in water for 2 hrs. (43,44).

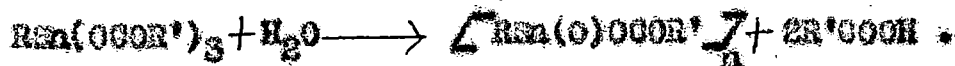


Oligomeric α -10 diacetoxy stannoxanes are also obtained by the reaction (45).



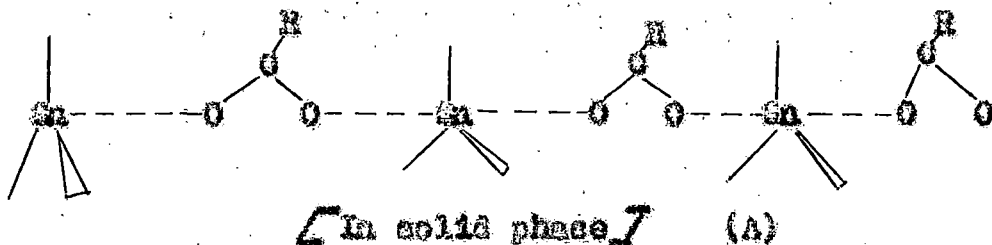
(X = 1,3,7,15).

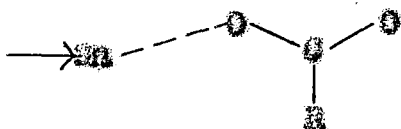
Organotin tricarboxylates are easily hydrolysed in benzene solution to give polymeric organotin carboxylates (46).



III. Structure of organotin complex

Structural features of organotin carboxylates have been reviewed by Okawara and Wada (38) and by Okawara and Ohara (26). The possibility of chelation or bridging through oxygen atoms of carboxylate group was shown by Beattie and Gilson (49) as an alternative to the previously postulated ionic nature of bonding by Freeman (49) and Okawara and co-workers (49). More recent spectroscopic studies on tin carboxylates in the solid as well as in the solution phase (8,10,50-53) have confirmed that trialkyl tin carboxylates are polymeric in solid state with planar trialkyl tin groups with bridging carboxylate group in between two tin atoms (A) and are expected to be monomeric esters in non-polar solvents (B).





(B) [In solution phase]

IR spectra of trimethyl tin carboxylate in the solid state contain two C - O stretching band at about 1570 cm^{-1} and 1410 cm^{-1} indicating a symmetrical COO group (54). Appearance of a single Sn - O stretching frequency in Nujol mull is constant with a planar trimethyl tin group. In CCl_4 solution the carboxylate absorption bands are shifted to 1650 cm^{-1} and 1300 cm^{-1} respectively with the appearance of both $\nu_{\text{as}}(\text{Sn} - \text{O})$ and $\nu_{\text{s}}(\text{Sn} - \text{O})$ bands indicating the breakdown of polymeric structure (A) into monomers with essentially tetrahedral tin atoms having ester like carboxylate groups bonded to it (B). This is supported by the works of Hester (29) and Tagliavines work (55). Similar behaviour of trialkyl tin formates has been demonstrated by Okamura and Ohara (56, 57) from spectroscopic studies and molecular weight in cyclohexane by cryoscopy.

However, tri-cyclohexyl tin acetate, trineophyl tin formate, trineophyl tin acetate and tribenzyl tin acetate have been suggested to be tetra co-ordinated monomers probably due to steric hindrance arising from the bulky organic

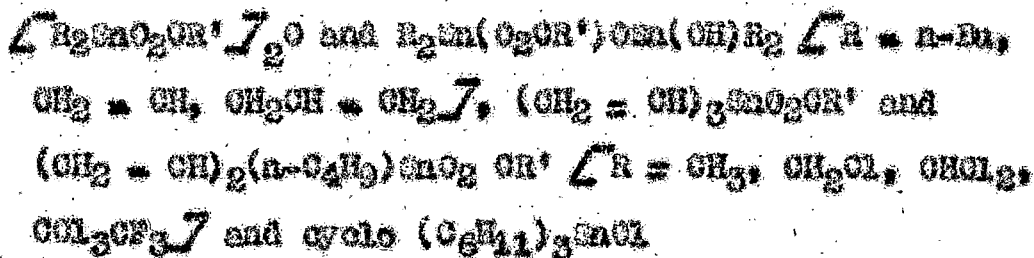
groups (53-60). Sano et al (10) have shown that branching at α -carbon atom generally prevent the formation of polymeric structure. Similarly, the trialkyl and aryl tin derivatives of halocarboxylic acids behave more like organic esters and thus possess monomeric structures (8, 61-63).

A monomeric penta co-ordinated structure (O) has been proposed for dialkyl chlorotin formates and acetates by Okawara et al (64)



(O)

Recently Calogero et al have undertaken systematic studies on organotin carboxylates by means of Mossbauer spectroscopy and X-ray crystal analysis. The compounds studied include:



It has been pointed out that the crystal data of some

tricyclohexyl tin derivatives do not agree well with the structure assigned on the basis of the Mossbauer quadrupole splitting values. The bulky cyclohexyl groups substantially modify the general structural pattern of the compounds of the R_3SnO_2OR' type, which usually have polymeric structure involving five co-ordinated tin atoms. Thus Mossbauer spectroscopic studies have been carried out on the series of tricyclohexyl tin halocarboxylates $(Cyclo C_6H_{11})_3SnO_2OR'$ with $R' = CH_3, CH_2Cl, CHCl_2, CCl_3, OP_3$ and X-ray crystal analysis has been carried out on the trifluoroacetate derivatives so that the results could be compared to those for the corresponding acetate. The crystals belong to orthorhombic, space group Pcm with unit cell parameters $a = 14.390 \pm 0.004$, $b = 5.427 \pm 0.004$, $c = 11.510 \pm 0.003 \text{ \AA}$.

The structure has been resolved by patterson methods and refined to an R value of 0.147. The co-ordination about the tin atom can be considered distorted trigonal pyramidal or distorted tetrahedral. Mossbauer data are explained in terms of distortions of bond angles about the tin atom (65).

Mossbauer data at liquid nitrogen temperature for the $(Cyclo C_6H_{11})_3SnO_2OR'$

Table - 2

R^+	$\delta_{a,b}$ (cm^{-1})	Δ^a (cm^{-1})	Δ^c (cm^{-1})	$O-Sn-O^d(\circ)$
CH_3	1.39	3.33	-2.96	106
CH_2Cl	1.42	3.33	-3.12	107
$CHCl_2$	1.53	3.60	-3.26	107
CCl_3	1.50	3.70	-3.30	106
CF_3	1.57	3.73	-3.36	106

$a \pm 0.03 \text{ cm}^{-1}$. Relative to SnO_2 at R.T.

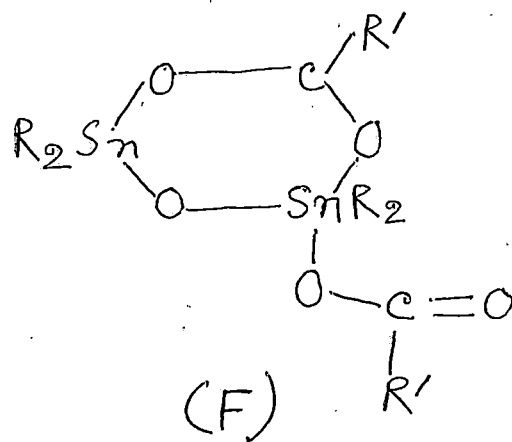
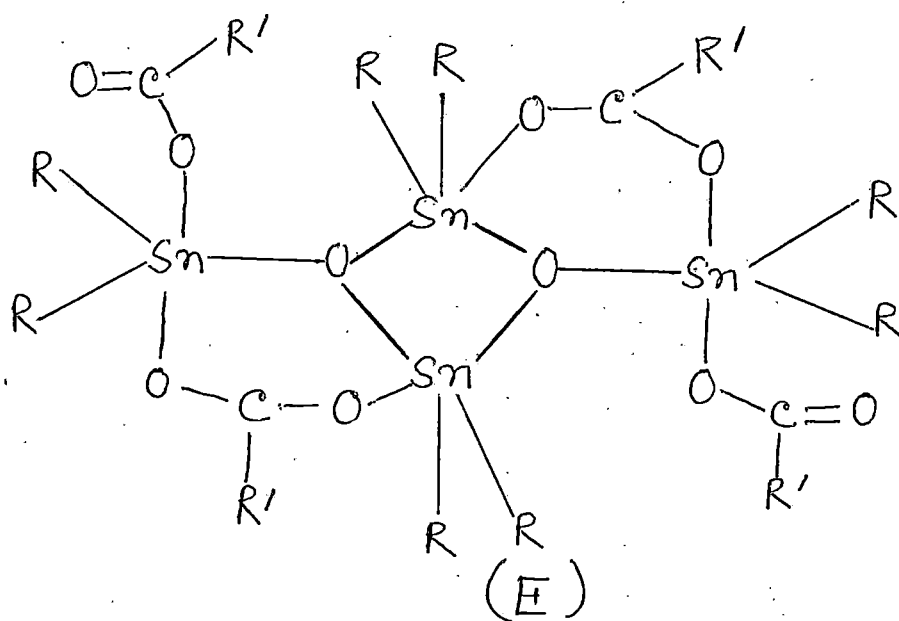
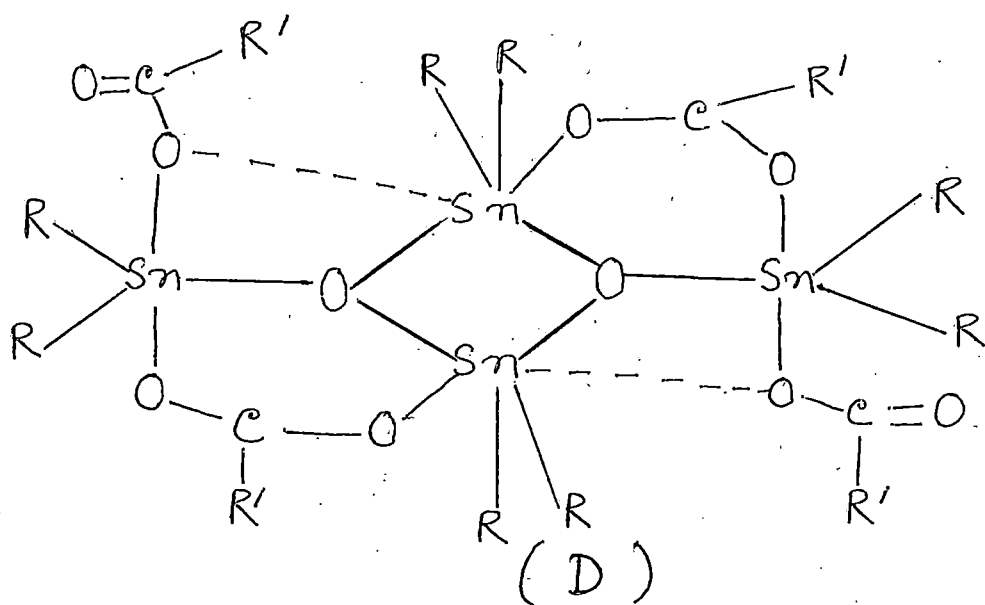
c predicted by simple point charge model. $\delta = 1.57$

and $\Delta = 3.27$

However, Alcock & Timms (69) have studied the structure of tribenzyl and tri-cyclohexyl tin acetate by x-ray diffraction method. This study confirms that the majority of organotin carboxylates have polymeric structure in the solid state. But with larger organic groups, the structure may become less polymeric and ultimately become monomeric.

The IR spectrum of a series of compounds $[n-Bu_2SnX_2]_x$ ($X = CH_2ClCOO$, $CHCl_2COO$, CCl_3COO) in chloroform solution, where these compounds exist in a dimer-monomer equilibrium

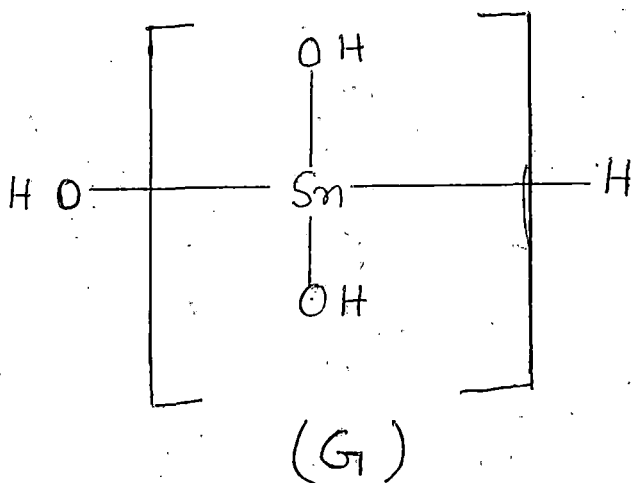
have shown that in dilute solution, a band at 1715 cm^{-1} arises from a stretching vibration of an ester like carboxylic group. From the behaviour of tetrabutyl-1,3-trichloro acetoxy distannoxane in solution, it appears that it is a dimer in non-polar solvent like carbon tetrachloride. Comparison of the IR spectra suggests that the same molecular structure is maintained in the solid and in CCl_4 solution. In fact, in the 600 asymmetric stretching region, only two bands are present (i) one near 1635 cm^{-1} must be attributed to the monodentate chloroacetate groups with the oxygen atom shared between the two tin atoms and (ii) one near 1650 cm^{-1} which arises from the chelate carboxylate group. In CCl_4 the weak Sn-O bond is preferentially broken, whereas the chelate ligands seem to remain unaffected. At varying concentrations, no change is observed in the position of the band centered at 1650 cm^{-1} , whereas that at 1635 cm^{-1} disappears on dilution and a strong band appears at 1715 cm^{-1} . The last band relates to the stretching vibrations of an ester like carboxylate group. It seems only that in CCl_4 , a dimeric ladder-type structure such as D is present whereas in chloroform, species like E and F are present (32).

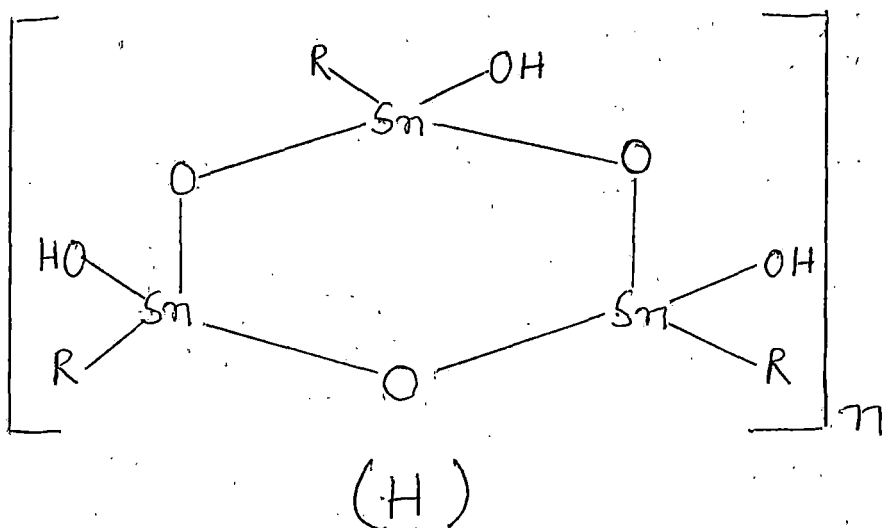


In the dimeric species D, in which two carboxylate groups are acting as bridging bidentate ligands and the other two as bridged monodentate ligands, the tin atoms are in different environments having co-ordination number of 6 and 5 in D, 5 in E and 5 and 4 in F. However, on the basis of IR, molecular wt. of diorganotin dicarboxylates ionic structure with R_2Sn cation, octahedral chelated structure with linear R_2Sn group as well as polymeric structure with bridging carboxylic groups have also been proposed by Okawara et al (49,66-68).

The structure of polymeric mono-organic stannic acids (69) and their carboxylate derivatives (8, 46, 10) have been studied in details. Herber et al (70) have shown that polymeric tin compounds are most likely to show a Monobauer effect at ambient temperature.

The stannous acids are infusible powders for which a polymeric structure (G) have been proposed (71,72). For the partially dehydrated material structure (H) has been proposed by Platt et al (73).





In both C and H, tin atom is 4 co-ordinated and is enclosed within the tetrahedra formed by the three oxygen atoms and the organic group R.

From the values of quadrupole splitting ($E_Q = 1.33 - 1.83$ mm/sec) in organo stannic acids Davies et al (67) have suggested a tetrahedral geometry at tin, though the possibility of association has not been completely excluded. The isomer shift values ($\delta = 0.40 - 0.73$ mm/sec.) are very small because of the very low 's' electron density at the tin atom resulting from electron attraction by the surrounding oxygens.

On the other hand, carboxylic acid derivatives [Rsn(O)OOCOR']_n of the stannic acids [Rsn(O)OH]_n show a

larger quadrupole splitting values ($B_q = 2.00 - 2.64$ mm/sec.) (46,10) indicating a 5 co-ordinated trigonal bipyramidal tin I which would be expected to give a quadrupole splitting of about 2.25 mm/sec. (73).

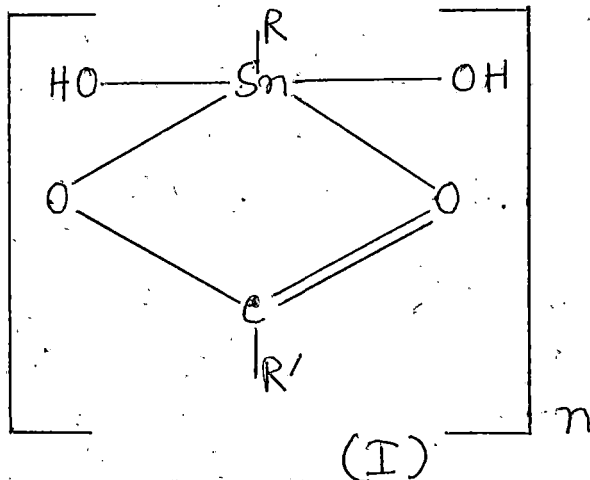


Table - 3

Hessbauer parameters for organotinanoic acid

Compound	δ mm/sec.	ΔB_q mm/sec.
$[Me_2Sn(O)OH]_n$	0.40	1.23
$[EtSn(O)OH]_n$	0.76 - 0.70	1.61 - 1.70
$[BuSn(O)OH]_n$	0.65 - 0.70	1.52 - 1.71
$[C_{12}H_{27}Sn(O)OH]_n$	0.66	1.62
$[PhSn(O)OH]_n$	0.73	1.23

(ΔB_q = quadrupole splitting, δ = isomer shift)

Table - 4

Mosebauer parameters for carboxylates of
the organotin(II) acids

Compound	δ mm/sec.	ΔE_Q mm/sec.
PhSn(O) $\left[\text{COO}(\text{CH}_2)_8\text{OH} = \text{CH}_2 \right]$	0.57	2.31
PhSn(O) $\left[\text{COO}(\text{CH}_2)_{16}\text{Me} \right]$	0.56	2.32
PhSn(O) $\left[\text{COO}(\text{CH}_3)_3 \right]$	0.53	2.00
PhSn(O) $\left[\text{COOCCl}_3 \right]$	0.72	2.35
PhSn(O) $\left[\text{COOCS}_3 \right]$	0.66	2.64
PhSn(O) $\left[\text{COOMe} \right]$	0.70	2.28
BuSn(O)OH	0.63	1.71

On the basis of this discussion the generalisation which could be made regarding the structure of organotin carboxylates are,

- (1) These compounds are usually polymeric in the solid state with the carboxy groups acting as the bridges.
- (2) Branching at the α -carbon atom of the carboxy group generally resists the formation of polymeric structure probably by steric effect.

(3) Electronegative substituents, e.g., halogens etc. when attached to the carboxy groups as in halocarboxylates diminishes the possibility of polymeric structures, possibly by decreasing the ability of the $\text{>C}=\text{O}$ group to co-ordinate with the tin atom, possibly due to withdrawal of electron from the oxygen atom via inductive effect.

(4) The polymeric structures are broken down in solution, the extent of splitting being determined by the nature of the solvent and the carboxylate and also on the concentration.

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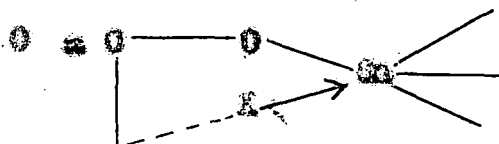
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CHAPTER - III

PREPARATION, ANALYTICAL DATA AND IR SPECTRUM
OF SOME NEW TRIORGANOTIN ARYLOXY ACETATES.

IIIA. Introduction

Recently Majee and Banerjee (12) have synthesised and studied the properties of organotin carboxylates where the carboxylate group forms a part of chelate ring.

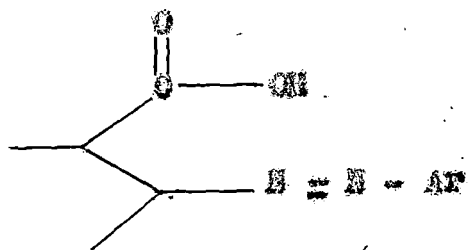


The organotin carboxylates of such type are of interest because:

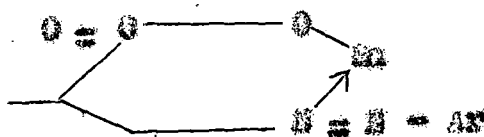
(1) Unlike organotin halides, organotin carboxylates are very reluctant to form addition compounds with Lewis basis and only a very few examples of such addition compounds are known (1,2). It is, therefore, of great interest to know whether such intramolecular co-ordination would occur in carboxylate derivatives having a suitable donor group in the carboxyl residue.

(2) The study of chelated carboxylates may lead to the preparation of triorganotin carboxylates with relatively greater stability towards cleavage by H^+ , OH^- and other reagents.

Majee and Banerjee have synthesised organotin compounds of *O*-aryleso carboxylic acids of the type II where the organotin derivative is very likely to have a 5 co-ordinated structure (12).

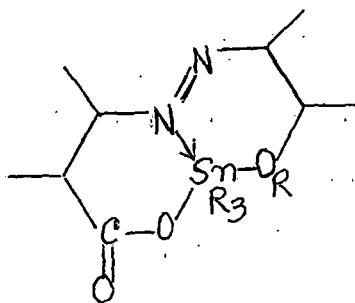


II



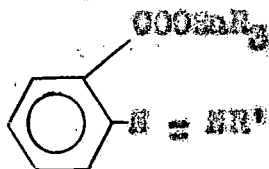
III

The hexa co-ordinated triorganotin compounds have also been prepared when the ligand has a -OR or -NR₂ type substituents at the *O'* - position (Fig. IV).

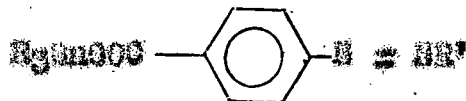


IV

A no. of organotin derivatives of the type V have been prepared and their properties compared with those of *p*-azo benzoic acids of the type VI in order to realise whether intramolecular co-ordination occurs in the former.



V



VI

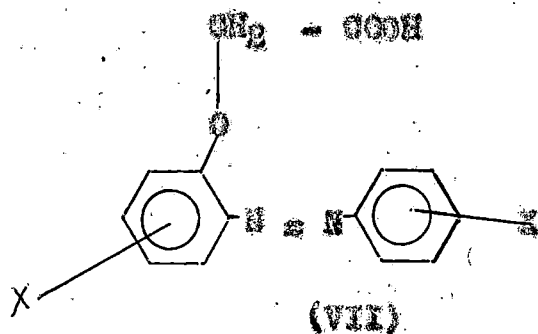
The organotin (O-arylate) benzoates are generally penta co-ordinated but those containing a hydroxyl group in the 2-position, e.g., triorganotin O-(2-hydroxy-5-methyl-benzene) benzoate, are hexa co-ordinated. The tetra carboxyl derivatives contain two different types of tin-carboxylate bonds, as shown by IR absorption at 1700 (ester like) and 1620 cm^{-1} (Chelated) (18).

In the present work we have tried to synthesise hitherto unknown 7-co-ordinated triorganotin carboxylates. A no. of 6-co-ordinated compounds have also been synthesised with a view to establish the nature of bonding through comparative studies of spectral properties and stabilities.

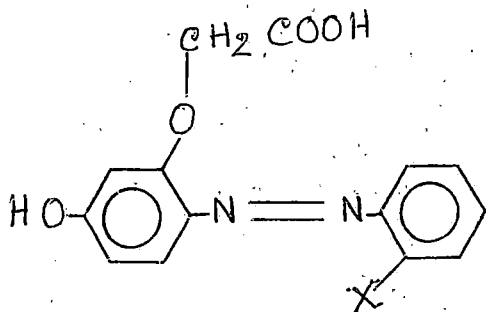
III. Choice of ligands

In view of the stability and ease of formation of penta as well as hexa co-ordinated derivatives of the 2'-substituted O-(arylate) benzoic acids; 2-carboxyethoxy 2'-hydroxy acetophenone and related molecules (VII) are expected to be ideal tetradentate ligands for the synthesis of hepta

co-ordinated chelates.

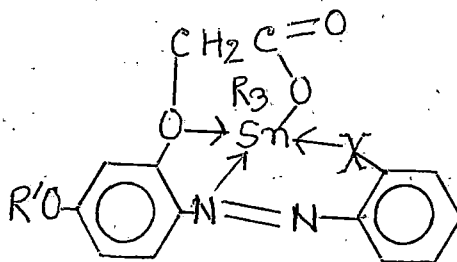


The synthesis of the ligand 2-carboxymethoxy 4-hydroxy-2'-hydroxy/chloro/fluoro (azobenzene) (VIII), has ultimately led to the preparation of the expected hepta co-ordinated compound (IX).



X = -OH, F, Cl

(VIII)



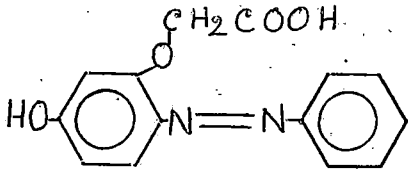
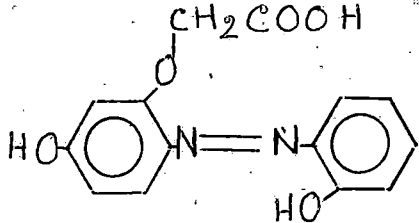
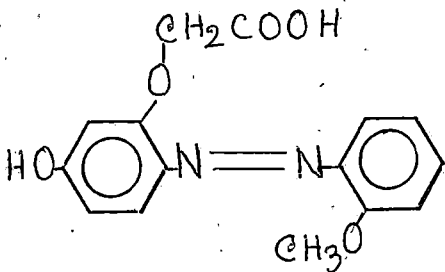
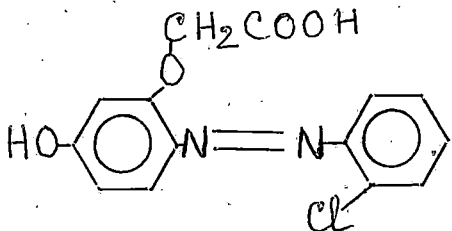
R' = R₃Sn, X = -OH;

R' = H, X = F, Cl.

(IX)

The ligands on which the studies were done are tabulated below:

Table - 1

Structure	Name	Abbreviation
1. 	2-(benzene azo) 5-hydroxy phenoxy acetic acid.	L ₁ H
2. 	2-(3'-hydroxy benzene azo) 5- hydroxy phenoxy acetic acid.	L ₂ H
3. 	2-(2'-methoxy benzene azo) 5-hydroxy phenoxy acetic acid.	L ₃ H
4. 	2-(2' chloro benzene azo) 5- hydroxy phenoxy acetic acid.	L ₄ H

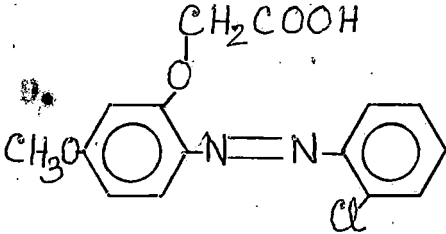
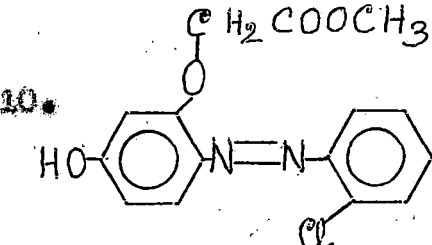
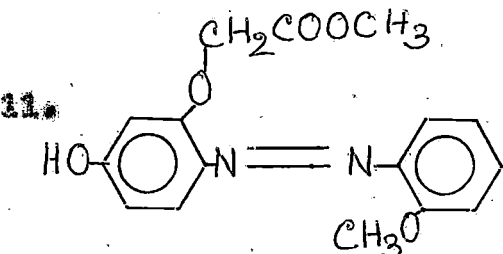
Contd..

Table - 1 (Contd..)

Structure	Name	Abbreviation
5.	2-(2' fluoro benzene azo) 5-hydroxy phenoxy acetic acid.	L ₅ H
6.	2-(4' nitro benzene azo) 5-hydroxy phenoxy acetic acid.	L ₆ H
7.	2-(4' methoxy benzene azo) 5-hydroxy phenoxy acetic acid.	L ₇ H
8.	2-(3' hydroxy benzene azo) 5-hydroxy phenoxy acetic acid.	L ₈ H

Contd..

Table - 1 (Contd..)

Structure	Name	Abbreviation
9. 	2-(2' chloro benzene azo) 5-methoxy phenoxy acetic acid.	L ₉ H
10. 	2-(2' chloro benzene azo) 5-hydroxy phenoxy methyl acetate	L ₁₀
11. 	2-(2' methoxy benzene azo) 5-hydroxy phenoxy methyl acetate	L ₁₁

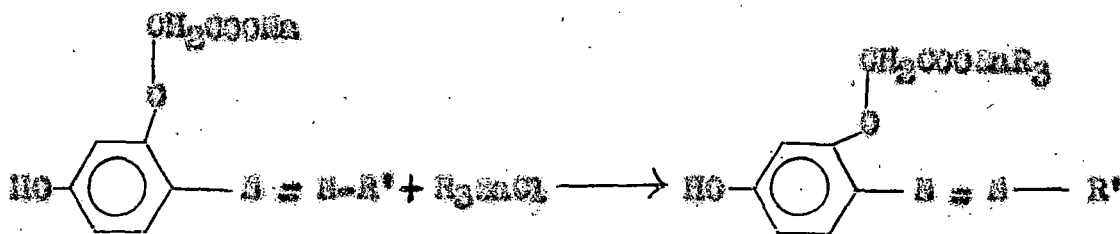
Except the compounds No. 10, 11 (which are the esters of L₉H and L₁₀H respectively) and 9 (the methoxy derivative of the compound No. 4), all other compounds were prepared by coupling 5-hydroxy phenoxy acetic acid with suitable diazotised components.

III. Methods of preparation

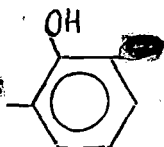
(A) In order to prepare the triorganotin carboxylates, the following methods were employed:

(1) Reaction of the organotin halides with the sodium salt of the 2-(benzene ring) 5-hydroxy phenoxy acetic acid and related compounds.

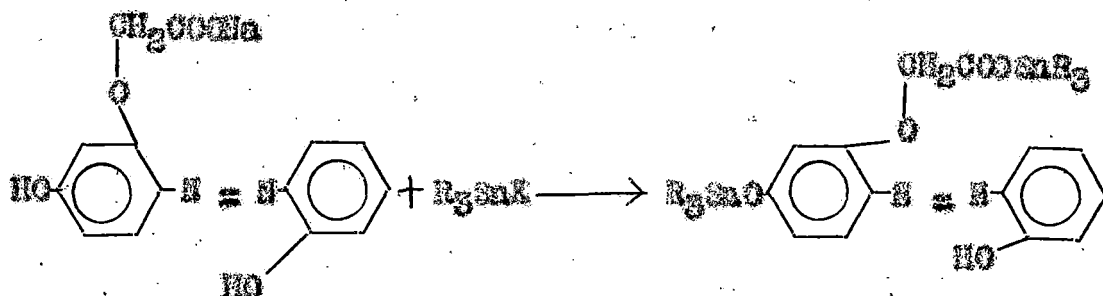
Na - salt of the ligand and R_3SnCl (1:1) were taken in dry benzene and the mixture was refluxed (sometimes stirred only). The reaction mixture was filtered off and the benzene solution was concentrated and then pet. ether was gradually added. The crystallized compound was purified from unreacted dye by extraction with cold benzene followed by recrystallization from benzene-pet. ether mixture. The reaction may be represented as follows:



where R = phenyl and butyl.

An interesting reaction occurs when $R' =$ 

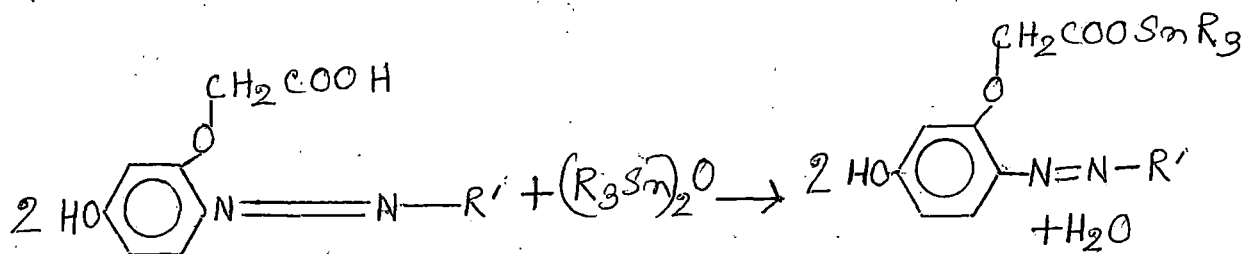
In this case only the bis(triorganotin) derivatives could be isolated. No simple (triorganotin) derivatives could be isolated as in the other cases. The reaction may be written as:



... (1)

(2) Reaction of hexaorganotin distannoxane with 2-(benzene ring) 5-hydroxy phenoxy acetic acid and related compounds.

The ligand and (R₃Sn)₂O (2:1) were taken in dry benzene and refluxed. The mixture was filtered and the solution was concentrated and the desired compound was obtained by crystallisation from benzene-pet. ether mixture.

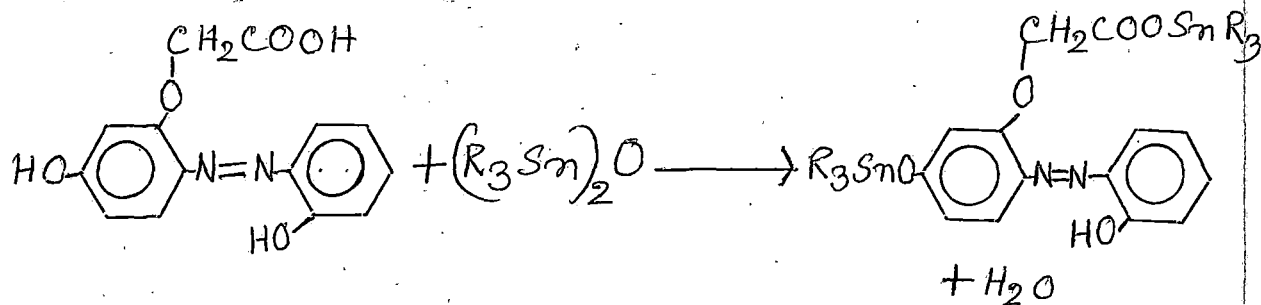


... (2)

where R = phenyl and butyl

In this case the addition of anhydrous sodium sulphate to the reaction mixture was found to improve the yield of the products. Apparently, this drove the reaction to the right hand side by removing the water formed.

As before, R' = 2'-hydroxy benzene always resulted in the formation of the bis (triorganotin) compound instead of the simple triphenyl tin carboxylates:

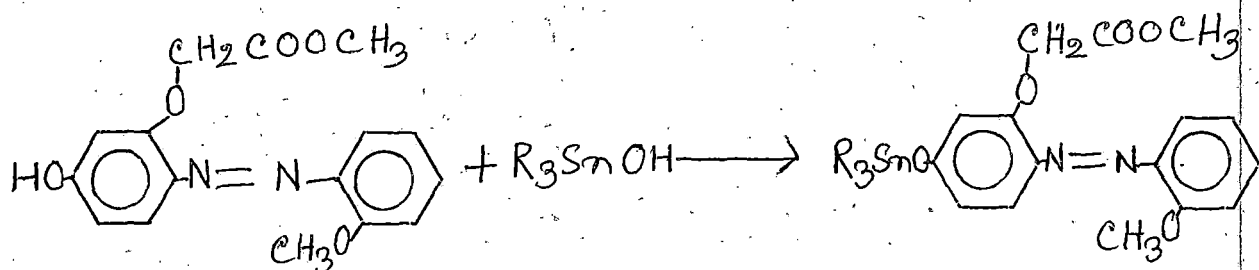


... (3)

(B) Stannylation of the -OH group on the benzene ring were achieved by the following methods:

(i) Reaction of triorganotin hydroxide with 2-(2'-methoxy benzene aso) 5-hydroxy phenoxy methyl acetate.

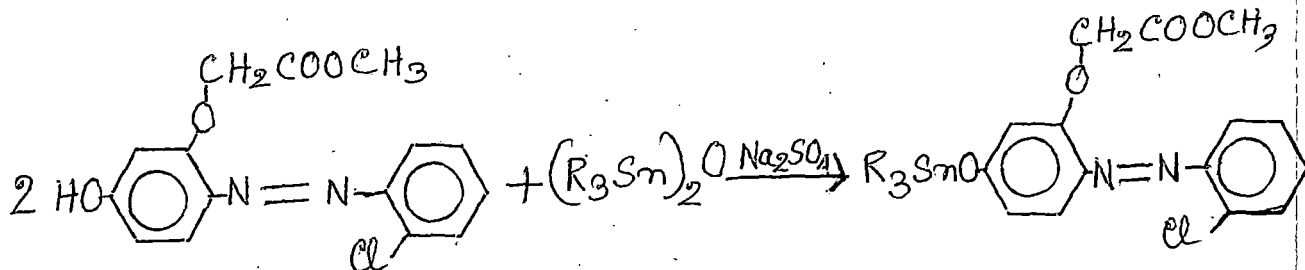
The ester and R_3SnOH were taken in dry benzene and stirred at R.T. On addition of petroleum ether to the concentrated benzene solution the triorganotin derivative could be obtained.



[R = Phenyl]

... (4)

(ii) $(R_3Sn)_2O$ in dry benzene was also found to be suitable. For example the stannylation of the phenoxy -OH group in 2-(2'-chloro benzene aso) 5-hydroxy phenoxy methyl acetate was achieved by the following reaction.

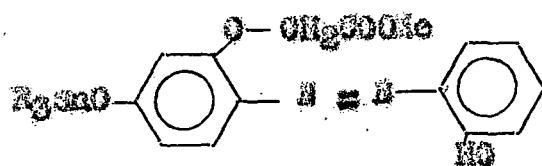


.... (5)

[where R = phenyl]

It may be pointed out methylation of the carboxyl group was necessary in order to avoid stannylation of the carboxylate group with occurs more easily in most of the cases.

All attempts to prepare (K) however failed.



(K)

A summary of the reaction products together with the yields and the experimental condition used in the present investigation are given in table 2.

Table -2

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield%)
1A. $I_1 - Na$ + Ph_3SnCl (1:1)	Stirring at RT for 8 hour in dry EtOH, product crystallised from benzene-pet. ether mixture.	Ph_3SnI_1 (154°, 60)
1B. I_1H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 6 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Ph_3SnI_1 (154°, 60)
2A. I_1Na + Bu_3SnCl (1:1)	Stirring at RT for 16 hours in dry EtOH, product crystallised from benzene-pet. ether mixture.	Bu_3SnI_1 (135°, 20)
2B. I_1H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 22 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Bu_3SnI_1 (128°, 40)
3A. $I_2 - Na$ + Ph_3SnCl (1:1)	Refluxing for 10 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	$(Ph_3Sn)_2I_2$ (141°, 50)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield %)
3B. LiH + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 20 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	$(\text{Ph}_3\text{Sn})_2\text{Li}_2$ (141°, 30)
4A. $\text{Li}_2 = \text{Na}$ + Bu_3SnOL (1:1)	Refluxing for 16 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	$(\text{Bu}_3\text{Sn})_2\text{Li}_2$ (88°, 30)
4B. LiH + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 20 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	$(\text{Bu}_3\text{Sn})_2\text{Li}_2$ (88°, 15)
5. LiH + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 6 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Ph_3SnLi_3 (170°, 30)
6. LiH + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 20 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Bu_3SnLi_3 (155°, 30)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield %)
7. I_3H + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing in dry benzene for 8 hours product crystallised from benzene- pet. ether mixture.	Ph_3SnI_4 (140°, 55)
8. I_4H + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 20 hours in dry benzene, product crystallised from benzene- pet. ether mixture.	Bu_3SnI_4 (90°, 30)
9. I_5H + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 6 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Ph_3SnI_5 (102°, 50)
10. I_3H + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 22 hours in dry benzene, product crystallised from benzene- pet. ether mixture.	Bu_3SnI_5 (75°, 20)
11. I_6H + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 12 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Ph_3SnI_6 (120°, 30)
12. I_6H + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 22 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Bu_3SnI_6 (83°, 20)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield %)
13. L_7H + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 10 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Ph_3SnL_7 (114°, 80)
14. L_7H + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 24 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Bu_3SnL_7 (79°, 25)
15. L_8H + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 8 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Ph_3SnL_8 (167°, 50)
16. L_9H + $(\text{Bu}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 30 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Bu_3SnL_9 (68°, 20)
17. L_9H + $(\text{Ph}_3\text{Sn})_2\text{O}$ (2:1)	Refluxing for 5 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Ph_3SnL_9 (78°, 70)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. [°] C, yield%)
12. I_{10} + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 10 hours in dry benzene, product crystallized from benzene - pet. ether mixture.	Ph_3SnI_{10} (83 [°] , 25)
19. I_{11} + Ph_3SnOH (1:1)	Stirring at RT for 24 hours, product crystallized from benzene - pet. ether mixture.	Ph_3SnI_{11} (70 [°] C, 50)

* = Decomposition point.

IIID. Analytical Data

Analytical data on the organotin derivatives are given in Table 3. Analytical data clearly indicates the formation of well defined organotin compounds.

Table - 3

Analytical data on organotin tin derivatives.

Formula	Found (Calculated) (%)			Sn
	C	H	N	
1. $C_{32}H_{26}O_4N_2Sn$ (Ph_3SnL_1)	62.32 (62.95)	4.31 (4.25)	4.56 (4.89)	19.13 (19.12)
2. $C_{26}H_{30}O_4N_2Sn$ (Bu_3SnL_1)	55.35 (55.71)	6.73 (6.72)	5.03 (5.00)	20.95 (21.16)
3. $C_{50}H_{40}O_6N_2Sn_2$ [$(Ph_3Sn)_2L_2$]	60.29 (60.8)	4.10 (4.06)	2.76 (2.84)	24.10 (24.09)
4. $C_{36}H_{64}O_4N_2Sn_2$ [$(Bu_3Sn)_2L_2$]	52.40 (52.69)	7.19 (7.39)	3.23 (3.23)	27.12 (27.43)
5. $C_{33}H_{28}O_6N_2Sn$ (Ph_3SnL_3)	61.40 (61.77)	4.26 (4.36)	4.22 (4.36)	18.29 (18.24)
6. $C_{27}H_{40}O_5N_2Sn$ (Bu_3SnL_3)	54.34 (54.35)	6.74 (6.77)	4.64 (4.74)	19.52 (20.09)
7. $C_{32}H_{25}O_4N_2SnCl$ (Ph_3SnL_4)	57.63 (58.01)	3.55 (3.81)	4.25 (4.27)	18.29 (18.11)

Contd..

Table - 3 (Contd..)

Formula	Found (Calculated) (%)			Sn
	C	H	N	
8. $C_{26}H_{37}O_4N_2SnCl$ (Bu_3SnL_2)	51.61 (52.40)	6.32 (6.22)	4.5 (4.70)	19.20 (19.94)
9. $C_{32}H_{26}O_4N_2SnF$ (Ph_3SnL_5)	59.02 (60.10)	3.72 (3.91)	4.40 (4.33)	18.29 (18.53)
10. $C_{26}H_{37}O_4N_2SnF$ (Bu_3SnL_5)	54.34 (54.90)	6.43 (6.39)	4.78 (4.84)	20.25 (20.51)
11. $C_{32}H_{26}O_6N_3Sn$ (Ph_3SnL_6)	57.29 (57.63)	3.67 (3.73)	6.23 (6.30)	17.71 (17.83)
12. $C_{26}H_{37}O_6N_3Sn$ (Bu_3SnL_6)	51.29 (51.60)	6.31 (6.10)	6.43 (6.00)	19.21 (19.59)
13. $C_{33}H_{26}O_5N_2Sn$ (Ph_3SnL_7)	61.26 (61.77)	4.31 (4.53)	4.23 (4.36)	17.93 (18.24)
14. $C_{27}H_{40}O_5N_2Sn$ (Bu_3SnL_7)	54.39 (54.85)	6.13 (6.77)	4.31 (4.74)	19.64 (20.09)
15. $C_{32}H_{26}O_5N_2Sn$ (Ph_3SnL_8)	59.10 (60.31)	4.14 (4.03)	4.31 (4.39)	17.93 (18.64)

Contd..

Table - 3 (Contd..)

Formula	<u>Found (Calculated) (%)</u>			Cl
	C	H	N	
16. $C_{26}H_{30}O_2Sn$ (Ph_3SnL_9)	54.62 (54.10)	6.33 (6.33)	4.31 (4.35)	20.16 (20.53)
17. $C_{33}H_{27}O_4SnCl$ (Ph_3SnL_9)	53.99 (53.17)	4.00 (4.03)	4.21 (4.13)	17.51 (17.73)
18. $C_{33}H_{27}O_4SnCl$ (Ph_3SnL_{10})	53.03 (53.17)	4.14 (4.03)	4.16 (4.13)	17.32 (17.73)
19. $C_{34}H_{30}O_3Sn$ (Ph_3SnL_{11})	61.22 (61.33)	4.43 (4.51)	4.37 (4.21)	17.76 (17.85)

III. Infrared spectra

The IR spectrum of the organotin azo carboxylates are very complex. Though complete assignment of the absorption bands in these compounds is not possible, important structural informations may be obtained from a qualitative assignment of bands due to $\nu_{as}(OCO)$, $\nu_{ss}(OCO)$, $\nu(Sn-O)$ and $\nu(H-H)$. Not all of these modes could be identified

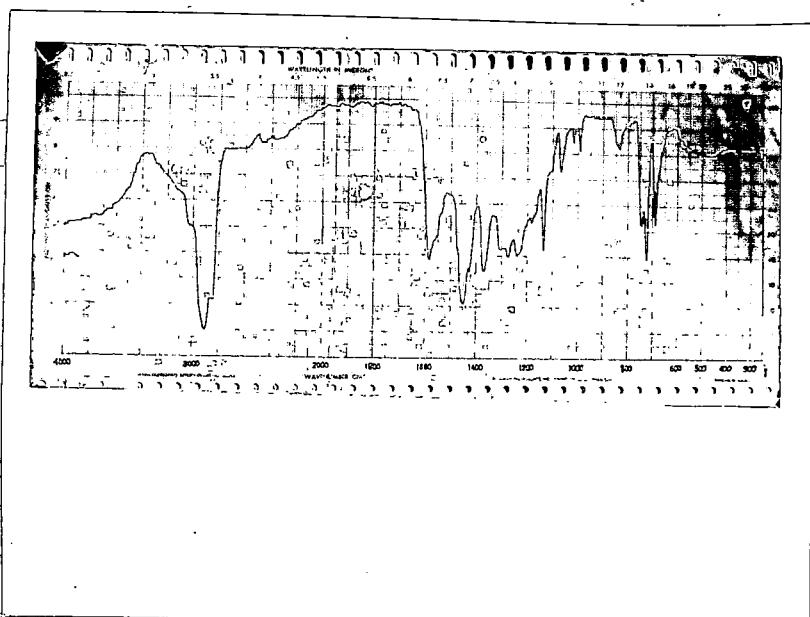


Fig. 1 IR spectra of $(\text{Pb}_3\text{Sn})_2$ in Nujol.

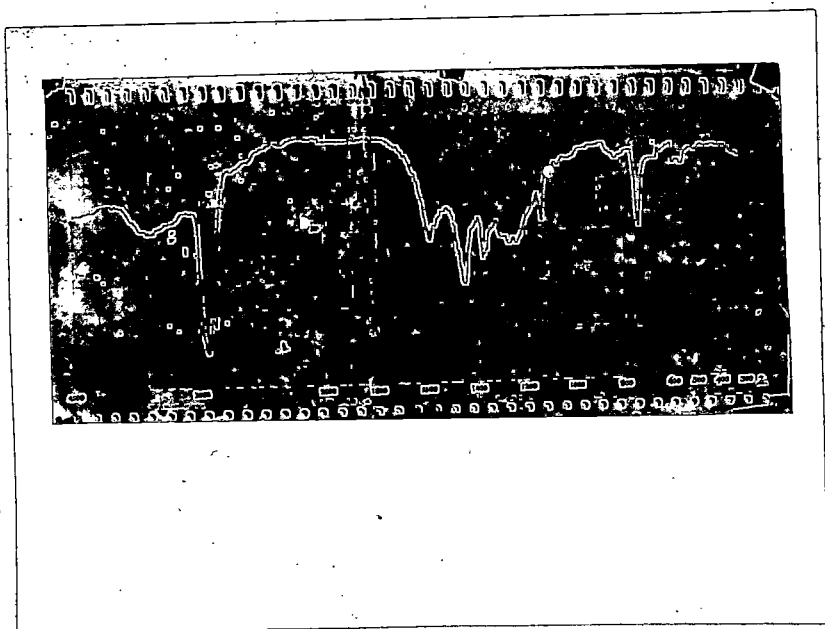


Fig. 2 IR spectra of $(\text{Mg}_3\text{Sn})_2$ in Nujol.

with certainty because of the presence of strong ligand vibrations in regions where these modes are expected. It is therefore useful to discuss the main features of the IR spectra in the different regions of interest. Some typical IR spectrum are shown in figs. 1-16.

(a) 1650 - 1750 cm^{-1} : In this region $\nu_{\text{as}}(\text{OCO})$ is expected (1,3,4,5) and all the compounds are characterized by the presence of a number of medium to strong intensity bands in this region. Asymmetric OCO vibrations have been identified by comparison of the IR spectra of the azo phenoxy acetic acids and its organotin derivatives. Because of the presence of strongly absorbing ring vibrational modes in this region which sometimes overlap with $\nu_{\text{as}}(\text{OCO})$, the identification of this mode has been made difficult in some cases and the peak positions are uncertain in these cases.

(b) 1250 - 1500 cm^{-1} region: Both $\text{N} = \text{N}$ stretch and symmetric OCO stretch are expected to occur in this region.

(1) $\text{N} = \text{N}$ stretch: The idea of correlating an IR band with $\text{N} = \text{N}$ stretch in azo dyes has been attractive one. However, substitution on the azo group in dyes are generally fairly symmetrical. $\text{N} = \text{N}$ stretch is, therefore, likely to be weak. Although the vibration has been reported to occur at 1400-1450 cm^{-1} (3). Miller has emphasized the absence of any diagnostically useful band in the region in azo dyes (6).

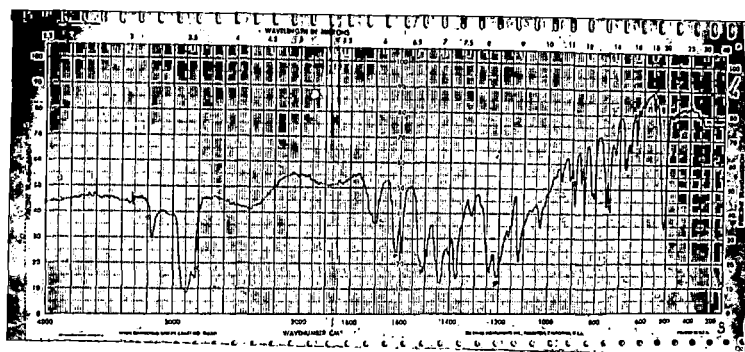


Fig. 5 IR spectra of L_1H in Nujol.

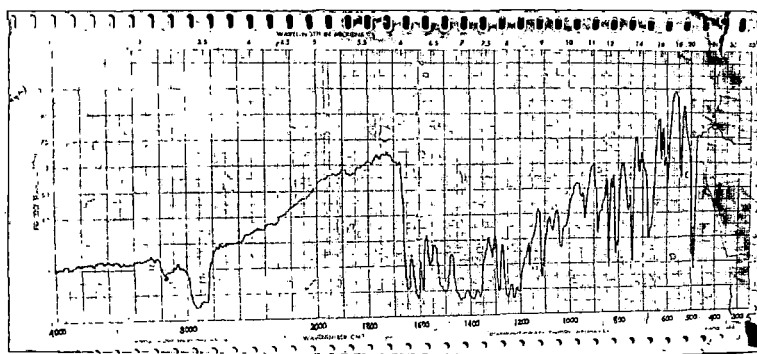


Fig. 4 IR spectra of Di_3SnH in Nujol.

The structure is more complex in the organotin derivatives because of the presence of strong aromatic bands in this region.

(ii) ~~(iii)~~ Symmetric OCO stretch: Because of the presence of a number of aryl-oxygen stretches in this region which are usually very strong, it has not been possible to identify the symmetric OCO stretch in the present compounds with any degree of certainty. Because of this, symmetric OCO stretch has not been considered in the present discussion.

(c) ~~450-600 cm⁻¹~~: Both $\dot{\nu}(\text{Sn}-\text{O})$ and $\dot{\nu}(\text{Sn}-\text{O})$ are expected in this region (1,13,3,4,8). Both $\dot{\nu}(\text{Sn}-\text{O})$ and $\dot{\nu}(\text{Sn}-\text{O})$ are probably very weak in these compounds since comparison with ligand spectra showed no new bands attributable to Sn-O or Sn-O stretch.

As all the spectra were run in nujol mull mostly with KBr windows, the region below 400 cm⁻¹, where stretching mode of $\text{N} \rightarrow \text{Sn}$ co-ordination bond is expected to occur (1,9,10), could not be explored. As such presence or absence of $\text{N} \rightarrow \text{Sn}$ co-ordination had to be deduced from other evidences to be discussed in the next chapter.

The absorption associated with Aryl -O-CH₂COOH moiety are, however, easily identifiable because of their intensity. Aryl-O-CH₂ vibrations generally lead to two easily identifiable absorption bands at 1310 - 1210 and 1030 - 1010 cm⁻¹ (7). The former may be looked upon as an aromatic

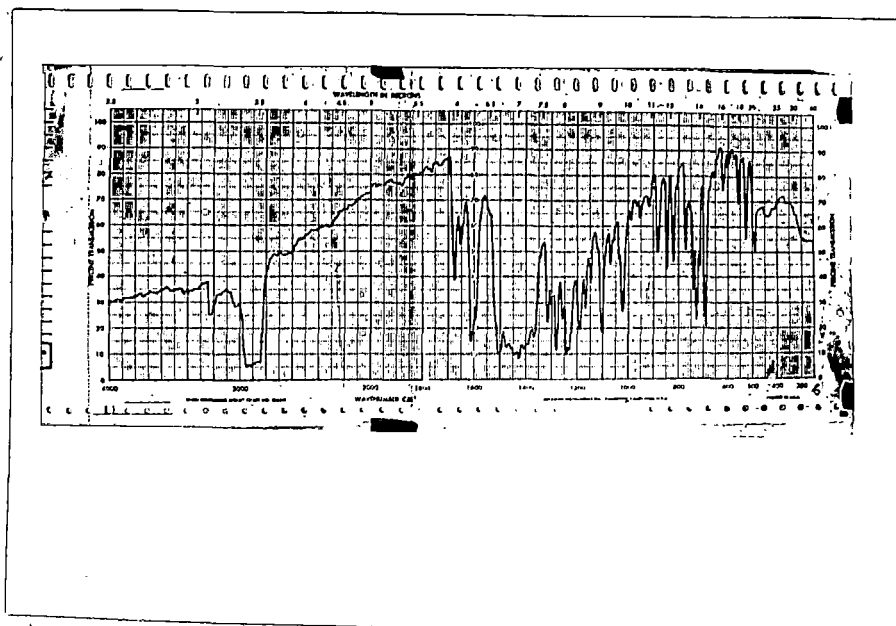


Fig. 5 IR spectra of Ph_3Al_3 in Nujol.

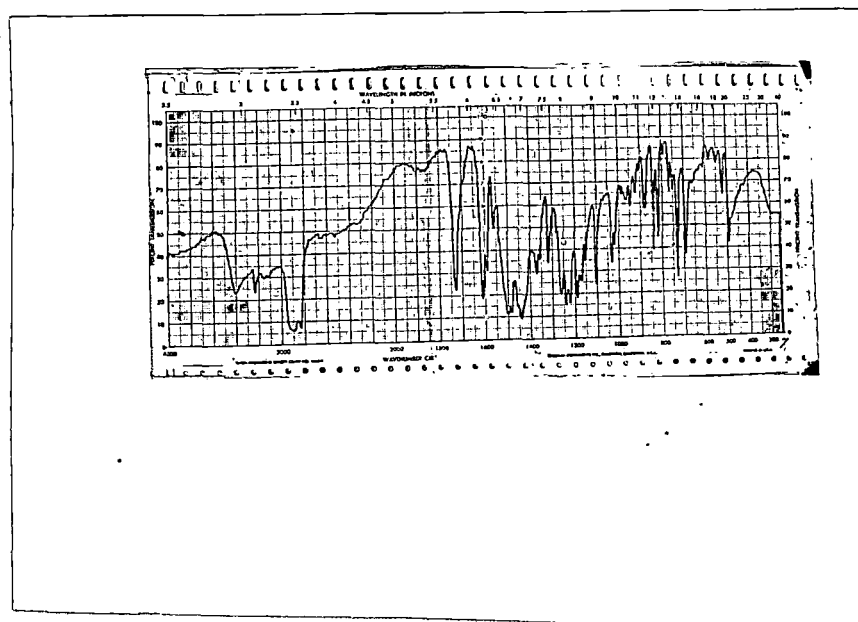


Fig. 6 IR spectra of L_3H in Nujol.

carbon-oxygen stretching frequency as in phenol while the low frequency band may be considered to be due to $O-CH_2$ vibration. The later band is expected to higher frequency to 1100 cm^{-1} in the present system due to mixing with adjacent $C-O$ stretch, the vibration being similar to the asymmetric $C-O-O$ stretch in alcohols. Co-ordination by the oxygen of the Aryl- $O-CH_2$ moiety is expected to affect these frequencies some what.

The important vibrational modes that could be identified with reasonable certainty are given in Table 4.

Table - 4

Important stretching frequencies in 2-(benzene etc) 5-hydroxy phenoxy acetic acids and their organotin derivatives in Nujol.

Compound	Frequencies (in cm^{-1}) of :		
	COO (as)	Aryl - OCH_2	$O-CH_2COOH$
1. L_2H	1700	1230	1120
2. Ph_3SnL_1	1655 (1660) ^a	1220	1100
3. Bu_3SnL_1	1645 (1660) ^a	1225	1110
4. L_2H	1660	1230	1130
5. $(Ph_3Sn)_2L_2$	1660 ^b	1230	1135
6. $(Bu_3Sn)_2L_2$	1660 ^b	1230	1130
7. L_2H	1750	1240	1100

Contd..

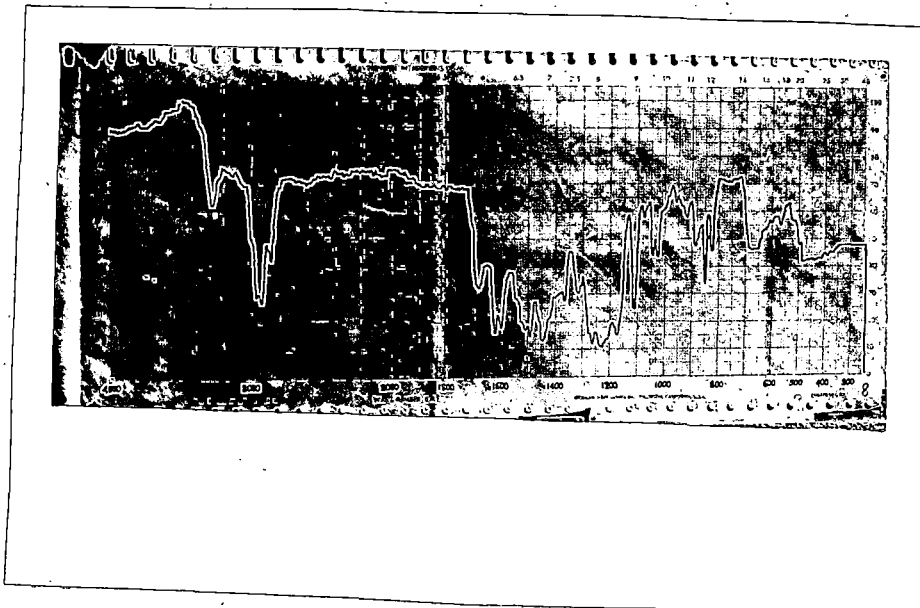


Fig. 7 IR spectra of Suganly in Chloroform.

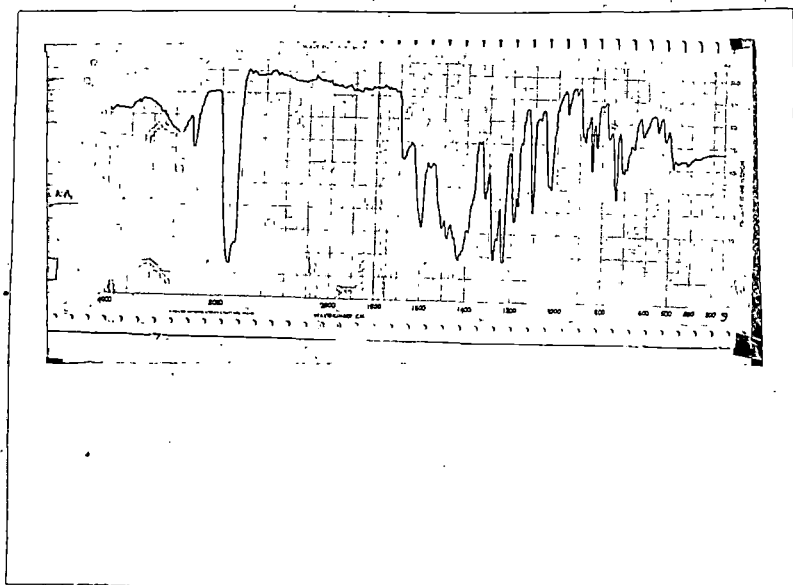


Fig. 8 IR spectra of Suganly in Nujol.

Table - 4 (Contd..)

Compound	Frequencies (in cm^{-1}) of:		
	COO (aa)	Aryl - COH ₂	G-CH ₂ COOH
8. Ph ₃ SnL ₃	1660	1220	1110
9. Bu ₃ SnL ₃	1660	1230	-
10. L ₄ H	1730	1240	1130
11. Ph ₃ SnL ₄	1690 ^b	1230	1100
12. Bu ₃ SnL ₄	1690 ^b	1225	1110
13. L ₅ H	1730	1240	1130
14. Ph ₃ SnL ₅	1690 ^b	1240	1110
15. Bu ₃ SnL ₅	1690 ^b	1230	1120
16. L ₆ H	1723	1240	1130
17. Ph ₃ SnL ₆	1670	1220	1110
18. Bu ₃ SnL ₆	1660	1220	1110
19. L ₇ H	1710	1230	1130
20. Ph ₃ SnL ₇	1660	1230	1120
21. Bu ₃ SnL ₇	1660	1240	1110
22. L ₈ H	1710	1240	1140
23. Ph ₃ SnL ₈	1660	-	-
24. Bu ₃ SnL ₈	1660	1240	1140
25. L ₉ H	1750	1260	1140
26. Ph ₃ SnL ₉	1570 ^b	1230	1130

a) In chloroform solution

b) Overlapping absorption with strong ring vibration near 1600 cm^{-1} , frequencies given are only approximate values.

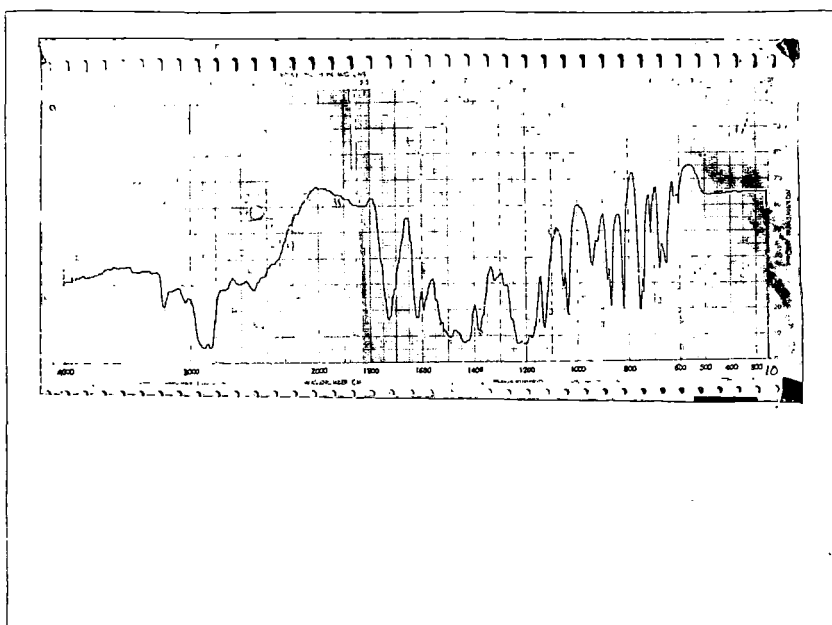


Fig. 9 IR spectra of L_2H in Nujol.

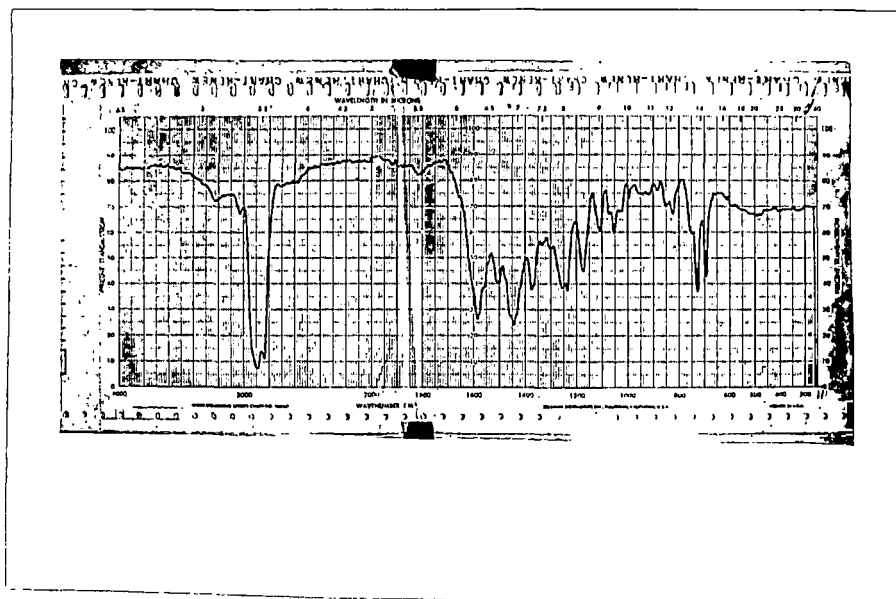


Fig. 10 IR spectra of Ph_3SnB_4 in Nujol.

As expected the asymmetric COO stretching frequency is lowered in the organotin derivatives. Excepting in ligands with a donor group at the orthoposition in the diene moiety (L_2H , L_4H , L_6H , and L_8H), the $\nu_{as}(COO)$ in the organotin derivatives occur in the range $1645 - 1680 \text{ cm}^{-1}$ both in the solid state (Nujol mols) as in chloroform solution. Unlike simple organotin carboxylates such as, formate, acetate etc., where $\nu_{as}(COO)$ occur in a much lower region due to polymeric structure (1), these derivatives are to be regarded as monomeric carboxylates.

The aryl-O-Mn₂ frequencies are also generally lowered to some extent in the organotin derivatives. This may be taken as an evidence in favour of O $\rightarrow$ Sn co-ordination.

Potentially tetracarboxylate ligand, such as, L_2H , L_4H , L_6H and L_8H , are characterized by organotin derivatives in which the $\nu_{as}(COO)$ is lowered to 1580 cm^{-1} and overlaps with the strong ring vibration near 1600 cm^{-1} . However, formation of polymeric structure through bridging carboxylate in these systems is unlikely because the stretching frequencies in the solid phase and solution (chloroform) are nearly same. Further, the presence of bulky substituted phenoxy group at α -position will not be conducive to the formation polymeric structure involving -COO- bridge. It therefore, appears that the most probable explanation for such lowering

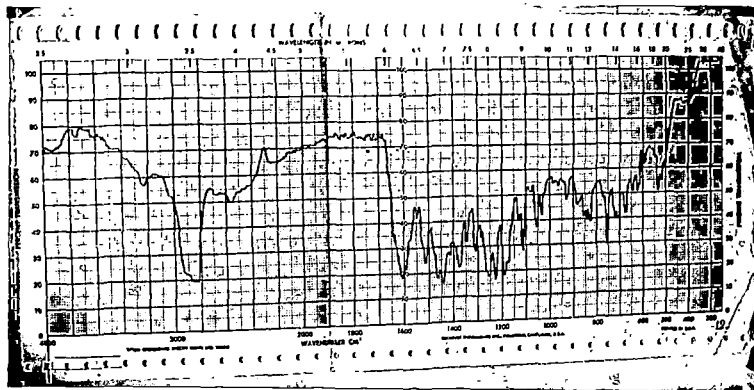


Fig. 11 IR spectra of Bu_3SnBr in Nujol.

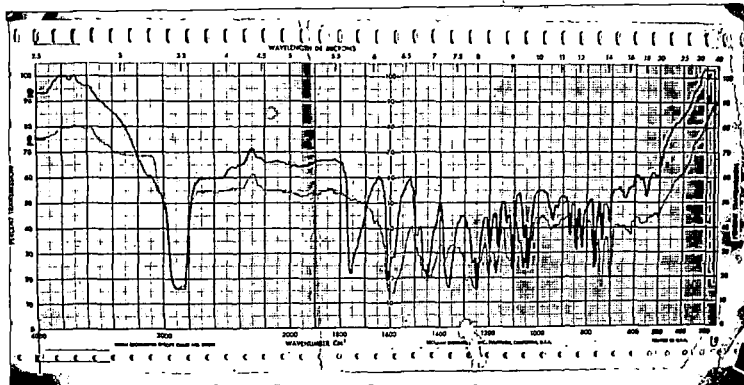
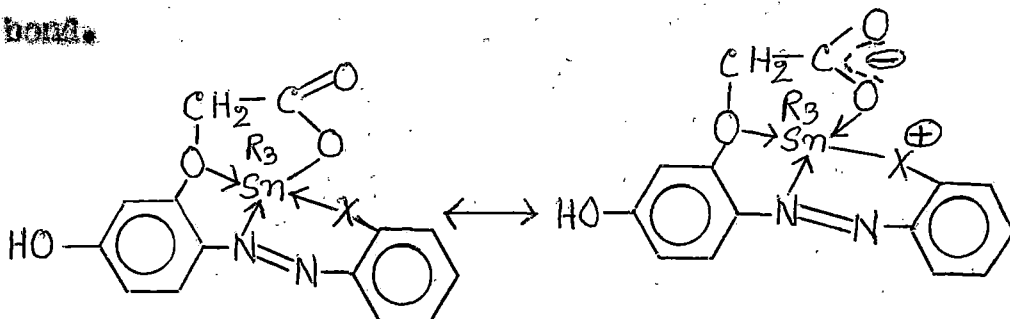


Fig. 12 IR spectra in Nujol of
1. Ph_3SnBr 2. Et_3SnBr

of C=O stretching frequency in the organotin derivatives is a resonance of the type (XI) which tends to weaken $>C=O$ bond.



(XI)

Such a resonance is not unreasonable since the formal +ve charge on the donor substituent X will be stabilized by interaction with the ring.

In view of this, it appears reasonable to regard the organotin derivatives of these ligands as examples of 7-co-ordinated chelates.

III. Experimental

Triphenyl tin chloride (Fluka A.G. Switzerland) was used after recrystallisation from petroleum ether, m.p. 105° - 106° (lit. m.p. 106°) and sometime triphenyl tin

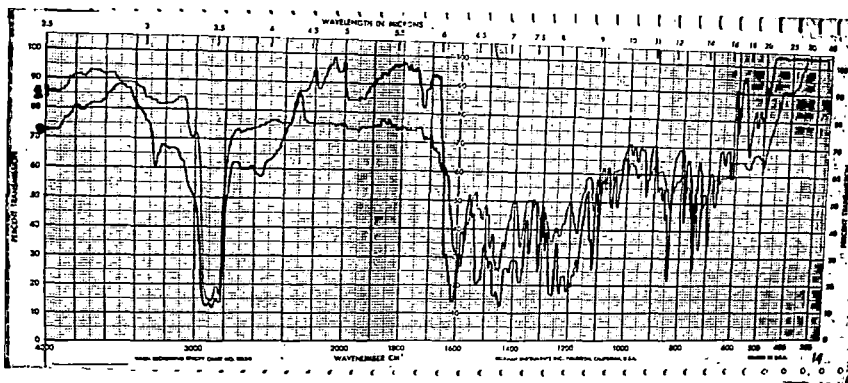


Fig. 13 IR spectra in Nujol of
 1. Ph₃NHClg 2. Bu₃NHClg

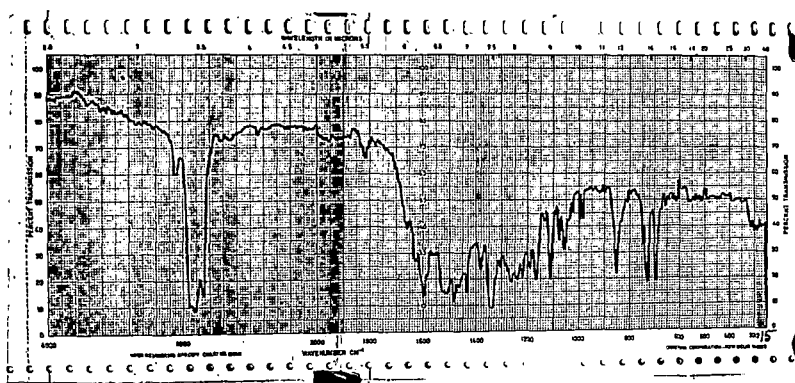


Fig. 14 IR spectra of Bu₃NHClg in Nujol

chloride was prepared from tetraphenyl tin by the reaction of stannic chloride (13). Triphenyl tin ether (m.p. 132 - 134°C) prepared by the reaction of triphenyl tin chloride and sodium hydroxide (14). Tributyl tin chloride b.p. 132°/10 mm bis-tributyl tin oxide, b.p. 210 - 4°/10 mm (Fluka A.G. Switzerland products) were used without further purification.

Unless otherwise stated petroleum ether (pet. ether) used in the present investigation refers to the fraction with the boiling range 60 - 80°C. All melting points are uncorrected.

Preparation of α -hydroxy phenoxy acetic acid (HPA)

20 gm. resorcinol was dissolved in 70 c.c. of 33% sodium hydroxide solution in a 250 ml. flask and was shaken till all the resorcinol dissolve. To this was added 17.2 gm. mono-chloro acetic acid in 100 ml. water. The reaction mixture was refluxed for 3-4 hrs. The reddish solution was cooled, acidified with conc. HCl with vigorous stirring. The product was extracted with ether in a separating funnel. Nearly complete extraction was achieved in 5-6 extractions. The ether extract was evaporated to dryness. The residue was taken in minimum volume of ether in order to make a homogeneous paste and to this when benzene was added, yellowish white powder obtained which when crystallised from benzene methanol mixture, α -hydroxy phenoxy acetic acid of m.p. 155°C was obtained.

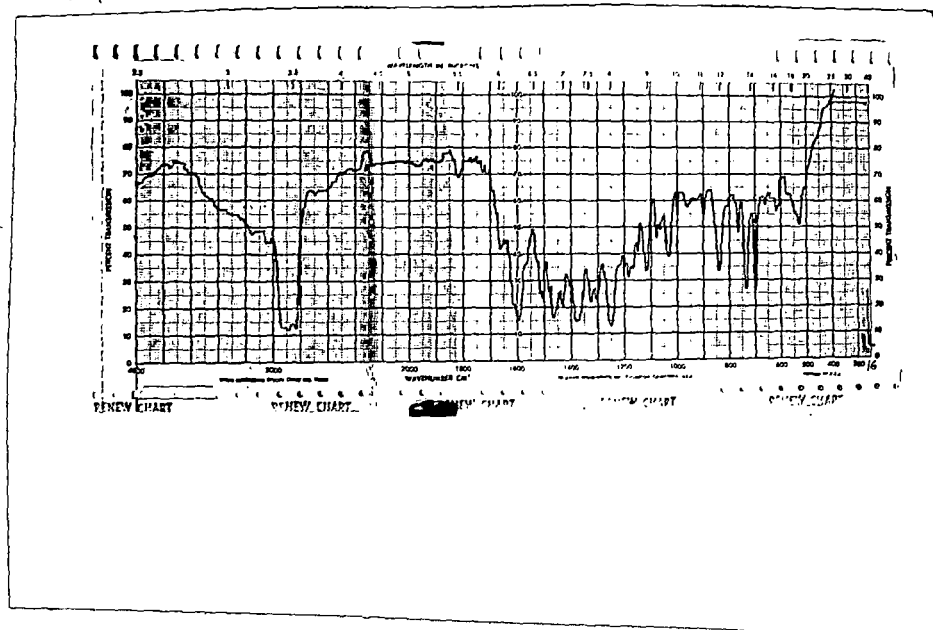


Fig. 15 IR spectra of Ph_3Al_7 in Nujol.

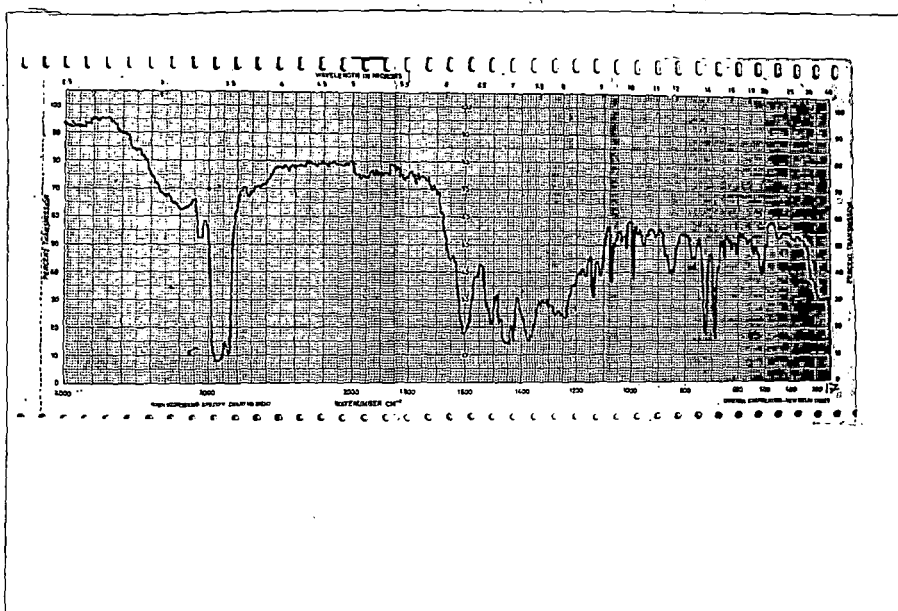


Fig. 16 IR spectra of $\text{Al}_3\text{Sn}_{13}$ in Nujol.

IR : $\nu_{as}(000)$

1710 cm^{-1}

Yield : 85%

(1) Preparation (benzene soln)- phenoxy acetic acids

1. Preparation of L₂H

11 gm. O-aminophenol was diazotised by the usual procedure (11). 10.5 gm HPA was dissolved in 50 ml. of 50% sodium hydroxide solution and was cooled to 5°C in an ice bath which was then added to the cold diazonium salt solution with vigorous stirring when a red colour developed. It was kept overnight in a refrigerator followed by 1 hr. at R.T. and then acidified with conc. hydrochloric acid when the deep red dye separated out. It was filtered, washed several times with water, dried in air. Crystallisation from acetone - pet. ether mixture yielded L₂H. decomposition point (D.P.) 200°C.

IR : $\nu_{as}(000)$

1680 cm^{-1}

Yield: 40%

2. Preparation of L₁H

By following the same procedure and taking the same quantity of other chemicals as described in 1, but using 9.5 gm. aniline as the diazotised component, brick red L₁H, m.p. 205°C was obtained.

IR: $\nu_{as}(000)$

1730 cm^{-1}

5. Preparation of L₃H

By following same procedure and taking the same quantity of other materials as described in 1 but using 12.3 gm. O-anisidine as the diazotised component, an orange red solid obtained which on crystallisation from acetone-pet. ether mixture afforded L₃H, m.p. 197°C.

IR : $\nu_{as}(000)$

1730 cm⁻¹

Yield : 60%

6. Preparation of L₄H

By following the similar method and taking the same quantity of other components, as described in 1, but using 12.7 gm O-Chloro aniline as the diazotised component, a solid obtained which on crystallisation from acetone - pet. ether mixture afforded the chocolate brown L₄H of m.p. 187°C.

IR : $\nu_{as}(000)$

1730 cm⁻¹

Yield : 50%

3. The preparation of L₂H

By following the same procedure and taking the same quantity of all other chemicals as described in 1, but using 11 gm of O-fluoro aniline as the diazotised material for diazotisation, a solid obtained which when crystallised from

acetone-pet. ether mixture offered the reddish brown L_6H of m.p. $195^{\circ}C$.

IR : $\nu_{as}(000)$

1730 cm^{-1}

Yield: 60%

6. The preparation of L_6H

7 gm p-nitro aniline was dissolved in 20 ml. of conc. sulphuric acid (Sp. Gr. 1.84) and was cooled to $5^{\circ}C$ in an ice bath and diazotised by the usual method (11). 9 gm. H_2A was dissolved in 20 ml. of 36% sodium hydroxide and was cooled to $5^{\circ}C$ which was then added to the cold diazonium salt solution with vigorous stirring when a red colour developed. The solution was kept overnight in a refrigerator followed by 5 hrs at R.T. and then slowly acidified with conc. hydrochloric acid when the brown dye separated out. It was filtered, washed several times with hot water, dried in air and finally dried in vacuum at room temperature. Crystallisation from acetone-pet. ether mixture yielded the dye L_6H of m.p. $184^{\circ}C$.

IR : $\nu_{as}(000)$

1725 cm^{-1}

Yield : 40%

7. The preparation of L₇H

By following the similar method and taking the same amount of all other materials as described in 1, but using 12.5 gm. p-aminidine as the component for diazotization, a chocolate brown solid obtained which after recrystallization from acetone-pet. ether mixture afforded the dye L₇H of m.p. 136°C.

IR : $\nu_{as}(000)$

1710 cm⁻¹

Yield : 50%

8. The preparation of L₈H

By following the previous procedure and taking all other materials in the same amount as directed in 1, but using 10.9 gm. m-aminic phenol as the component for diazotization, a brown solid obtained which on recrystallization from acetone-pet. ether mixture afforded the reddish brown dye L₈H of m.p. 200°C.

IR : $\nu_{as}(000)$

1710 cm⁻¹

Yield : 70%

9. The preparation of L₉H

(The methoxy derivative of L₈H)

6 gm of L₈H was dissolved in 20 ml. of 10% sodium hydroxide solution, and was cooled to 10°C. 5.3 gm. of dimethyl sulphate was added slowly to the alkaline solution

at 10°C with vigorous stirring. The product was extracted with ether and the ethereal solution was washed with 10% sodium hydroxide solution and water. After evaporation of ether the residue was hydrolysed by 5% sodium hydroxide solution followed by acidification with dil. hydrochloric acid when an orange solid separated. After several recrystallisation from benzene-pet. ether mixture, the bright orange L_9H , m.p. 120°C, was obtained.

IR spectrum: ν_{as} (C=O) 1760 cm^{-1}

Yield : 80%

10. Preparation of L_{10}

1 gm. of L_9H , was dissolved in absolute methanol and cooled. To this was added the ethereal solution of 0.2 gm. diazomethane. After evaporation of ether the only residue was extracted with ether and the ethereal solution was washed with 50% sodium bicarbonate solution. After evaporation of ether, the brownish yellow ester L_{10} (smell like green mango) was obtained.

IR spectrum : ν_{as} (C=O) 1740, 1760 cm^{-1}

Yield : 40%

11. Preparation of L₁₁

By following the similar procedure and taking the same amount of all other materials as described in 10, but using 1 gm L₃H instead of L₄H, the deep red ester L₁₁ was obtained.

IR : $\nu_{\text{as}}(1000)$

1760 cm^{-1}

Yield: 40%

(ii) Reactions for the preparations of organotin derivatives:

1A. Reaction of triphenyl tin chloride with Na-salt of L₁H

A mixture of 1 gm. of Na-salt of L₁H and 1.4 gm. of triphenyl tin chloride in 300 ml. dry ethyl alcohol was stirred for eight hours at R.T. and cooled, filtered off. After evaporation of the alcohol from the filtrate, the residue was taken in cold benzene and filtered. The solution was concentrated and to this was added pet. ether when an orange solid of m.p. 131°C separated which after several recrystallization from benzene-pet. ether mixture afforded the bright orange product of m.p. 134°C, yield 60%. The percentage of

Found:

C	H	Cl	Sn
62.42	4.21	4.46	19.52

Calculated for
C₃₂H₂₆O₄Sn :

62.95	4.26	4.53	19.12
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IR spectrum:

$\nu_{\text{as}}(1000)$

1655 cm^{-1}

1B. Reaction of bis-(triphenyl tin) oxide with L_1H

A mixture of 1 gm. L_1H , 1.3 gm bis-(triphenyl tin) oxide, 0.5 gm. of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 12 hours and then cooled, filtered off. The filtrate was concentrated and pet. ether was added when a reddish orange solid m.p. $160^{\circ}C$, separated. The product was purified by recrystallising from benzene-pet. ether mixture. The yield of the purified product, m.p. $184^{\circ}C$, was about 80%. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	62.32	4.31	4.56	19.18
Calculated for				
$C_{32}H_{26}O_4S_2Na$:	62.95	4.26	4.59	19.12

IR spectrum : $\gamma_{as}(000)$ 1655 cm^{-1}

8A. Reaction of tributyl tin chloride with Na - salt of L_1H

A mixture of 1 gm. Na-salt of L_1H and 1.3 gm. tributyl tin chloride in 200 ml. dry ethanol was stirred for 16 hours at R.T. and then filtered. The alcohol was removed completely from the filtrate and the residue was taken in cold, dry benzene and filtered when pet. ether was added to the concentrated filtrate, a solid m.p. $125^{\circ}C$, separated which on

several recrystallisation from benzene-pet. ether mixture yielded the bright orange organotin compound of m.p. 128°C , yield 20%. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	55.56	6.73	5.03	20.98
Calculated for				
$\text{C}_{26}\text{H}_{38}\text{O}_4\text{N}_2\text{Sn}$	55.71	6.73	5.00	21.16

IR spectrum : $\nu_{\text{as}}(1000)$ 1645 cm^{-1}

23. Reaction of bis-(tributyl tin) oxide with I_2H

A mixture of 1 gm. I_2H , 1.1 gm. ^{^ b.s. -} (tributyl tin) oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. benzene was refluxed for 23 hours and then it was cooled, filtered off. On addition of the pet. ether to the concentrated filtrate a solid, m.p. 122°C separated which after several recrystallisation from benzene-pet. ether mixture afforded the bright orange organotin derivative of m.p. 128°C , yield 40%. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	55.46	6.70	5.1	21.38
Calculated for				
$\text{C}_{26}\text{H}_{38}\text{O}_4\text{N}_2\text{Sn}$	55.71	6.73	5.00	21.16

IR spectrum: $\nu_{\text{as}}(1000)$ 1645 cm^{-1}

3A. Reaction of Na-salt of LgH with triphenyl tin chloride.

A mixture of 1.1 gm of the sodium salt and 1.8 gm triphenyl tin chloride in 200 ml. benzene was refluxed for 10 hrs. cooled and filtered. The benzene was completely evaporated from the deep violet filtrate and the residue was taken in cold benzene and the concentrated benzene solution afforded a deep violet compound on addition of pet. ether to it. On recrystallisation the product from benzene-pet. ether mixture, the deep violet, shining crystals of triphenyl tin derivative (0.8 gm) of D.P. 141° was obtained.

	%	<u>C</u>	<u>H</u>	<u>S</u>	<u>Na</u>
Found:		60.2	4.1	2.76	24.3
Calculated for					
$C_{20}H_{15}O_2SNa_2$		60.2	4.06	2.80	24.00
IR spectrum:	ν_{as} (980)	1560 cm^{-1}			

3B. Reaction of Bis-(triphenyl tin)oxide with LgH

A mixture of 1 gm. LgH and 1.2 gm. bis-(triphenyl tin) oxide in 200 ml dry benzene was refluxed for 20 hours in presence of 0.5 gm. anhydrous sodium sulphate and then filtered. To the concentrated filtrate was added pet. ether when a reddish violet solid separated out and it was filtered off. The solid was taken in cold benzene and the

solution was concentrated. On addition of pet. ether to the benzene solution, the deep violet crystal of triphenyl tin derivative (0.5 gm) of D.P. 141°C was obtained. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found :	63.1	3.76	2.72	24.00
Calculated for				
$\text{C}_{20}\text{H}_{15}\text{N}_3\text{Sn}_2$:	60.8	4.24	2.84	24.09
IR spectrum :	$\nu_{\text{as}}(000)$ 1560 cm^{-1}			

4A. Reaction of tributyl tin chloride with Na-salt of LgH

A mixture of 1.1 gm tributyl tin chloride and 1.1 gm sodium salt in 200 ml. dry benzene was refluxed for 16 hours and then cooled, filtered. The benzene was evaporated completely from the filtrate and the residue, after washing several times with hot. pet. ether, was taken in cold benzene. To the concentrated benzene solution when pet. ether was added, a reddish violet compound separated. Several crystallization from benzene pet. ether mixture, afforded the deep violet organotin derivative (0.6 gm) of D.P. 83°C . The percentage of

	<u>g</u>	<u>H</u>	<u>Cl</u>	<u>Sn</u>
Found:	52.72	7.26	3.12	27.61
Calculated for				
$C_{38}H_{64}O_4H_2Sn_2$	52.69	7.33	3.23	27.43
IR spectrum:	$\gamma_{as}(933)$	1560 cm^{-1}		

4B. Reaction of Bis-(tributyl tin) oxide with LgH

A mixture of 1 gm LgH , 1 gm bis-(tributyl tin) oxide and 0.5 gm of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 22 hours and then cooled, filtered off. On addition of pet. ether to the concentrated filtrate, a reddish violet solid was obtained and washed with hot pet. ether. After several crystallization of the product from benzene-pet. ether mixture, the deep violet organotin derivative (0.4 gm) of D.P. 86⁰ was obtained. The percentage of

	<u>g</u>	<u>H</u>	<u>Cl</u>	<u>Sn</u>
Found:	52.40	7.19	3.23	27.12
Calculated for				
$C_{38}H_{64}O_4H_2Sn_2$	52.49	7.33	3.23	27.43
IR spectrum :	$\gamma_{as}(933)$	1560 cm^{-1}		

5. Reaction of bis-(triphenyl tin) oxide with LgH

A mixture of 1 gm LgH , 1.2 gm bis-(triphenyl tin) oxide and 0.5 gm of anhydrous sodium sulphate in 200 ml. dry benzene

was refluxed for 6 hours and then was cooled, filtered off. On addition of pet. ether to the concentrated filtrate, an orange red solid (1.3 gm, m.p. 173°C) separated which after several recrystallisation from benzene-pet. ether mixture afforded the desired product (1.1 gm) of m.p. 179°C . The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Pounds:	61.40	4.26	4.22	18.29
Calculated for				
$\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_2\text{Sn}$	61.77	4.36	4.36	18.24

IR spectrum : $\nu_{\text{as}}(600)$ 1680 cm^{-1}

6. Reaction of bis-(tributyl tin) oxide with L_3H

A mixture of 1 gm L_3H , 1 gm bis-(tributyl tin) oxide and 0.5 gm anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 50 hours and then after cooling was filtered. The filtrate was concentrated and to it was added pet. ether when a red solid (1.8 gm, m.p. 151°C) separated and was filtered off. After several crystallisation from benzene-pet. ether mixture, the deep red organotin compound (1.5 gm), m.p. 135°C , was obtained. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	54.34	6.74	4.64	19.83
Calculated for				
$C_{27}H_{40}O_2Sn_2$:	54.85	6.77	4.74	20.09
IR spectrum: $\bar{\nu}_{as}(OCO)$	1680 cm^{-1}			

7. Reaction of bis-(triphenyl tin)oxide with L_4H

A mixture of 1 gm L_4H , 1.2 gm bis-(triphenyl tin) oxide and 0.5 gm of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 3 hours and then was cooled, filtered off. The filtrate was concentrated and when pet. ether was added to it, an orange yellow solid (1.2 gm), m.p. $138^{\circ}C$, separated. After recrystallisation from benzene-pet. ether mixture, the desired organotin derivative (1.8 gm), m.p. $140^{\circ}C$, was obtained. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	57.63	5.85	4.23	18.20
Calculated for				
$C_{32}H_{25}O_4Sn_2$:	58.61	5.81	4.27	18.11
IR spectrum : $\bar{\nu}_{as}(OCO)$	1680 cm^{-1}			

8. Reaction of bis-(tributyl tin)oxide with L_4H

A mixture of 1 gm. L_4H , 1 gm bis (tributyl tin) oxide, 0.5 gm anhydrous sodium sulphate in 200 ml. benzene was refluxed for 20 hours and then filtered. The solution was concentrated and to it was added pet. ether when a reddish gummy mass separated. On keeping the benzene-pet. ether mixture for 3 days at R.T., an orange yellow product (0.7 gm), m.p. $82^{\circ}C$, was deposited on the wall of the container (having the gummy mass at the bottom). The solid, after recrystallization from benzene-pet. ether mixture, afforded the desired organotin compound (0.6 gm) of m.p. $90^{\circ}C$. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	51.6	6.32	4.5	19.20
Calculated for				
$C_{26}H_{37}O_4N_2Sn_2$	52.4	6.22	4.7	19.94
IR spectrum :	$\gamma_{25}(1000) \quad 1590 \text{ cm}^{-1}$			

9. Reaction of bis-(triphenyl tin)oxide with L_4H

A mixture of 1 gm L_4H , 1.2 gm bis-(triphenyl tin) oxide, 0.5 gm of anhydrous sodium sulphate in 200 ml. benzene was refluxed for 6 hours and then filtered. On addition of pet. ether to the concentrated solution, an orange yellow

solid (2 gm), m.p. 99°C , separated which after recrystallization from benzene-pet. ether mixture, afforded the bright orange-yellow triphenyltin derivative (1.8), m.p. 102°C . The percentage of

	<u>C</u>	<u>H</u>	<u>Sn</u>	<u>Sn</u>
Found:	59.02	3.72	4.40	18.29
Calculated for				
$\text{C}_{22}\text{H}_{25}\text{O}_4\text{H}_2\text{Sn}_2$	60.1	3.91	4.38	18.58

IR spectrum: $\nu_{\text{as}}(\text{OOO})$ 1590 cm^{-1}

10. Reaction of bis-(tributyl tin) oxide with I_2H

A mixture of 1 gm I_2H , 1 gm bis-(tributyl tin) oxide and 0.5 gm of anhydrous sodium sulphate in 250 ml. benzene was refluxed for 22 hours and then cooled, filtered off. Then pet. ether was added to the concentrated solution, a gummy separated. After keeping the solution for 2 days at R.T., an yellowish orange solid (0.6 gm), m.p. 73°C , deposited on the wall of the container having the gummy mass at the bottom. The solid was recrystallised from benzene-pet. ether mixture when the tributyl tin derivative (0.5 gm), m.p. 73°C separated. The percentage of

	<u>C</u>	<u>H</u>	<u>H</u>	<u>Sn</u>
Found:	54.54	0.45	4.78	20.26
Calculated for				
$C_{26}H_{37}O_4H_3Sn$:	54.9	6.39	4.84	20.61
IR spectrum :	$\nu_{as}(OCO)$	1600 cm^{-1}		

11. Reaction of bis-(triphenyl tin)oxide with L_2H

A mixture of 1 gm. L_2H , 1.2 gm bis (triphenyl tin) oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 12 hours. The benzene solution was concentrated and when pet. ether was added, a brown solid (0.7 gm), m.p. $117^{\circ}C$, separated which after recrystallization from benzene-pet. ether mixture yielded the brownish-orange organotin carboxylate (0.6 gm) of m.p. $120^{\circ}C$. The percentage of

	<u>C</u>	<u>H</u>	<u>H</u>	<u>Sn</u>
Found:	57.29	3.07	6.28	17.71
Calculated for				
$C_{32}H_{29}O_6H_3Sn$:	57.63	3.75	6.5	17.63
IR spectrum :	$\nu_{as}(OCO)$	1670 cm^{-1}		

18. Reaction of bis-(tributyl^{tin}) oxide with L_6H

A mixture of 1 gm L_6H , 2gm. bis-(tributyl tin) oxide and 0.5 gm of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 23 hours, when pet. ether was added to the concentrated benzene solution, an orange solid (0.6 gm) m.p. $84^{\circ}C$ obtained. After several crystallization from benzene-pet. ether mixture, the desired tributyl tin derivative (0.4 gm) m.p. $83^{\circ}C$, was obtained. The percentage of

	<u>C</u>	<u>H</u>	<u>Sn</u>	<u>Na</u>
Found:	51.21	6.31	6.43	19.21
Calculated for				
$C_{26}H_{37}O_2Sn$:	51.50	6.10	6.90	19.59
IR spectrum :	$\nu_{as}(OCO) \quad 1650 \text{ cm}^{-1}$			

19. Reaction of bis-(triphenyl tin) oxide with L_7H

A mixture of 1 gm. L_7H , 1.2 gm. bis-(triphenyl tin) oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed 10 hours. The benzene solution was concentrated and when pet. ether was added to it, a red solid (1.2 gm), m.p. $112^{\circ}C$ separated which after recrystallisation from benzene-pet. ether mixture yielded the bright-red crystals of the organotin derivative (1.7 gm), m.p. $114^{\circ}C$. The percentage of

	<u>C</u>	<u>H</u>	<u>H</u>	<u>Sn</u>
Found:	61.26	4.31	4.23	17.08
Calculated for				
$C_{33}H_{29}O_5H_2Sn$:	61.77	4.30	4.36	13.24
IR spectrum :	$\nu_{as}(OCO)$	1660	cm^{-1}	

14. Reaction of bis-(tributyl tin) oxide with L_7H

A mixture of 1 gm. bis-(tributyl tin) oxide, 1 gm. L_7H and 0.5 gm. of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 24 hours. The benzene solution was concentrated and pot. ether was added to it when a gummy mass separated. On keeping the solution for 4 days at R.T., an reddish orange solid (0.7 gm), m.p. $73^{\circ}C$, deposited on the wall of the container which was recrystallized from benzene-pot. ether mixture resulting in the formation of the orange crystals of the tributyl tin carboxylate (0.5 gm), m.p. $73^{\circ}C$. The percentage of

	<u>C</u>	<u>H</u>	<u>H</u>	<u>Sn</u>
Found:	54.60	6.19	4.61	19.64
Calculated for				
$C_{27}H_{40}O_5H_2Sn$:	54.53	6.77	4.74	20.09
IR spectrum :	$\nu_{as}(OCO)$	1660	cm^{-1}	

15. Reaction of bis-(triphenyl tin) oxide with LgH

A mixture of 1 gm. LgH , 1.2 gm. bis-(triphenyl tin) oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. benzene was refluxed for 3 hours. The reaction mixture was then cooled and filtered. On addition of pet. ether to the concentrated solution, an orange solid (2.6 gm), m.p. 104°C , separated which after recrystallisation from benzene-pet. ether mixture afforded the organotin derivative (1.1 gm), m.p. 107°C . The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found :	59.10	4.14	4.31	17.98
Calculated for				
$\text{C}_{32}\text{H}_{26}\text{O}_5\text{Sn}$:	60.31	4.03	4.39	18.64

IR spectrum: $\bar{\nu}_{\text{as}}(1000)$ 1660 cm^{-1}

16. Reaction of bis-(tributyl tin) oxide with LgH

A mixture of 1 gm. LgH , 1 gm. bis-(tributyl tin) oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 30 hours and then cooled, filtered. When pet. ether was added to the concentrated solution, a gummy mass separated. On keeping the solution for 5 days at R.T., an orange solid (0.6), m.p. 66°C , deposited on the wall of the container which after recrystallisation from

benzene-pet. ether mixture yielded the desired product (0.4 gm), m.p. 63°C. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	54.62	6.38	4.81	20.16
Calculated for				
$C_{26}H_{38}O_2N_2Sn$:	54.1	6.58	4.85	20.58

IR spectrum: $\nu_{as}(000)$ 1630 cm^{-1}

17. Reaction of bis-(triphenyl tin)oxide with H_2N

A mixture of 1 gm H_2N , 1.1 gm bis-(triphenyl tin)oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 5 hours and cooled and filtered. On addition of pet. ether to the concentrated solution, an orange solid (1.6 gm), m.p. 77°C, separated out which after recrystallization from benzene-pet. ether mixture, afforded the triphenyl tin carboxylate (1.4 gm), m.p. 78°C. The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found :	58.89	4.00	4.21	17.51
Calculated for				
$C_{33}H_{27}O_4N_2SnCl$:	59.17	4.05	4.18	17.73

IR spectrum: $\nu_{as}(000)$ 1570 cm^{-1}

18. Reaction of bis-(triphenyl tin) oxide with L₁₀

A mixture of 1 gm. L₁₀, 1.1 gm bis-(triphenyl tin) oxide and 0.5 gm. anhydrous sodium sulphate in 200 ml. dry benzene was refluxed for 10 hours and cooled, filtered. On addition of pet. ether to the concentrated benzene solution, an orange solid (0.7 gm), m.p. 82°C, separated out which after recrystallisation from benzene-pet. ether mixture afforded the triphenyl tin derivative (0.5 gm), m.p. 83°C. The percentage of

	<u>C</u>	<u>H</u>	<u>H</u>	<u>Sn</u>
Found:	59.03	4.14	4.10	17.82
Calculated for				
C ₃₃ H ₂₇ O ₄ SnCl	59.17	4.03	4.18	17.73

IR spectrum : $\gamma_{as}^{+}(000)$ 1755 cm⁻¹

19. Reaction of triphenyl tin hydroside with L₁₁

A mixture of 1 gm. L₁₁, 1.2 gm triphenyl tin hydroside in 200 ml. dry benzene was stirred at R.T. for 24 hours and then filtered. On addition of pet. ether to the concentrated benzene solution, a red solid (0.5 gm), m.p. 85°C, appeared which after recrystallisation from benzene-pet. ether mixture afforded the triphenyl tin derivative (0.6 gm), m.p. 70°C.

The percentage of

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found:	61.22	4.48	4.27	17.76
Calculated for				
$C_{24}H_{30}O_5Sn$	61.33	4.51	4.21	17.85

IR spectrum : $\gamma_{ss}(000)$ 1750 cm^{-1}

(iii) Infrared Spectra: IR spectra reported in the present work were recorded with Beckman IR-20 infra red spectrophotometer using Nujol. Chloroform used for the solution phase spectra was of spectroscopic grade (S. Merck).

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CHAPTER - IV

ABSORPTION SPECTRA AND STRUCTURE OF THE
ORGANOTIN (ARYL AZO) PHENOXY ACETATES.

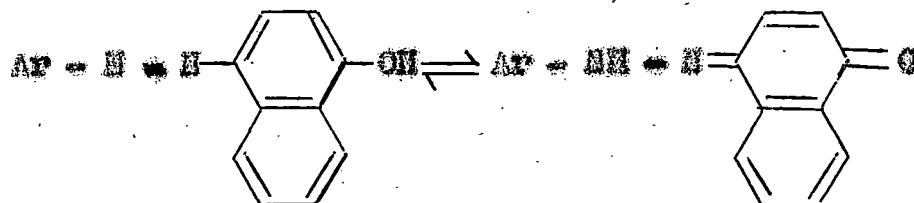
IVA. Introduction

The electronic spectra of azobenzene and related compounds have been studied extensively by several workers (1-14) and have been interpreted in terms of molecular orbital description (1,2,15,16). On the basis of these studies, the absorption bands in the UV - Visible region, which are generally, three to four in number, may be divided into two types. The longest wavelength, weak to moderate intensity band in azo benzene and related compounds ($\epsilon_{\text{max}} \approx 10^2 - 10^3$), is ascribed to the $n-\pi^*$ transition and the other more intense absorption bands ($\epsilon_{\text{max}} \approx 10^4$) are ascribed to $\pi-\pi^*$ transitions. While the position of the first $\pi-\pi^*$ band varies considerably from compound to compound, the position of the $n-\pi^*$ band is almost unaffected by the aryl groups and occurs at about 440 - 460 nm. This is easily explained in terms of MO treatment of the azo benzene system. The upper MO for the first $n-\pi^*$ and $\pi-\pi^*$ transitions is the perturbed orbital originating from the antibonding π orbital of the azo group and its energy is almost independent of the nature of the aryl groups. The lower orbital of the first $\pi-\pi^*$ transition is the orbital arising from the perturbation of the higher bonding π orbitals of the aryl groups and hence its energy largely depends on the aryl

groups. On the other hand, the lower orbital of the $n \rightarrow \pi^*$ transition being a non-bonding orbital of the azo group its energy is unaffected by the aryl groups.

Substituents like $-NH_2$, $-NMe_2$, $-OH$, $-COOH$ etc. which are capable of producing large bathochromic shift of the $\pi \rightarrow \pi^*$ transitions by extending the conjugation, may often shift the first $\pi \rightarrow \pi^*$ band in the azo compounds to such an extent that the characteristic $n \rightarrow \pi^*$ absorption is masked by the strong absorption. Thus methyl red which contains $-COOH$ and $-NMe_2$ groups in 3 and 4 positions respectively, no weak absorption band could be observed in the 440 - 460 nm region due to the presence of strong $\pi \rightarrow \pi^*$ absorption in this region (6). All the acetic acids and their derivatives investigated in the present work belong to this category and no separate band due to $n \rightarrow \pi^*$ transition could be observed in these compounds.

In the absence of specific solvent - solute interactions the electronic absorption spectra of the azo compounds do not show any strong solvent dependence apart from a small red shift of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands (1,17). However, the presence of $-OH$ group in the aryl part of the azo compounds often leads to a strongly solvent dependent absorption spectrum due to the possibility of (a) hydrogen bond formation by the phenolic $-OH$ group and/or (b) azo-hydrazone tautomerism as shown below (1).

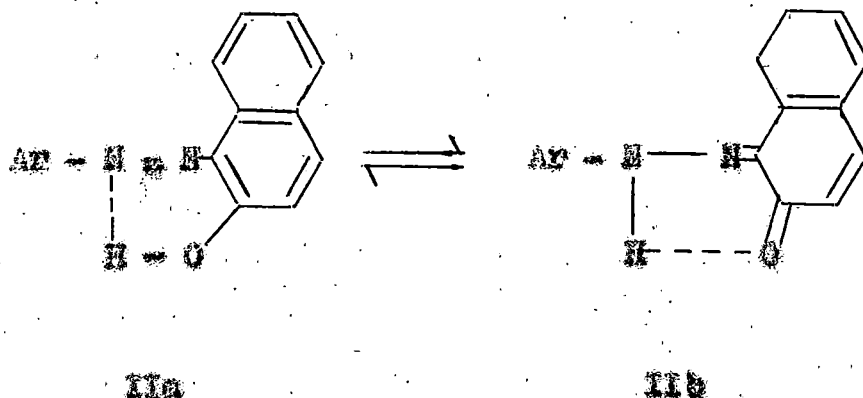


I

The azo-hydrazone tautomerism in hydroxy azo derivatives has been studied in great detail by several workers (3,7, 9,10,18). It has been found that the azo-hydrazone tautomeric equilibria, e.g., I, is important only in the azo naphthol series while no indication of the presence of hydrazone form could be found in the hydroxy azo-benzene and phenyl azonaphthols (3,19, 20).

In phenyl azonaphthols, the presence of an isobestic point in the visible absorption curves measured in a variety of solvents has been given as an evidence for the presence of the equilibrium I in phenyl azonaphthols (7). Both the azo and hydrazone forms may be stabilized in suitable donor solvents by external hydrogen bonds formed by the -OH and -NH group respectively. However, with a given solvent, the phenolic hydrogen generally forms stronger bonds than the -NH group and the concentration of azo form increases in the order : hexane < ethyl alcohol < benzene < chloroform < 50% ethyl alcohol < acetic acid, in contrast to observation in

aryl and 2-naphthol series. This effect is considerably enhanced by ortho substituents which sterically inhibit the formation of the external hydrogen bonds in the hydrazone tautomer and thus, unexpectedly low concentration of the phenyl hydrazone form is present in the ortho substituted 1-aryl and 4-naphthols (9). On the other hand, both the tautomers in 1-aryl and 2-naphthols (IIa, IIb) are unable to form external hydrogen bonds and the concentration of the more polar ketonic structure increases in the order of solvents:



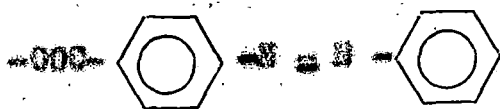
hexane < benzene < ethyl alcohol < chloroform < acetic acid < water, approximately in line with increasing dielectric constants (9).

Though a large number of metal complexes, particularly those of chromium, nickel, cobalt and copper, of

hydrazo and O-carboxy azo compounds have been prepared because of their importance in the dye industry, comparatively little attention has been paid to the study of the electronic spectra of the metal derivatives (5, 21-25). No detailed general account of the effect of co-ordination on the electronic spectra of the azo compounds is so far available. In the early work by Ernster and Brode (21), a comparison of the absorption spectra of a series of phenyl azo p-cresol, β -naphthol and β -naphthylamine derivatives with those of the copper, nickel and cobalt compounds has been made. The metal derivatives were found to exhibit a new band in the visible region together with the absorption bands corresponding to those found in the parent azo dye. The new bands in the metal complexes occur at the same position for a given metal, regardless of the dye with which it is combined and may therefore be ascribed to an electronic transition within the metal atom only.

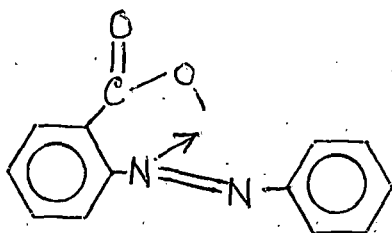
Absorption spectra of organotin derivatives of (aryl azo) benzoic acids have been reported by Majee and Banerjee (26) where it is shown that organotin (aryl azo) benzoates may be classified into three categories, viz., (i) derivatives of O-(aryl azo) benzoic acids where the coupling component has no donor groups (e.g., $-\text{NR}_2$, $-\text{OH}$, OMe etc.) at the ortho position, (ii) derivatives of O-(aryl azo) benzoic acids where the coupling component have a donor group at the

ortho position and (iii) derivatives of the p-(aryl azo) benzoic acids. This classification actually corresponds to ligating ability of the compounds. Thus the first group of compounds represent the derivatives of the ligands which are potentially bidentate, the second group represent potentially tridentate ligands while the p-carboxy ligands are only monodentate (III-V).



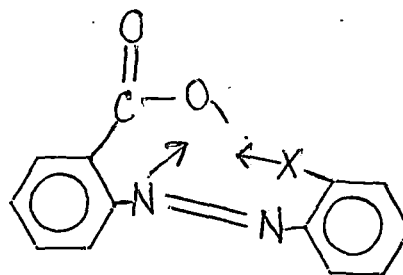
Monodentate

III



Bidentate

IV



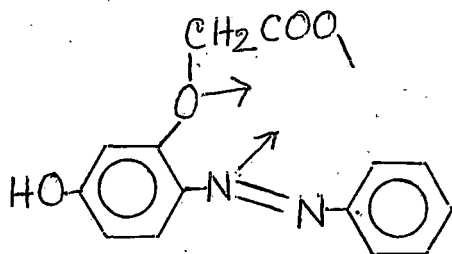
(X = -NR₂, -OH, -Ole)

Tridentate

V

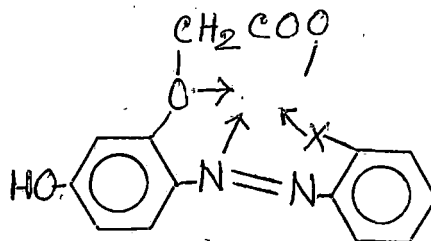
Because the stability of the complexes generally increase with the number of annelated chelate rings, complexes derived from V are usually more stable than those formed by IV, which in turn, is more stable than the p-(aryl azo) benzoates where $N(azo) \rightarrow N$ co-ordination is not possible. This is reflected in the solvent sensitivity of the absorption spectra of organotin complexes (26).

Although none of the aryloxy acetic acids used in the present investigation are terdentate (type VI), the O-substituted derivatives (type VII) are potentially tetradentate.



Terdentate

(VI)



Tetradentate

X = OH, OCH₃, F, Cl etc.

(VII)

Another interesting possibility is the azo-hydrazone tautomeric equilibrium of the following type.

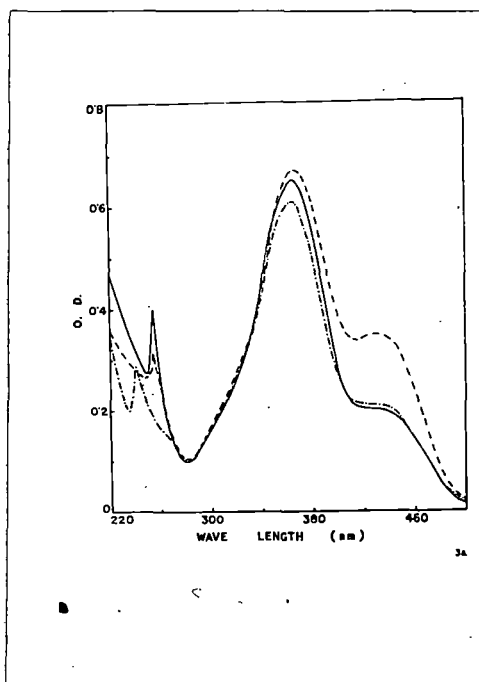


Fig. 1 Absorption spectra in methanol of
 1. L_1H ($3.6 \times 10^{-5} M$, - - - - -)
 2. Ph_3SnL_1 ($4.1 \times 10^{-5} M$, ————)
 3. Ru_3SnL_1 ($3.7 \times 10^{-5} M$, - · - · -)

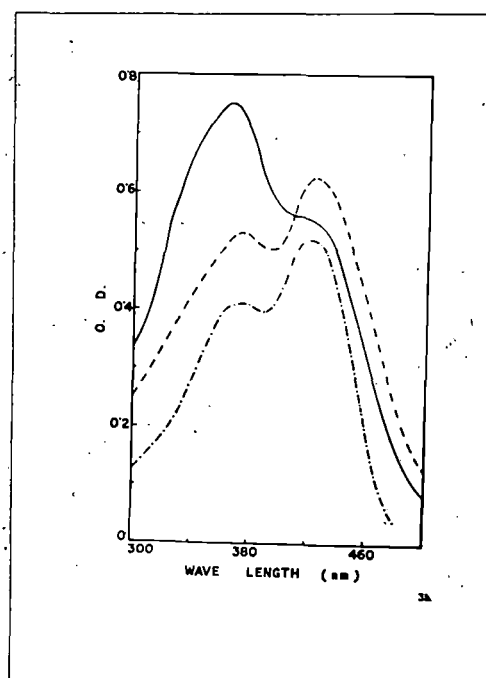
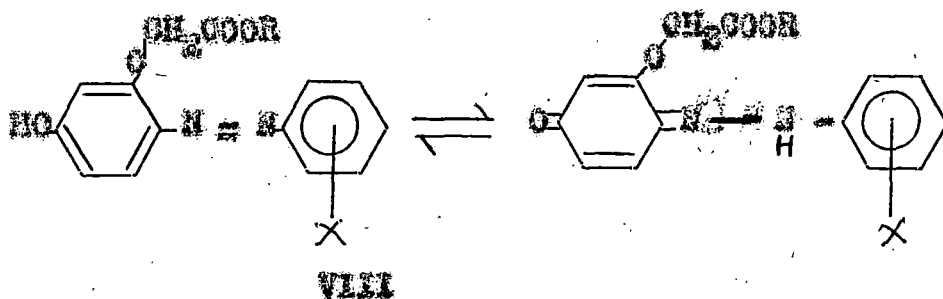


Fig. 2 Absorption spectra in benzene of
 1. L_1H (—————)
 2. Ph_3SnL_1 ($2.8 \times 10^{-5} M$, - - - - -)
 3. Ru_3SnL_1 ($3.76 \times 10^{-5} M$, - · - · -)



We shall now present electronic absorption spectral data which support the formation of π -coordinated triorganotin chelates in some cases.

IVB. Electronic Absorption spectra of the ligands and the abbreviation used for ligands are given in the preceding chapter. The spectral data for the aryloxy acetic acids and their organotin derivatives are given in Table 1. Absorption curves are also shown in figs. 1-24.

Table 1

Absorption Maxima in (Aryl ary) phenoxy acetic acids and their organotin derivatives.

Compound	Solvent	$\lambda_{\max}$ (m μ)	(log ϵ)	
1. I_3H	Methanol	240 (3.09)	365 (4.23)	430 ^a
	Benzene		365	420
2. Ph_3Sn-I_3	Methanol	265 (3.1)	365 (1.19)	150 ^a
	Benzene		370 (4.16)	420 (4.25)

Contd..

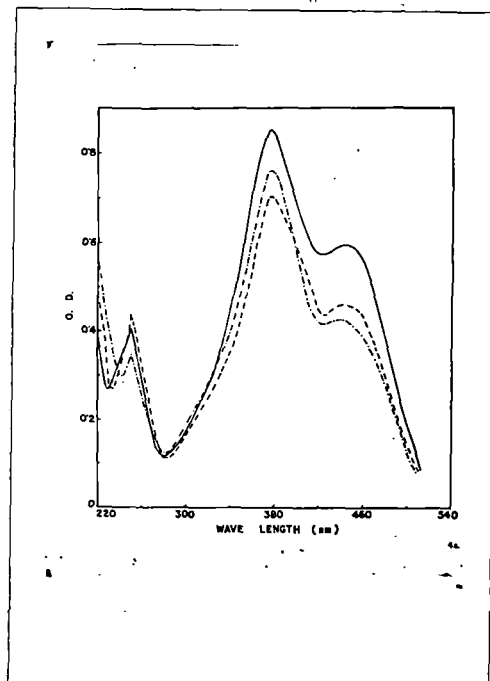


Fig. 3 Absorption spectra in methanol of
 1. L_3H (3.68×10^{-3} M, — — — —)
 2. Ph_3Al (5×10^{-5} M, — • — • —)
 3. Bu_3Al (3.26×10^{-5} M, — — — —)

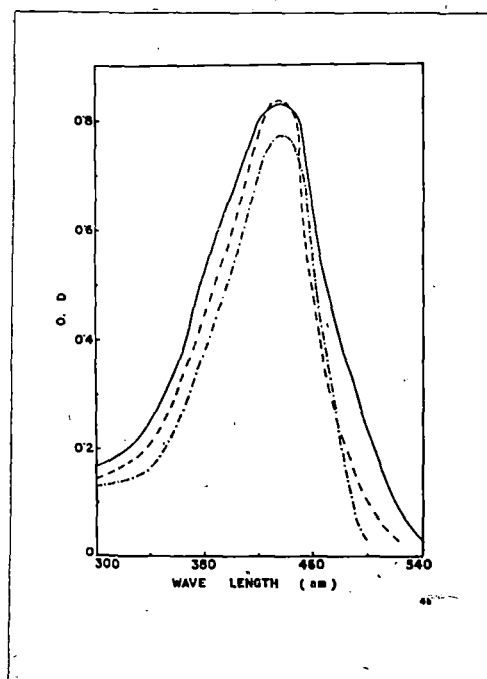


Fig. 4 Absorption spectra in benzene of
 1. L_3H (— — — —)
 2. Ph_3Al (3.7×10^{-5} M, — — — —)
 3. Bu_3Al (4×10^{-5} M, — • — • —)

Table - 1 (Contd..)

Compound	Solvent	λ_{max} (nm)	(log ϵ)	
3. $\text{Bu}_3\text{Sn-I}_2$	Methanol	235 (4.03)	363 (4.25)	430 ^a
	Benzene		372 (4.14)	422 (4.22)
4. I_2H	Methanol	270 (4.00)		450 (4.03)
	Benzene		372 (4.14)	422 (4.22)
5. $(\text{Ph}_3\text{Sn})_2\text{I}_2$	Methanol	274 (4.09)	375 (3.06)	530 (4.3)
			397 (3.09)	560 (4.31)
6. $(\text{Bu}_3\text{Sn})_2\text{I}_2$	Methanol	270 (4.36)	330 (4.2)	525 (4.36)
			325 (4.2)	360 (4.32)
7. I_3H	Methanol	230 (3.02)	374 (4.31)	437 (4.03)
			435	
8. Ph_3SnI_3	Methanol	250 (4.14)	375 (4.36)	437 (4.17)
	Benzene			435 (4.34)
9. Bu_3SnI_3	Methanol	250 (4.03)	375 (4.41)	440 (4.25)
	Benzene			435 (4.23)

Contd..

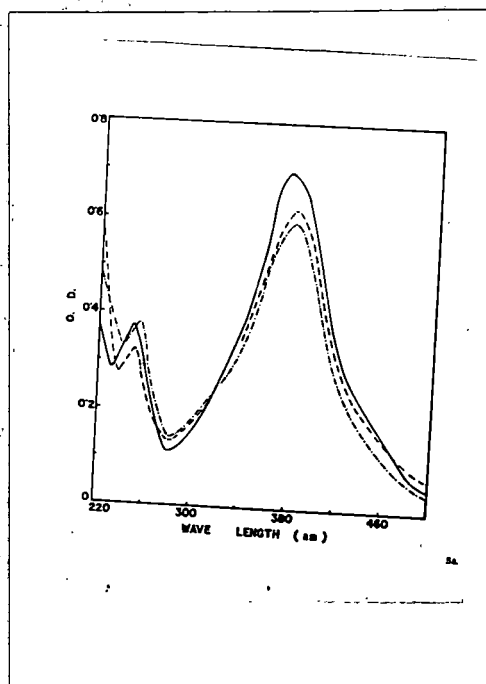


Fig. 5 Absorption spectra in methanol of
 1. L_4H ($3.55 \times 10^{-5} M$, ———)
 2. Ph_3SnL_4 ($3.3 \times 10^{-5} M$, - - - - -)
 3. Et_3SnL_4 ($3.9 \times 10^{-5} M$, - · - · -)

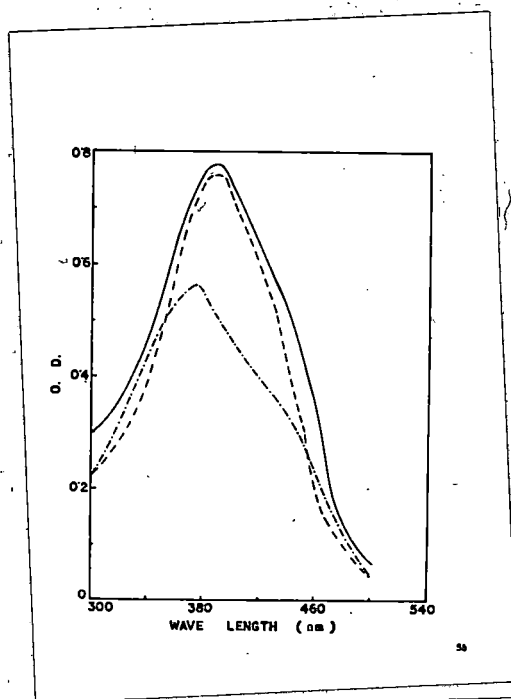


Fig. 6 Absorption spectra in benzene of
 1. L_4H (- - - - -)
 2. Ph_3SnL_4 ($4.7 \times 10^{-5} M$, - · - · -)
 3. Et_3SnL_4 ($4.1 \times 10^{-5} M$, ———)

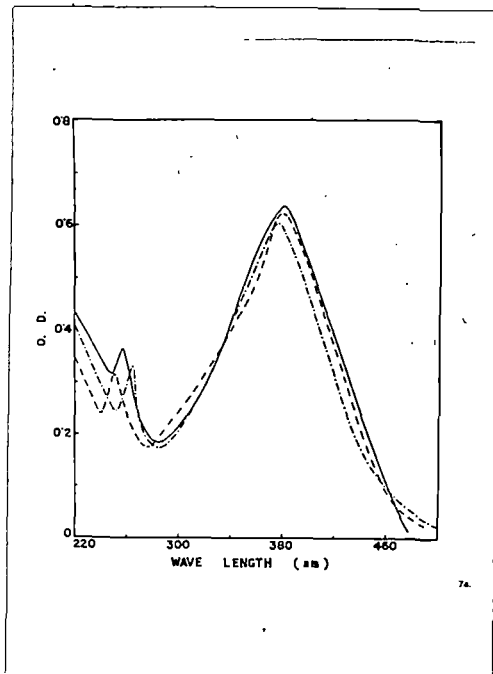


Fig. 7 Absorption spectra in methanol of
 1. L₅H (4.8×10^{-5} M, - · - · -)
 2. Ph₃SnL₅ (3.9×10^{-5} M, - - - - -)
 3. Bu₃SnL₅ (4.6×10^{-5} M, —————)

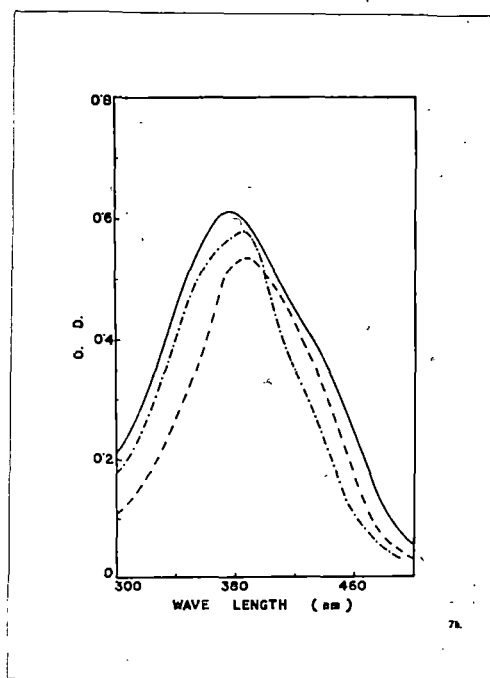


Fig. 8 Absorption spectra in benzene of
 1. L₅H (—————)
 2. Ph₃SnL₅ (3.2×10^{-5} M, - · - · -)
 3. Bu₃SnL₅ (3.1×10^{-5} M, - - - - -)

Table - 1 (Contd..)

Compound	Solvent	λ_{max} (nm)	(log ϵ)
10. I_2H	Methanol	250(4.02)	377(4.3)
	Benzene	375	430 ^a
11. Ph_3SnI_4	Methanol	254(4.06)	380(4.25)
			387(4.2) 430 ^a
12. Bu_3SnI_4	Methanol	250(3.09)	380(4.2)
			387(4.28) 440 ^a
13. I_3H	Methanol	265(3.15)	375(4.09)
		375	440 ^a
14. Ph_3SnI_5	Methanol	250(3.03)	380(4.2)
			387(4.26) 435 ^a
15. Bu_3SnI_5	Methanol	253(3.1)	380(4.14)
			387(4.53) 440 ^a
16. I_6H	Methanol	260(3.22)	435 (4.23)
	Benzene		415
17. Ph_3SnI_6	Methanol	270(3.39)	435 (4.19)
	Benzene		440 (4.52)
18. Bu_3SnI_6	Methanol	270(3.36)	434 (4.24)
	Benzene		440 (4.37)

Contd..

Table - 1 (Contd..)

Compound	Solvent	λ_{max} (nm)	(log ϵ)	
19. L_7H	Methanol	250(4.04)	370(4.24)	450 ^a
	Benzene		370	450 ^a
20. Ph_3SnL_7	Methanol	253(4.2)	370(4.26)	450 ^a
	Benzene		370(4.26)	450 ^a
21. Bu_3SnL_7	Methanol	256(4.13)	370(4.22)	450 ^a
	Benzene		370(4.3)	450 ^a
22. L_8H	Methanol	250(3.09)	370(4.14)	435 (4.00)
23. Ph_3SnL_8	Methanol	250(4.08)	370(4.26)	435 (4.04)
	Benzene		370 ^a	425 (4.33)
24. Bu_3SnL_8	Methanol	250(4.05)	370(4.24)	435 (4.01)
	Benzene		373 ^a	425 (4.36)
25. L_9H	Methanol	250(4.02)	372(4.33)	
	Benzene		370(4.11)	
26. Ph_3SnL_9	Methanol	250(3.06)	372(4.32)	
	Benzene		372(4.08)	

Contd..

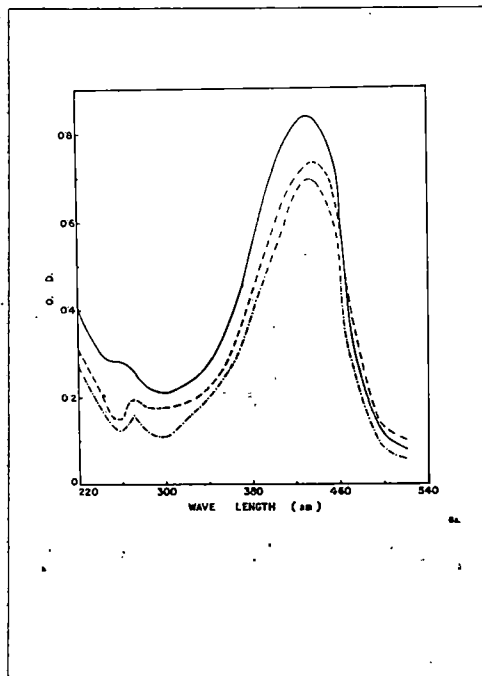


Fig. 9 Absorption spectra in methanol of
 1. LgH ($4.4 \times 10^{-5} M$, ———)
 2. Ph₃SnLg ($4.7 \times 10^{-5} M$, - - - -)
 3. Bu₃SnLg ($3.9 \times 10^{-5} M$, - . - . -)

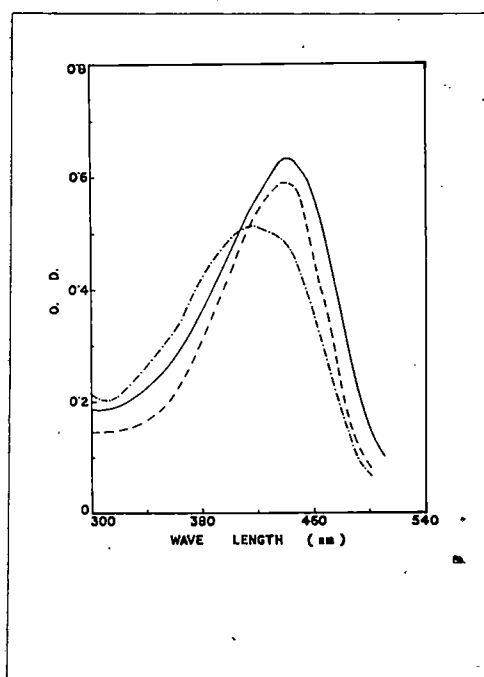


Fig. 10 Absorption spectra in benzene of
 1. LgH (- . - . -)
 2. Ph₃SnLg ($2.8 \times 10^{-5} M$, - - - -)
 3. Bu₃SnLg ($2.76 \times 10^{-5} M$, ———)

Table - 1 (Contd..)

Compound	Solvent	λ_{max} (nm)	(log ϵ)	
27. L_{10}	Methanol	258	375	
	Benzene		376	440 ^a
28. $\text{Ph}_3\text{SnL}_{10}$	Methanol	260(4.15)	375(4.35)	
	Benzene		375(4.40)	
29. L_{11}	Methanol	260	375	445
	Benzene			440
30. $\text{Ph}_3\text{SnL}_{11}$	Methanol	260(3.92)	375(4.26)	
	Benzene		375(4.24)	

a) Inflection or shoulder.

The electronic absorption spectra of almost all the compounds are characterized by the presence of three absorption bands in the UV - visible region. The lowest wave length peak in the 250-270 nm region undoubtedly originates from perturbed local excitation in the aryl groups, while the absorption in the visible region is associated with the $\pi - \pi^*$ (azo) transition.

An examination of the data given in Table 1 shows that the absorption characteristic of the organotin derivatives are generally very similar to that of the free ligands

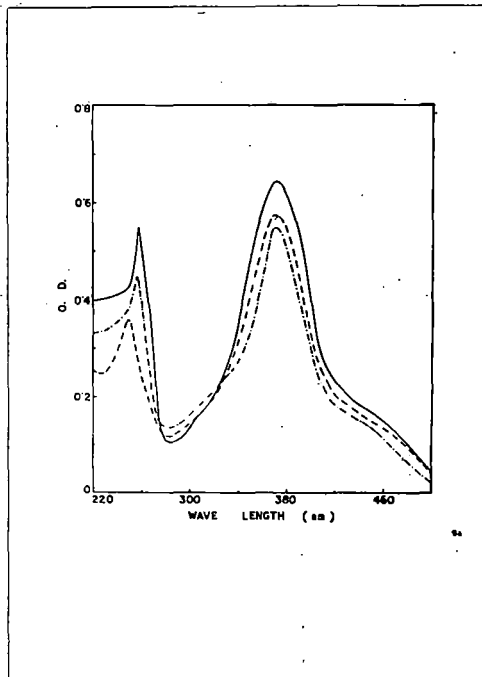


Fig. 11 Absorption spectra in methanol of
 1. L₇H (3.26×10^{-5} M, - - - - -)
 2. Ph₃NL₇ (3.6×10^{-5} M, ———)
 3. Bu₃NL₇ (3.3×10^{-5} M, - . - . -)

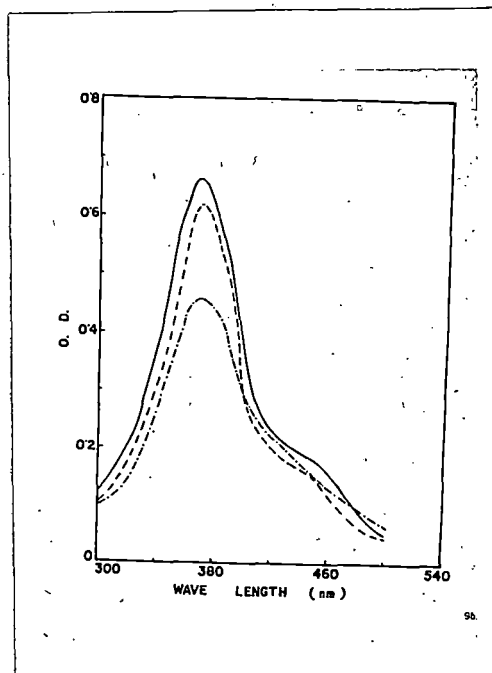
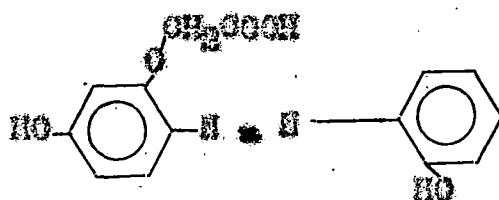


Fig. 12 Absorption spectra in benzene of
 1. L₇H (- . - . -)
 2. Ph₃NL₇ (3.6×10^{-5} M, ———)
 3. Bu₃NL₇ (3.3×10^{-5} M, - - - - -)

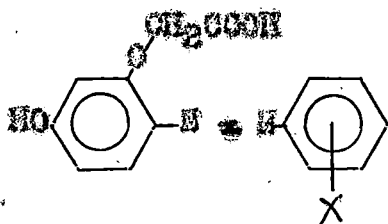
except where the ligand is a hydroxyl group at ortho position in the diazo moiety as in IX.



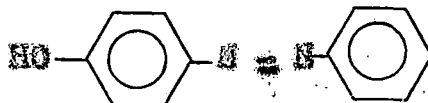
IX

A general feature of the absorption spectra of almost all the compounds is two absorption maxima in the visible region which suggests the presence of tautomeric equilibrium in solution.

In the absence of any tautomeric or solvent - solute equilibria, the absorption spectrum of the (2-benzene azo)-5-hydroxy phenoxy acetates (X) is expected to be closely similar to that of the 4-hydroxy azo benzene (XI) except for a small bathochromic shift that may arise due to the substituents in the aryl moiety of (X).



(X)



(XI)

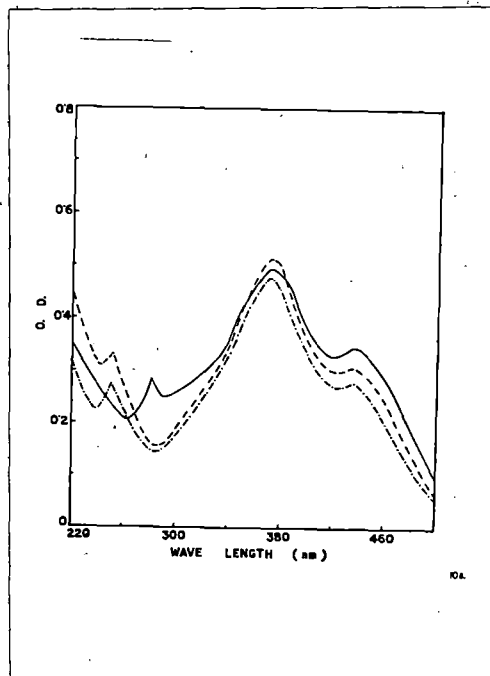


Fig. 13 Absorption spectra in methanol of
 1. L_pH ($3.5 \times 10^{-5} M$, ———)
 2. Ph_3SnHg ($2.8 \times 10^{-5} M$, - - -)
 3. Bu_3SnHg ($2.7 \times 10^{-5} M$, - . - .)

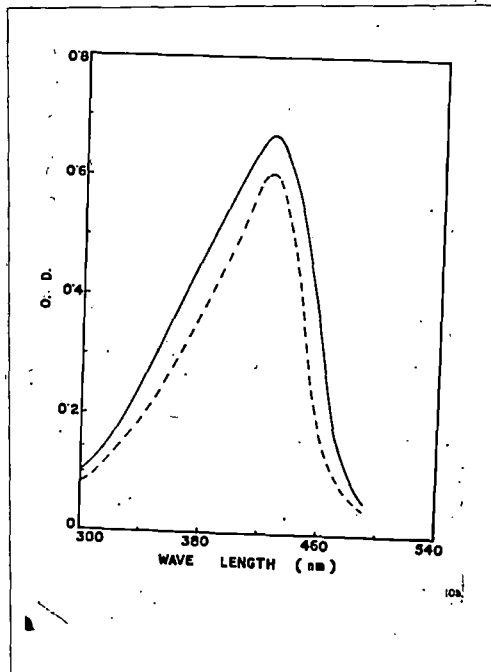


Fig. 14 Absorption spectra in benzene of
 1. Ph_3SnHg ($3.1 \times 10^{-5} M$, ———)
 2. Bu_3SnHg ($2.6 \times 10^{-5} M$, - - -)

The absorption spectrum of XI shows the presence of only one strong transition around 380 nm due to $\pi - \pi^*$ transition with a weak band at 436 nm due to $n - \pi^*$ transition.(1) All substituted derivatives of XI also show the presence of a single strong absorption band which occur in the range 350-390 nm depending on the substituent. Since compound (X) differs from the substituted 4-hydroxy azo benzene only by an acetoxy group which is not expected to show absorption in the same region if it exists in the azo form like the 4-hydroxy azo benzenes. In fact, almost all the compounds show an intense absorption in 360 - 390 nm. Obviously, this absorption is associated with $\pi - \pi^*$ transition in the azo form. The additional band at much longer wave length should be attributed to the presence of the hydrazone form in equilibrium with the azo form. This is consistent with known behaviour of the hydrazone form which always absorb at longer wave length compared to the corresponding azo form(23).

That azo-hydrazone equilibrium is responsible for the presence of two absorption bands in the visible region in the present compounds is conclusively demonstrated by the following observations.

Replacement of the H atom of the hydroxyl group by a methyl or octanyl group as shown in (XII) which eliminates the possibility of azo-hydrazone tautomerism results in a

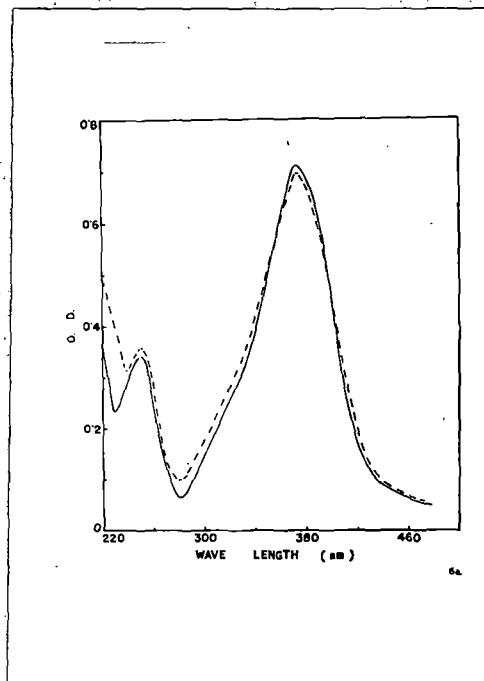


FIG. 15 Absorption spectra in methanol of
 1. LgH ($3.3 \times 10^{-5} M$, —))
 2. Ph_3SnH ($4.2 \times 10^{-5} M$, - - - -)

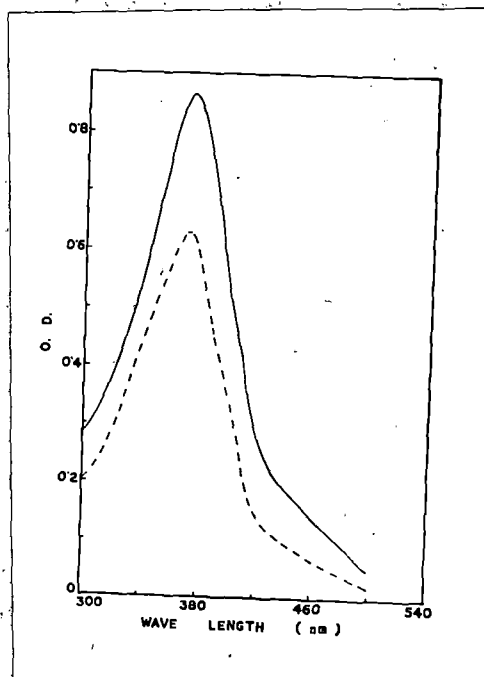
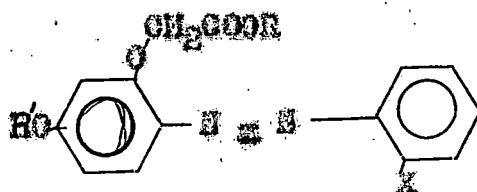


FIG. 16 Absorption spectra in benzene of
 1. LgH ($4.3 \times 10^{-5} M$, - - - -))
 2. Ph_3SnH ($3.5 \times 10^{-5} M$, —)

single absorption band at 370 nm.



$R = H, Ph_3Sn$; $R' = CH_3Ph_3Sn$

and $X = Cl, OCH_3$

(XII)

The long wave length absorption around $430 \overset{nm}{\mu s}$, thus eliminated whenever the possibility hydrazone form is eliminated clearly, the longest wave length absorption band around 420 - 450 nm region, when present, must be attributed to the presence of the hydrazone form. The data given in Table - 2 demonstrates this.

Table - 2

Visible absorption maxima in compounds of type XII.

Sl. No.	R	R'	X	Solvent	$\lambda_{max}(nm)$	Tautomer(s) present in solution
1.	H	H	Cl	Benzene	375, 430 ^a	Azo & Hydrazone
				Methanol	377	Azo

Contd..

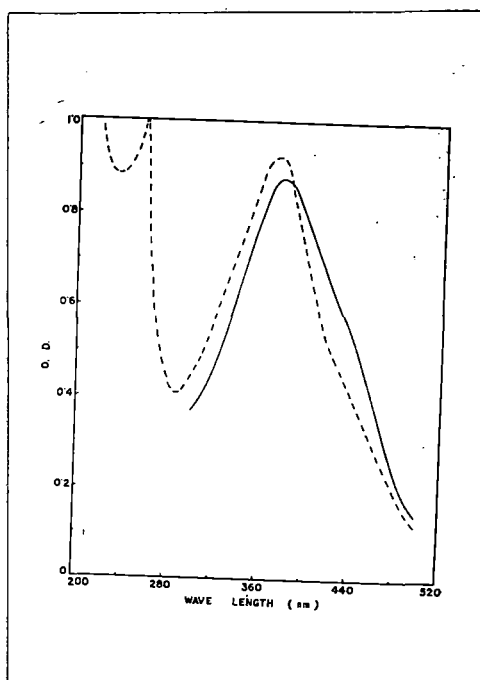


Fig. 17 Absorption spectra of

1. I_{10} in methanol (- - - -)
2. I_{10} in benzene (———)

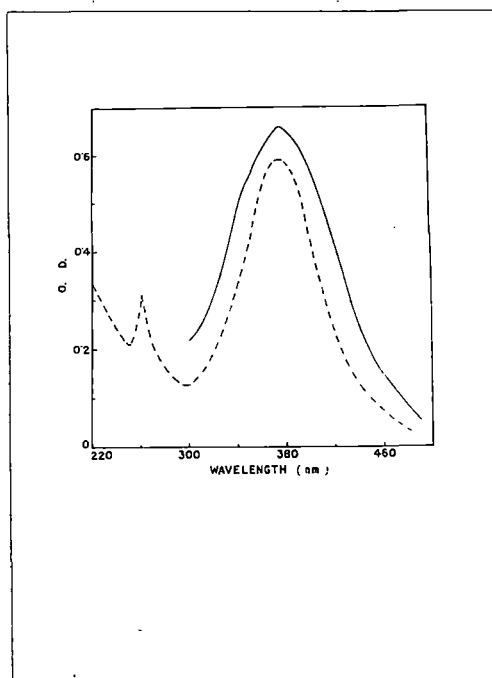


Fig. 18 Absorption spectra of

1. Ph_3SnI_{10} in methanol ($2.3 \times 10^{-5} M$, - - - -)
2. Ph_3SnI_{10} in benzene ($4.1 \times 10^{-5} M$, ———)

Table - 2 (Contd..)

Sl. No.	R	R'	X	Solvent	λ_{max} (nm)	Isomer(s) present in solution
2.	Ph ₃ Sn	H	Cl	Benzene	357, 438 ^a	Azo & Hydrazone
				Methanol	380	Azo
3.	Bu ₃ Sn	H	Cl	Benzene	367, 440 ^a	Azo & Hydrazone
				Methanol	380	Azo
4.	H	CH ₃	Cl	Benzene	370	Azo
				Methanol	370	Azo
5.	Ph ₃ Sn	CH ₃	Cl	Benzene	372	Azo
				Methanol	372	Azo
6.	CH ₃	Ph ₃ Sn	Cl	Benzene	375	Azo
				Methanol	375	Azo
7.	H	H	OCH ₃	Benzene	435	Hydrazone
				Methanol	374, 437	Azo & Hydrazone
8.	CH ₃	H	OCH ₃	Benzene	440	Hydrazone
				Methanol	373, 445	Azo & Hydrazone
9.	CH ₃	Ph ₃ Sn	OCH ₃	Benzene	375	Azo
				Methanol	375	Azo

a = Inflection or shoulder.

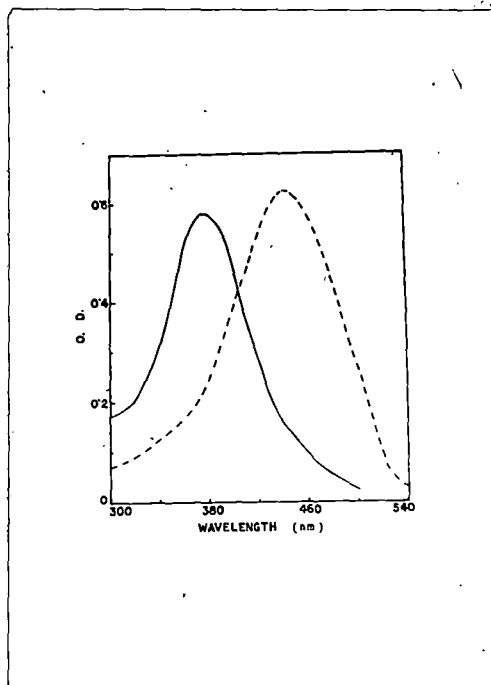


Fig. 19 Absorption spectra in benzene of
 1. L_{11} (- - - -)
 2. $\text{Ph}_3\text{SnL}_{11}$ (3.5×10^{-5} M, ———)

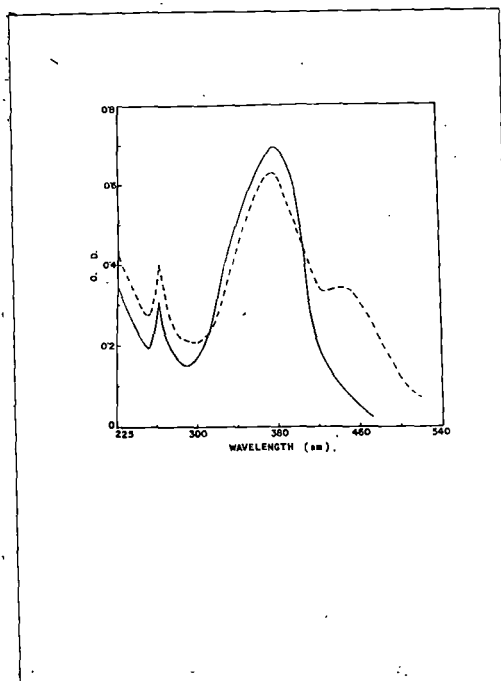


Fig. 20 Absorption spectra in methanol of
 1. L_{11} (- - - -)
 2. $\text{Ph}_3\text{SnL}_{11}$ (3.77×10^{-5} M, ———)

The data given in table - 2, clearly shows that presence of azo-hydrazones tautomeric equilibria in solution, the hydrazone form being favoured in the non polar solvent benzene. A quantitative study of this equilibrium is discussed in the next section.

IVC. Quantitative study of the Azo-hydrazone tautomeric equilibria in 2-(benzene azo) 5-hydroxy phenoxy acetic acids and their organotin derivatives.

It is of interest to make a quantitative study of the azo-hydrazone tautomeric equilibria in the 2-(benzene azo) 5-hydroxy phenoxy acetic acid, related molecules and their organotin derivatives in order to determine how this equilibrium is affected by the organotin group.

Let us represent the equilibrium as



where the tautomeric equilibrium constant K_T is given by

$$K_T = [H] / [A] \quad \dots (2)$$

$[H]$ and $[A]$ respectively, denote the equilibrium concentration of the hydrazone form, H and the azo form, A.

Spectrophotometric estimation of the equilibrium constant is quite simple in principle provided the molar

extinction co-efficients of each form is known at suitable wave lengths, preferably at the absorption maximum of the azo form or that of the hydrazene form.

Assuming the validity of Beer's law, the optical density, D_λ at any wave length λ , of a solution having a molar concentration C , is given by

$$D_\lambda = \{ \epsilon_\lambda^A [A] + \epsilon_\lambda^H [H] \} \cdot l \quad \dots (3)$$

where ϵ_λ^A and ϵ_λ^H are the molar extinction of the azo and the hydrazene form respectively, l is the path length of the cell.

The total concentration of the solute is given by

$$C = [A] + [H] \quad \dots (4)$$

Combining equation (3) and (4) we obtain

$$[A] = [D_\lambda / l - \epsilon_\lambda^H \cdot C] / [\epsilon_\lambda^A - \epsilon_\lambda^H] \quad \dots (5)$$

and

$$[H] = [C \cdot \epsilon_\lambda^A - D_\lambda / l] / [\epsilon_\lambda^A - \epsilon_\lambda^H] \quad \dots (6)$$

Substituting in equation (3), we get

$$K_T = (0. \epsilon_{\lambda}^A - D_{\lambda}/l) / (D_{\lambda}/l - \epsilon_{\lambda}^B . 0) \quad \dots (7)$$

Thus the equilibrium constant can be easily determined from a single spectrophotometric measurement provided the molar extinction co-efficient of each form is separately known.

The problem is, however, complicated by the fact that the solution in any solvent contains both the forms in equilibrium making it difficult to determine the molar extinction co-efficient of each form separately without a knowledge of the equilibrium constant. Further, the equilibrium cannot be shifted almost completely in any direction except by changing the solvent often the change in solvent not only introduces drastic change in absorption maxima and molar extinction co-efficient, it is not always possible to find a solvent in which only one form exists.

In order to overcome this difficulty the following approach has been adopted in the present work.

It is well known that the integrated molar absorption is not only theoretically significant (1,27), but is a more reliable experimental measure of absorption than the molar extinction co-efficient which is affected by a variety of parameters. Unlike molar extinction, the integrated molar absorption of a compound is not strongly affected by change of solvent though the band maximum may undergo considerable

shift. Experimental determination of integrated absorption is, however, more difficult. Fortunately, the absorption bands of most compounds may be closely approximated by gaussian curve of the following type

$$A_{\nu} = A_{\max} \exp \left[-b \left\{ (\nu - \nu_{\max}) / \Delta\nu_{1/2} \right\}^2 \right] \quad \dots (3)$$

where

A_{ν} = absorbance at the frequency

$A_{\max}$ = absorbance at the band maximum

$\nu_{\max}$ = frequency of the band maximum

$\Delta\nu_{1/2}$ = band half width

and $b = \log e^2 = 2.772$

The advantage of expressing the experimental band shape in terms of analytical functions, such as equation (3), lies in the calculation of integrated absorbance (A) which is given by,

$$A = \int_{\text{band}} A_{\nu} d\nu = 1.065 \cdot A_{\max} \cdot \Delta\nu_{1/2} \quad \dots (3)$$

The absorbance data over the visible region of the spectrum were fitted to gaussian curve given by equation (3) by least square method. It was observed that the absorbance data of compounds showing only a single absorption peak in this region (without any inflexion or marked band) can be expressed by equation (3). In case of compounds showing evidence of azo-hydrazone tautomerism, the optical data can be fitted by a linear combination of two such curves, one corresponding to the azo form and the other corresponding to the hydrazone form. The integrated absorbance corresponding to each band can then be taken to be proportional to the concentration of each tautomer in the solution. That such an assumption is experimentally justified may be seen from the data given in Table 3. The data clearly shows that total integrated absorption of a given ligand or its organotin derivatives remain nearly constant although the intensity of the two bands vary widely due to variation in the relative concentrations of the azo and the hydrazone form which vary from compound to compound and also from solvent to solvent. The constancy of the total integrated intensity, therefore, shows that the integrated molar absorbance of the two forms are equal.

Table - 3

Integrated molar absorbances of the visible absorption band of 2-(benzene azo) 5-hydroxy phenoxy acid, related compounds and their organotin derivatives.

Compound	Solvent	$\lambda_{\max}$ (nm)	Total integrated molar absorbance $\times 10^3$ (litre mole ⁻¹ cm ⁻¹ sec ⁻¹)
1. Ph ₃ SnL ₁	Benzene	370,420	1.3
2. Bu ₃ SnL ₁	Methanol	366,430	1.3
3. Ph ₃ SnL ₂	Benzene	367,430	1.1
4. L ₂ H	Benzene	370	1.00
5. Ph ₃ SnL ₃	Benzene	372	1.00
	Methanol	372	1.1
6. L ₇ H	Methanol	370,460	1.12
7. Ph ₃ SnL ₇	Methanol	370,450	1.16
	Benzene	370,450	1.12
8. Bu ₃ SnL ₇	Benzene	370,450	1.06
9. Ph ₃ SnL ₈	Methanol	370,435	1.44
	Benzene	370,425	1.43
10. Bu ₃ SnL ₈	Methanol	370,435	1.6
11. Ph ₃ SnL ₁₀	Methanol	375	1.38
	Benzene	375	1.47
12. Ph ₃ SnL ₁₁	Methanol	375	1.29
	Benzene	375	1.19

It is, therefore, reasonable to use the following relations:

$$K_T = \frac{[H]}{[A]} = \frac{A_h}{A_a} \quad \dots (10)$$

where $[H]$ and $[A]$ are the equilibrium concentrations of the hydrazones and the azo form respectively and A_h and A_a are the corresponding integrated absorbance in a given solution.

Using a computer programme which fits the absorbance data over the visible region of spectrum in terms of two superimposed gaussian bands such that the square of the residual is minimum, the integrated absorbance as well as their ratio which is equal to the equilibrium constant K_T were determined. These are given in Table 4. The calculated absorption maxima of the azo and the hydrazone forms are also included in table 4.

Table - 4

Integrated absorbance and azo-hydrazone tautomeric equilibrium constant in 2-(benzene azo) 6-hydroxy phenoxy acetic acid, related compounds and their organotin derivatives.

Compound	Solvent	Azo form		Hydrazone form		K_T
		λ_{max}^{a*} (nm) $A_a \times 10^3$	$A_a \times 10^3$	λ_{max}^{a*} (nm) $A_h \times 10^3$	$A_h \times 10^3$	
1. I_2H	Methanol	358	3.79	440	0.30	0.08
	Benzene	347	3.53	426	1.50	0.37

Contd..

Table - 4 (Contd..)

Compound	Solvent	azo form		Hydrazone form		K_T
		ϵ^* λ_{max}	(nm) $A_{\epsilon} \times 10^3$	ϵ^* λ_{max}	(nm) $A_{\epsilon} \times 10^3$	
2. Ph_3SnL_1	Methanol	358	3.33	454	0.44	0.11
	Benzene	380	2.31	420	1.52	0.68
3. Bu_3SnL_1	Methanol	363	4.26	445	0.54	0.13
	Benzene	346	3.24	425	2.62	0.51
4. L_2H	Methanol	371	5.04	461	0.73	0.14
5. Ph_3SnL_2	Methanol	376	4.97	460	0.65	0.13
6. Bu_3SnL_2	Methanol	376	5.96	460	0.94	0.16
7. L_2H	Benzene	355	5.07	434	0.32	0.04
8. Ph_3SnL_2	Benzene	374	4.97	430	0.21	0.04
9. Bu_3SnL_2	Benzene	346	5.40	440	0.23	0.04
10. L_2H	Benzene	369	5.37	457	0.14	0.03
11. Ph_3SnL_3	Benzene	373	4.43	424	0.25	0.05
12. Bu_3SnL_3	Benzene	373	3.52	430	0.39	0.11
13. L_2H	Methanol	367	3.45	463	0.21	0.06
	Benzene	368	2.79	463	0.31	0.11
14. Ph_3SnL_7	Methanol	367	3.75	463	0.25	0.07
	Benzene	365	3.76	459	0.30	0.08
15. Bu_3SnL_7	Methanol	366	2.91	437	0.23	0.08
	Benzene	363	3.13	452	0.27	0.08

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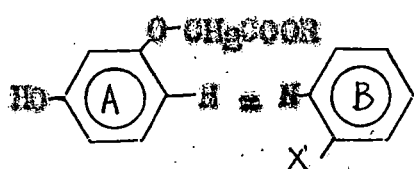
Table - 4 (Contd..)

Compound	Solvent	Azo form	λ_{max}	$A_{\text{max}} \times 10^3$	Hydrazone form	λ_{max}	$A_{\text{max}} \times 10^3$	K_T
		λ_{max}			λ_{max}			
16. L_9H	Methanol	371		3.77	457		0.52	0.13
17. Ph_3SnL_9	Benzene	355		1.67	420		2.77	1.6
18. Ph_3SnL_9	Methanol	264		3.50	450		0.23	0.06
	Benzene	376		1.64	426		1.62	1.00
19. L_9H	Methanol	366		4.33	-		-	-
	Benzene	360		4.30	-		-	-
20. Ph_3SnL_9	Methanol	366		4.54	-		-	-
	Benzene	365		3.3	-		-	-
21. L_{10}	Methanol	362		9.2	-		-	-
	Benzene	371		8.4	4.23		0.20	0.02
22. $\text{Ph}_3\text{SnL}_{10}$	Methanol	371		3.6	-		-	-
	Benzene	372		6.1	-		-	-

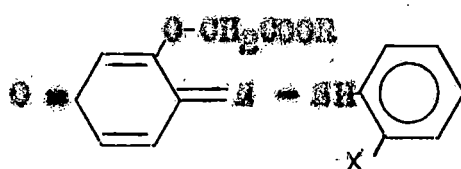
λ_{max} - The absorption maxima given in this table were obtained by least square fit of the optical density data in the visible region in terms of gaussian functions [eqn. ² (8)]

Data given in table 4 shows the following trends:

(i) The azo form predominates over the hydrazone form both in polar and non-polar solvents in compounds where the Diazo moiety (ring B) contains a substituent in the ortho position as shown below:



(XIII A)



(XIII B)

R = H, CH₃, Et, Sn -, Ph, Sn -

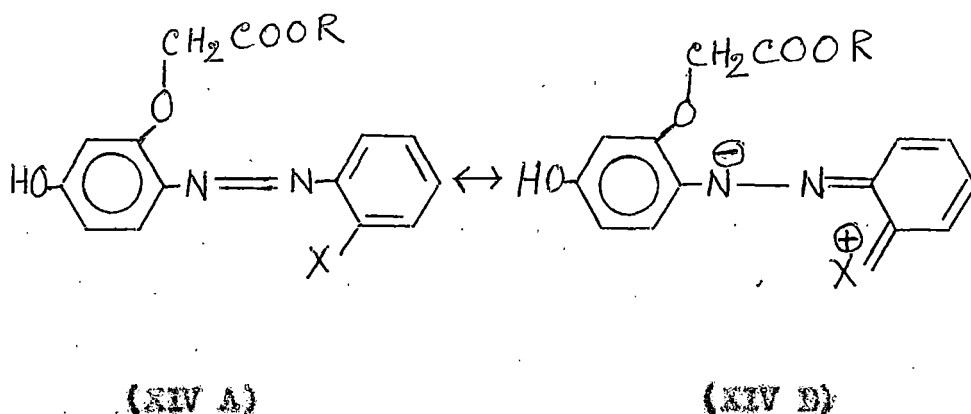
X = Cl, F, OCH₃

(ii) The absence of O-substituent (X = H in XIII) shifts the equilibrium markedly, in favour of the hydrazone form in the organotin derivatives (compounds Nos. 3, 5, 17, 18, Table 4).

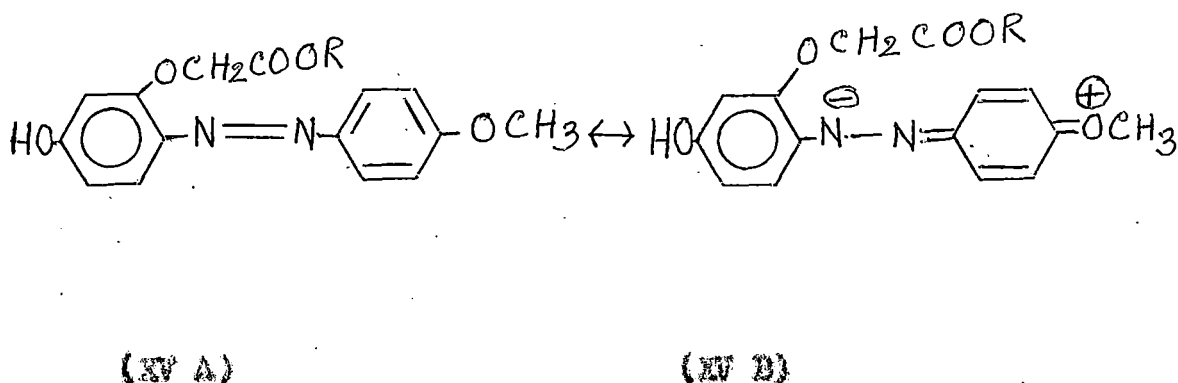
(iii) As expected non polar solvent like benzene stabilizes the hydrazone form compared to that in methanol as shown by the marked increase in the equilibrium constant.

The predominance of the azo form in O-substituted compounds in other series have been attributed to steric factors (9). While steric factors may have some role, another more likely reason for the increased stability of the azo -

form compared to the hydrazone form in O - substituted compounds in the possibility of resonating structure of the type XIVB.

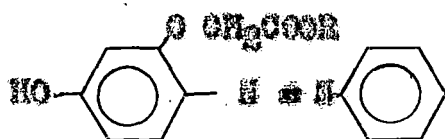


Since resonance structure of type XIVB is not possible in the hydrazone form, this would tend to destabilize the hydrazone form compared to the azo form. That this is contributing factor is shown by p-substituted compounds where the azo form again predominates

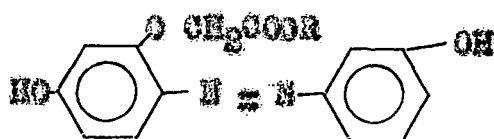


R = H, PhCON -, Et3CN -

For example, the equilibrium constant of the p-methoxy derivatives (compounds nos. 13,14,15) and o-methoxy derivatives (compound nos. 4,5,6) are nearly equal. In fact, calculated equilibrium constants are somewhat lower in the p-methoxy derivatives. Since steric factors cannot be involved in the p-methoxy compounds, the effect must be attributed to resonance shown in (XIV) and (XV). The equilibrium constants of (XVI) and (XVII) lend further support to this



(XVI)



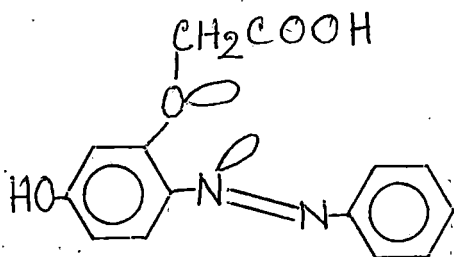
(XVII)

The equilibrium constants of (XVI) and (XVII) respectively, in methanol are 0.09, 0.13 (R = H); 0.11, 0.12 (R = Ph₃Sn -) and 0.13, 0.06 (R = Bu₃Sn -). Thus, the meta substituent, in contrast to ortho - or para substituent, has no effect on the eno - hydrazone tautomeric equilibrium. This, however, is not surprising since resonance of the type shown in (XIV) and (XV) are not possible in the m-substituted derivatives.

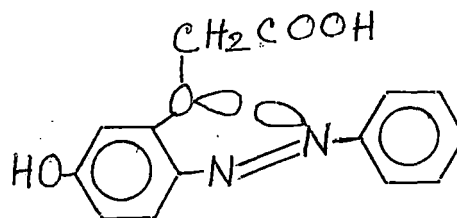
IVD. Electronic spectra of the organotin derivatives and probable structure.

Excepting the organotin derivatives of ligand (IX) which will be separately discussed because of the many interesting features associated with them, the spectra of the organotin derivatives are very similar to that of the ligand in the position of the absorption maxima except for some modification in the azo-hydrazone equilibria as discussed in the preceding section.

The steric effects of ortho substituents in the azo azo dyes and their preferred geometry has been discussed by Griffiths (23). The same considerations show that to minimize steric interaction between the nitrogen lone pair electrons and the ortho acetoxy group (the oxygen atom has also lone pairs) structure (XVIII) will be preferred to (XIX) since a very strong lone pair lone pair interaction is expected in the later.



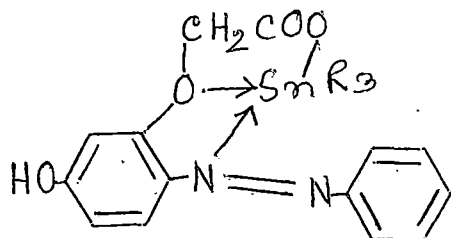
(XVIII)



(XIX)

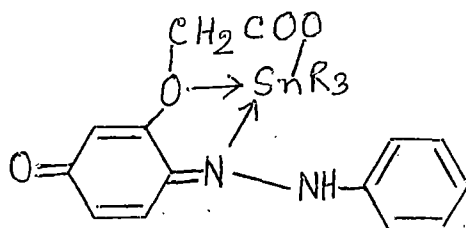
The possible conformation of the ligands showing lone pair lone pair interaction.

For steric reasons, the organotin derivatives are therefore likely to have structure (XX) in the azo form and (XXI) in the hydrazone form.



(XX)

Probable structure of the azo form of the organotin derivatives.

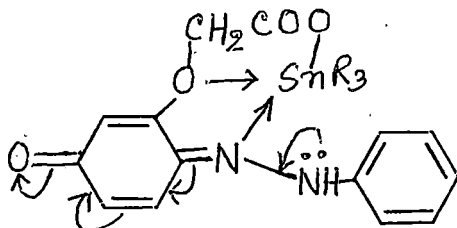


(XXI)

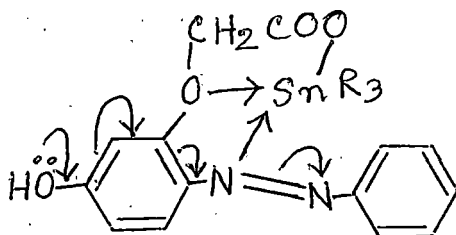
Probable structure of the hydrazone form of the organotin derivatives.

As shown in (XXII), the visible transition in the hydrazone form is typically a donor - acceptor transition.

the amino group being the donor and the carboxyl group, the acceptor (28). The direction of charge migration is opposite to that in the azo form (XXIII).



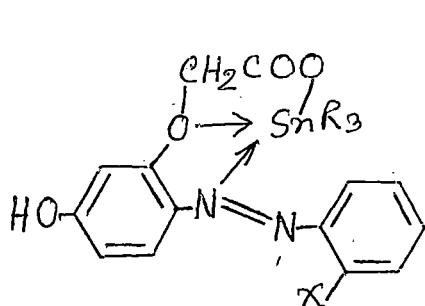
(XXII)



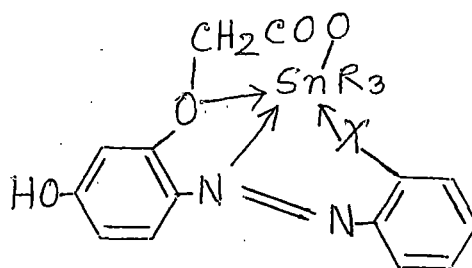
(XXIII)

In both the case π -atom co-ordinated to the organotin group is not directly involved in the charge migration and the co-ordination by the organotin group is therefore likely to have very little effect on the visible spectrum, a fact amply borne out by the experimental data given in Table -1.

In the presence of a donor substituent in the ortho position to the azo group in the other benzene ring (diazobenzene), the organotin derivatives may have two possible structures (XXIV) and (XXV) (only the azo form is shown), the tin atom is 6-co-ordinated in the former and 7-co-ordinated in the later.



(XXIV)



(XXV)

Structure (XXIV) being similar to (XXIII), the visible spectrum of the organotin derivative is expected to be almost similar to that of the free ligand in line with the other compounds where the substituent X is absent. However, co-ordination by the group/atom X which renders the tin atom 7-co-ordinated as in (XXV) is expected result in a bathochromic shift because of the expected formal

positive charge on the donor on co-ordination. This would facilitate electron migration from the hydroxyl group to the azo group as shown in (XXIII) resulting in a bathochromic shift. Examination of the absorption data given in Table I show such bathochromic shift in ortho fluoro- and ortho-chloro compounds (No. 11,12,14,15), although no such shift is observed in the ortho methoxy compound. This is not surprising as an examination of a model shows steric over crowding in a structure of type (XIV) when $X = \text{OCH}_3$, but not with $X = \text{F}$ or Cl . Thus, the chloro and fluoro substituted organotin derivatives are to be regarded as 7-co-ordinated while that of the methoxy derivative is most likely a 6-co-ordinated compound of type (XXII) or (XXIII).

IVB. Absorption spectra and probable structure of Bis-(trioorganotin) derivatives of 2-(2'-hydroxy benzene azo), 5-hydroxy phenoxy acetic acid (IX).

As mentioned in Chapter III, 2-(2'-hydroxy benzene azo), 5-hydroxy phenoxy acetic acid always furnished a bis (trioorganotin) derivative which may be formulated as follows:

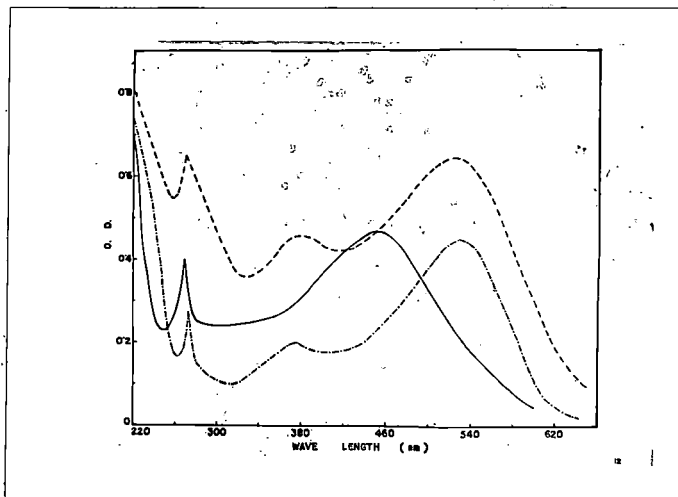


Fig. E1 Absorption spectra in methanol of
 1. I_2H ($3.2 \times 10^{-5} M$, —))
 2. $(Ph_3Sn)_2I_2$ ($2.24 \times 10^{-5} M$, - - - -))
 3. $(Bu_3Sn)_2I_2$ ($2.3 \times 10^{-5} M$, - . - . -))

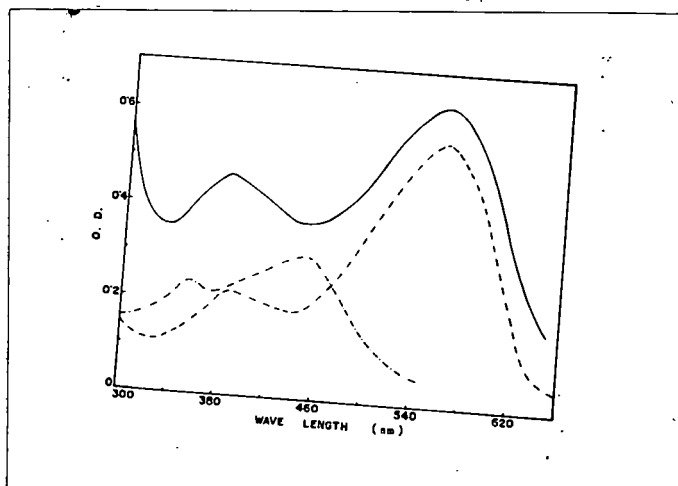
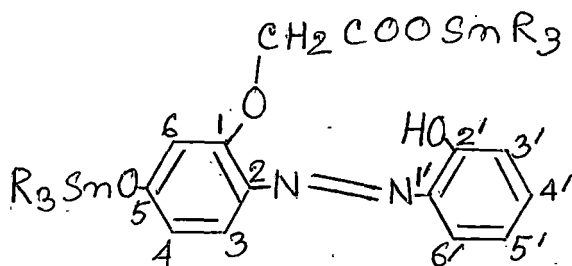


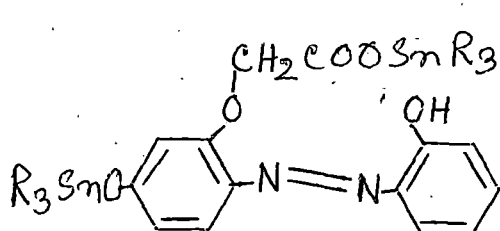
Fig. E2 Absorption spectra in benzene of
 1. I_2H (- . - . -))
 2. $(Ph_3Sn)_2I_2$ ($2.73 \times 10^{-5} M$, - - - -))
 3. $(Bu_3Sn)_2I_2$ ($3 \times 10^{-5} M$, —))



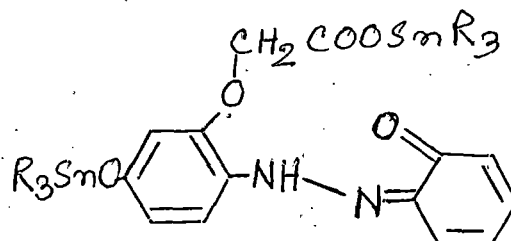
(XVI)

These derivatives are characterized by an extremely large bathochromic shift of the longest wave length visible absorption maxima in the free ligand (figs. 21, 22). For example, the longest wave length absorption in the ligand occurs at 450 mμ in benzene while the absorption maxima occurs at 560 mμ in the same solvent in the Bis (tributyl tin) or Bis (triphenyl tin) derivatives.

The ligand as well as the organotin derivatives show two absorption maxima in the visible region. In view of our discussion, this is to be expected because of the presence of keto-hydrazone equilibrium as shown below:



(XVII A)



(XVII B)

It should be noted that it is the -OH group in the diazo component that takes part in azo-hydrazone tautomerism in contrast to other compounds so far discussed where the -OH group is present on the coupler component. The hydrate form in these compounds may be regarded as ortho quinone derivatives (XVIII) in contrast to (XII) which may be regarded as para quinone derivatives.

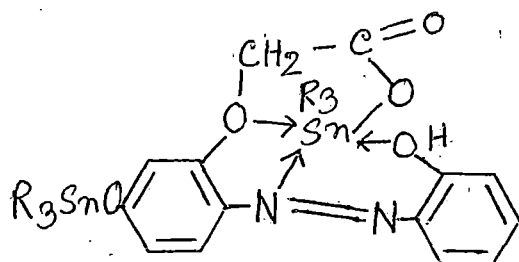
A summary of the absorption data is shown in Table 1 and the equilibrium constant for the tautomeric equilibrium calculated according to the method discussed in Sec. IV C is given in Table 5.

Table - 5

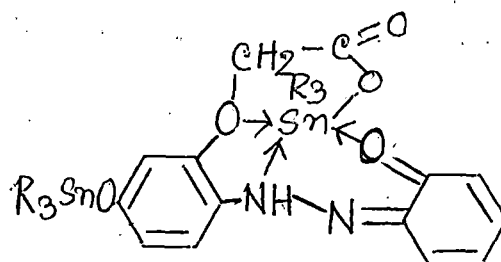
Visible absorption maxima and tautomeric forms of the ligand and organotin derivatives of type XVI.

Compound	Solvent	Azo form		Hydrazone form		λ_T
		$\epsilon \times 10^3$	$\lambda_{max} (nm)$	$\epsilon \times 10^3$	$\lambda_{max} (nm)$	
1. Ligand (IX) (LgH)	Methanol	-	-	2.55	450	-
	Benzene	1.55	555	2.15	430	1.56
2. (DugH) ₂ Lg	Methanol	1.55	580	2.14	526	1.37
	Benzene	1.43	585	2.60	560	1.51
3. (Ph ₃ H) ₂ Lg	Methanol	1.35	575	1.84	530	1.36
	Benzene	1.33	597	2.37	560	1.78

Considerable bathochromic shift of the absorption maxima both in the azo form and the hydrazone form suggests strong co-ordination with 7-co-ordinated structure as shown below:



Azo form



Hydrazone form

A strong co-ordinate bond by the ketonic oxygen atom in the hydrazone form would increase its acceptor strength thereby facilitating the charge migration during the transition depicted in (XVII). This explains the large bathochromic shift observed in the organotin compounds.

IVF. Effect of alkali on the absorption spectra of organotin derivatives.

It has been shown by Majee and Banerjee (29) by spectrophotometric titration of organotin (aryl azo) benzoates that the case of cleavage of the Sn-O bond by $\text{OH}^{(-)}$ represented by the eqn. (11) is related to the co-ordination no. of the tin atom.

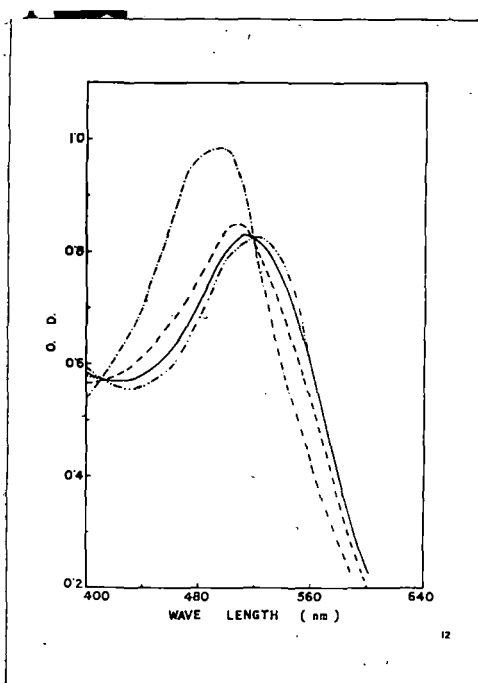
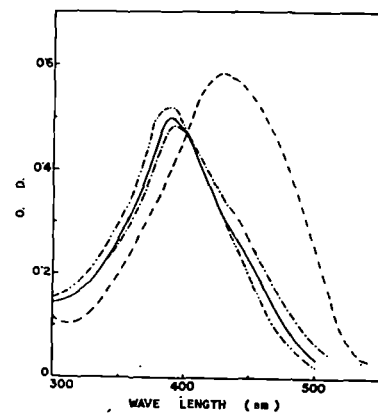


Fig. 23 Absorption spectra in methanol of

1. $(\text{Ph}_3\text{Sn})_2\text{I}_2$ ($3.8 \times 10^{-5} \text{ M}$, - - - - -)
2. " 0.5 equivalent NaOH (———)
3. " 1 " " (———)
4. " 2 " " (- - - -)
5. " 10 " " (- . . . -)

Fig. 24 Absorption spectra in methanol of

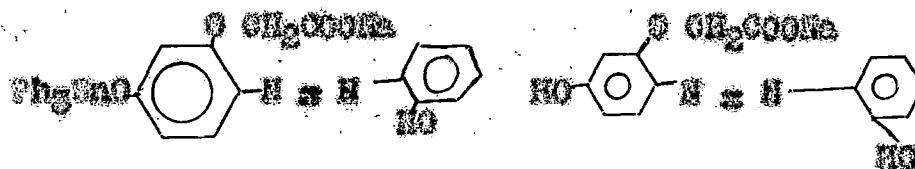
1. Ph_3SnI_2 ($2.9 \times 10^{-5} \text{ M}$, - - - - -)
2. " 1 equivalent NaOH (———)
3. " 10 " " (- . . . -)
4. " 30 " " (- - - -)





For example, the penta co-ordinated derivatives were found to cleave almost quantitatively by equivalent amount alkali whereas the 6-co-ordinated compounds were very stable towards alkali. It is therefore expected that the 7-co-ordinated compounds, if formed should be more resistant to cleavage by alkali.

The effect of methanolic NaOH on B10 (triphenyl) tin derivative is shown in fig. 23. The presence of isobestic point implies an equilibrium involving two absorbing species. Use of even tenfold excess of NaOH does not, however, change the spectrum into that of the ligand under same alkali concentration. Obviously both the triphenyl tin groups are not cleaved by alkali. The cleavage of the Ph_3Sn group bound to the carboxyl group as in XXVIII should result in a spectrum similar to that of the Na salt of the dye (XXIX)



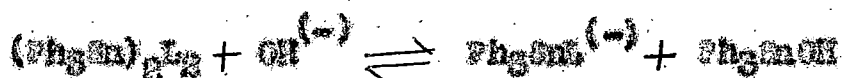
$$\lambda_{\text{max}} = 455 \text{ nm}$$

(XVIII)

$$\lambda_{\text{max}} = 450 \text{ nm}$$

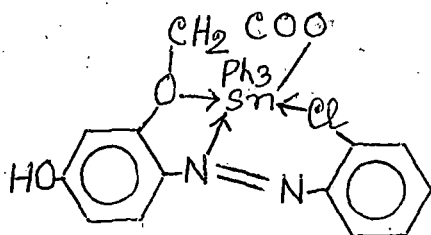
(XIX)

The large difference in the absorption maxima clearly indicates the Ph_3Sn group bond to the $-\text{COO}$ group is not cleaved, instead phenoxy $-\text{SnPh}_3$ bond is cleaved. This is to be expected in view of facile of $\text{Sn}-\text{O}$ bonds. Thus the action of $\text{OH}^{(-)}$ on $(\text{Ph}_3\text{Sn})_2\text{L}_2$ ($\text{L}_2\text{H} =$ ligand IX) can be represented as



The bis (triphenyl tin) derivative also shows the same behaviour.

The effect of alkali on compound (XIX) is shown in fig. 24. Again, it can be seen that very large excess of $\text{OH}^{(-)}$ is required to hydrolyse the stannyl group indicating a strong co-ordination. Even an 10 fold excess of alkali have only slight effect on the spectrum.



(XXV)

IVG. Conclusion

On the basis of electronic absorption spectra of the organotin derivatives of the 2-(aryl aceto) 5-hydroxy phenoxy acetic acids studied in the present work it may be concluded:

- (i) In the absence of a donor group (Cl, F, OH) in the ortho position of diazo component of the ligand, it behaves as tridentate forming 6-co-ordinated triorganotin chelates.
- (ii) The presence of Cl, F or -OH in the ortho position of diazo component makes the ligand tetradentate leading to the formation of 7-co-ordinated triorganotin chelates. It may be pointed out that the present examples constitute the first examples of 7-co-ordinated triorganotin chelates.

(iii) In solution, the ligands as well as the organotin complexes exist generally as a equilibrium mixture of the azo and the hydrazono tautomers.

IVH. Experimental

1. Synthesis : The synthesis of (benzene azo) phenoxy acetic acids and their organotin derivatives used in the present spectrophotometry study are given in Chapter-III.

2. UV - visible spectra: The UV - visible spectra were recorded with Beckman DU-2 spectrophotometer using 1 cm quartz cells.

All solvents used were of Uvasol (E. Merck, West Germany) grade.

3. Computation of Integrated Absorbance and equilibrium constants: Integrated absorbance and constants were computed according to the standard least square technique using DII Microsystem - 1121.

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