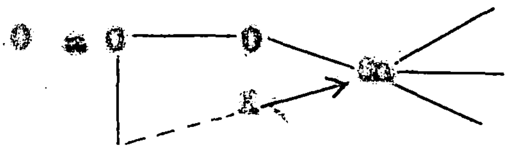
CHAPTER - III

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.



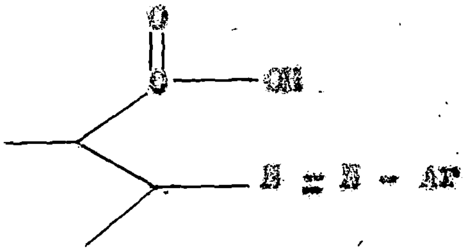
I

The organotin carboxylates of such type are of interest because:

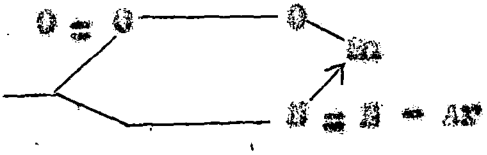
(1) Unlike organotin halides, organotin carboxylates are very reluctant to form addition compounds with Lewis bases and only a very few examples of such addition compounds are known (1,2). It is, therefore, of great interest to know whether such intramolecular co-ordination would occur in carboxylate 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-arylazo carboxylic acids of the type II where the organotin derivative is very likely to have a 5 co-ordinated structure (12).

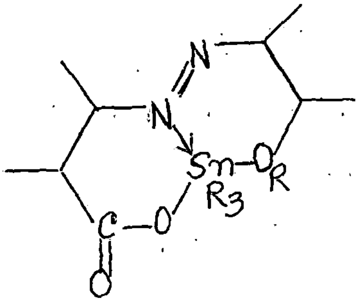


II



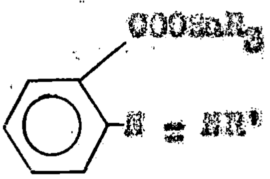
III

The hexa co-ordinated triorganotin compounds have also been prepared when the ligand has a -OR or $-NR_2$ type substituents at the O' - position (Fig. IV).

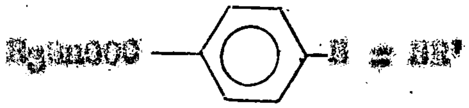


IV

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



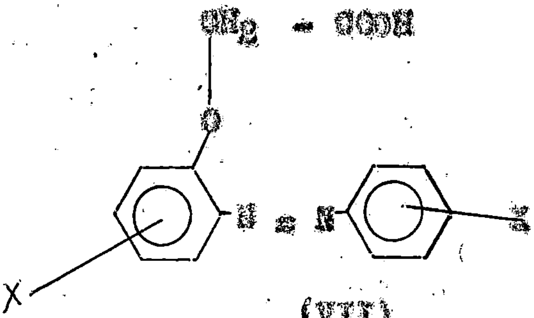
VI

The organotin (O-arylazo) benzoates are generally penta co-ordinated but those containing a hydroxyl group in the 2-position, e.g., triorganotin O-(2-hydroxy-5-methyl-benzeneazo) 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.

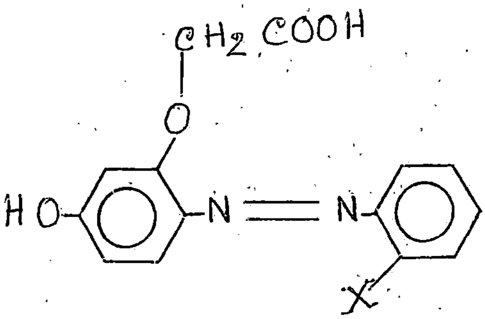
IIID. Choice of ligands

In view of the stability and ease of formation of penta as well as hexa co-ordinated derivatives of the 2'-substituted O-(arylazo) benzoic acids, 2-carboxymethoxy 2'-hydroxy azobenzene and related molecules (VII) are expected to be ideal tetradentate ligands for the synthesis of hepta co-ordinated chelates.



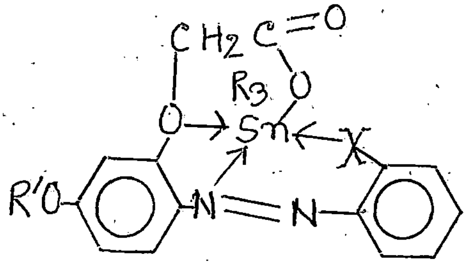
(VII)

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)



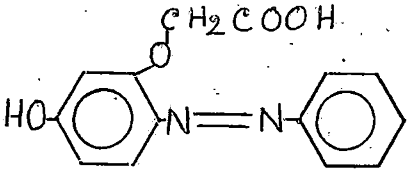
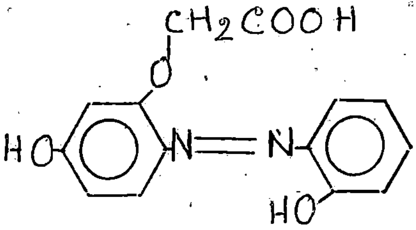
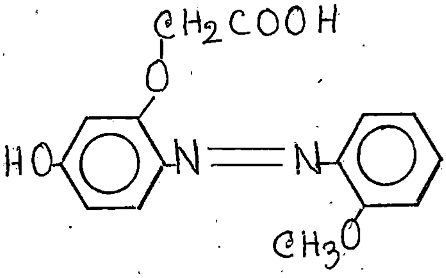
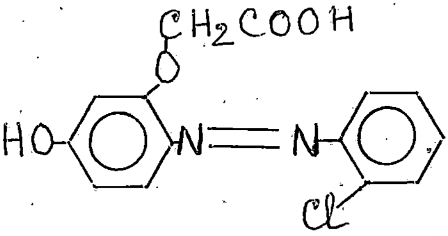
R' = R_3Sn , ; X = -OH;

R' = H , X = F, Cl.

(IX)

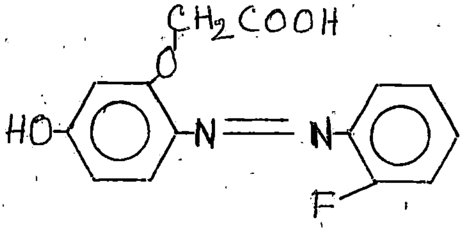
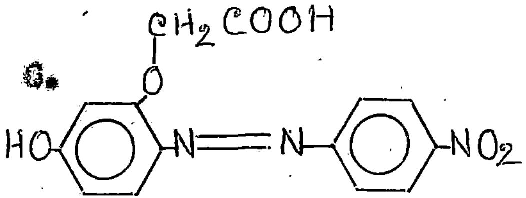
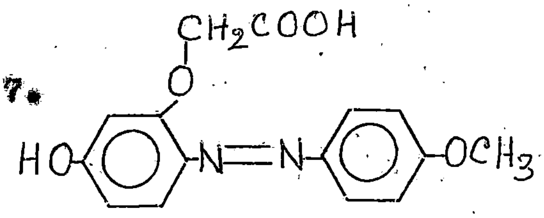
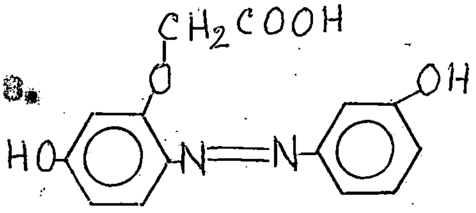
The ligands on which the studies were done are tabulated below:

Table - 1

	Structure	Name	Abbreviation
1.		2-(benzene azo) 5-hydroxy phenoxy acetic acid.	L_1H
2.		2-(2'-hydroxy benzene azo) 5-hydroxy phenoxy acetic acid.	L_2H
3.		2-(2'-methoxy benzene azo) 5-hydroxy phenoxy acetic acid.	L_3H
4.		2-(2' chloro benzene azo) 5-hydroxy phenoxy acetic acid.	L_4H

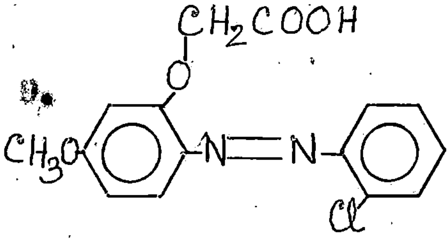
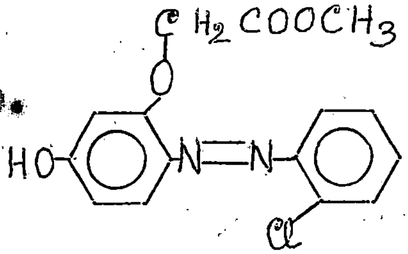
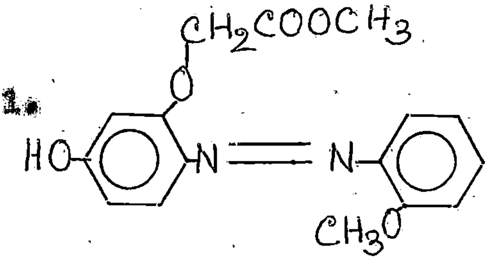
Contd..

Table - 1 (Contd..)

	Structure	Name	Abbreviation
5.		2-(2' fluoro benzene azo) 5-hydroxy phenoxy acetic acid.	L_5H
6.		2-(4' nitro benzene azo) 5-hydroxy phenoxy acetic acid.	L_6H
7.		2-(4' methoxy benzene azo) 5-hydroxy phenoxy acetic acid.	L_7H
8.		2-(3' hydroxy benzene azo) 5-hydroxy phenoxy acetic acid.	L_8H

Contd..

Table - 1 (Contd..)

Structure	Name	Abbreviation
9. 	2-(2' chloro benzene azo) 5-methoxy phenoxy acetic acid.	L_9H
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}

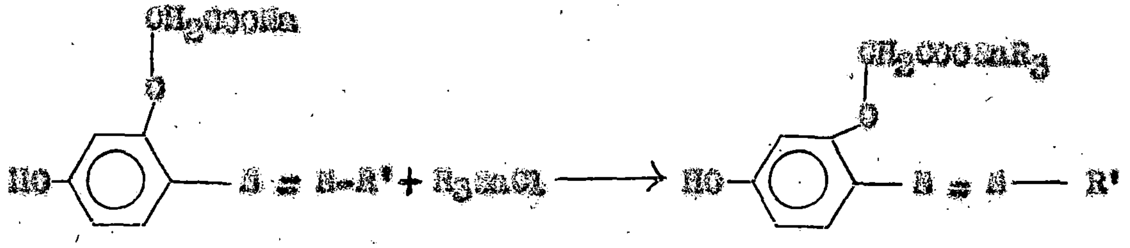
Except the compounds No. 10, 11 (which are the esters of L_3H and L_8H respectively) and 9 (the methoxy derivative of the compound No. 4), all other compounds were prepared by coupling 5-hydroxy phenoxy acetic acid with suitable diazotised components.

IIIC. Methods of preparation

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

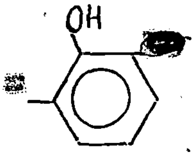
(1) Reaction of the organotin halides with the sodium salt of the 2-(benzene azo) 5-hydroxy phenoxy acetic acid and related compounds.

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

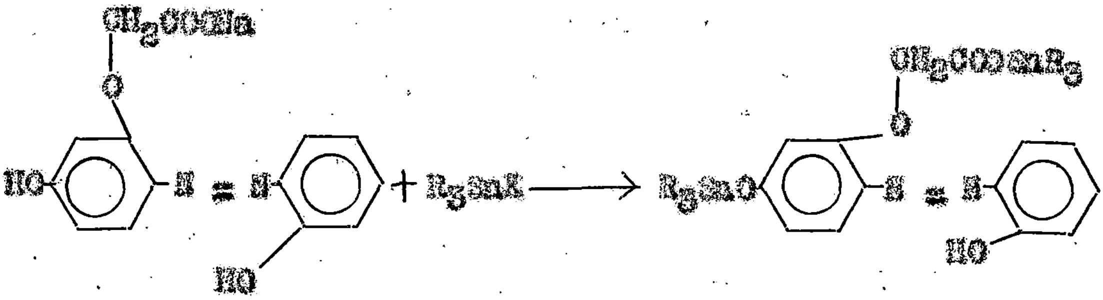


where R = phenyl and butyl.

An interesting reaction occurs when R' =



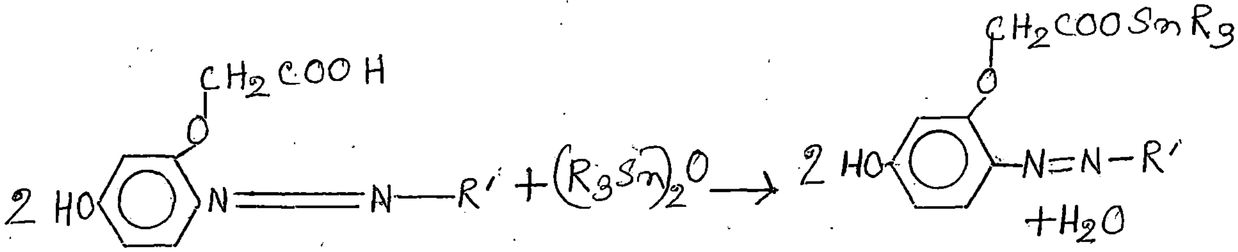
In this case only the bis(triorganotin) derivatives could be isolated. No simple (triorganotin) derivatives could be isolated as in the other cases. The reaction may be written as:



... (1)

(2) Reaction of hexaorgano distannoxanes with 2-(benzene azo) 5-hydroxy phenoxy acetic acid and related compounds.

The ligand and $(R_3Sn)_2O$ (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.

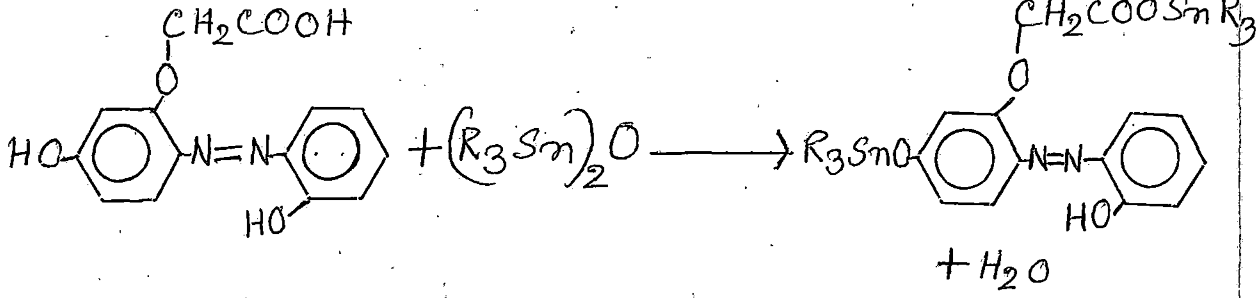


... (2)

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:

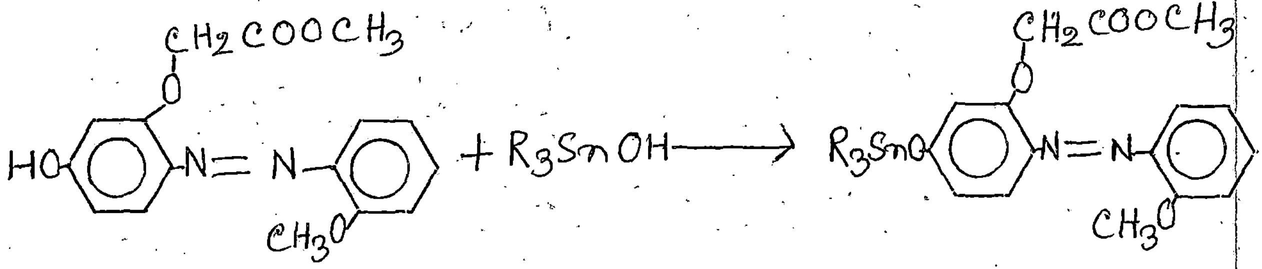


... (3)

(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 azo) 5-hydroxy phenoxy methyl acetate.

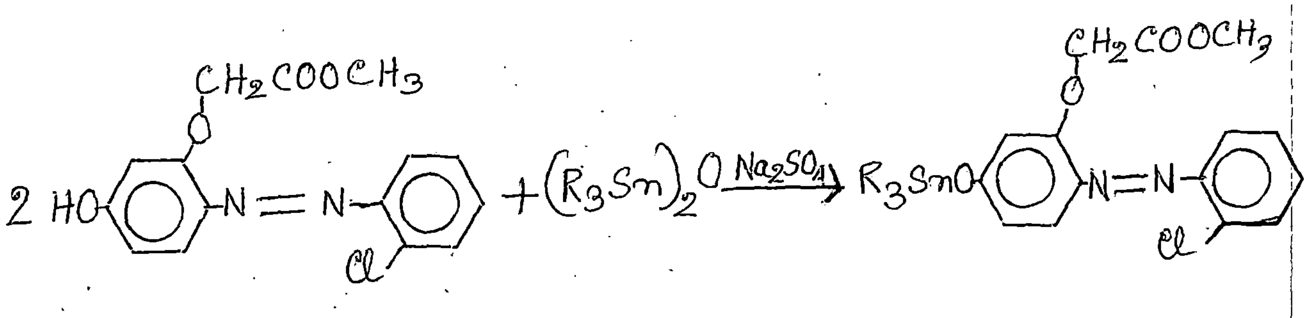
The ester and R_3SnOH were taken in dry benzene and stirred at R.T. On addition of petroleum ether to the concentrated benzene solution the triorganotin derivative could be obtained.



... (4)

[R = Phenyl]

(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 azo) 5-hydroxy phenoxy methyl acetate was achieved by the following reaction.

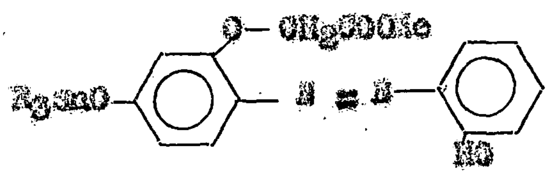


.... (5)

[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 (X) however failed.



(X)

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. L_1 - Na + Ph_3SnCl (1:1)	Stirring at RT for 8 hour in dry EtOH, product crystallised from benzene-pet. ether mixture.	Ph_3SnL_1 (184°, 60)
1B. L_1H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 6 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Ph_3SnL_1 (184°, 60)
2A. L_1Na + Bu_3SnCl (1:1)	Stirring at RT for 16 hours in dry EtOH, product crystallised from benzene-pet. ether mixture.	Bu_3SnL_1 (125°, 20)
2B. L_1H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 22 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Bu_3SnL_1 (128°, 40)
3A. L_2 - Na + Ph_3SnCl (1:1)	Refluxing for 10 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	$(Ph_3Sn)_2L_2$ (141°*, 50)

Contd..

Table – 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield%)
3B. L_2H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 20 hours in dry benzene, product crystallised from benzene – pet. ether mixture.	$(Ph_3Sn)_2L_2$ (141°*, 30)
4A. L_2 – Na + Bu_3SnCl (1:1)	Refluxing for 16 hours in dry benzene, product crystallised from benzene – pet. ether mixture.	$(Bu_3Sn)_2L_2$ (83°*, 20)
4B. L_2H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 26 hours in dry benzene, product crystallised from benzene – pet. ether mixture.	$(Bu_3Sn)_2L_2$ (85°*, 15)
5. L_3H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 6 hours in dry benzene, product crystallised from benzene – pet. ether mixture.	Ph_3SnL_3 (170°, 60)
6. L_3H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 30 hours in dry benzene, product crystallised from benzene – pet. ether mixture.	Bu_3SnL_3 (155°, 80)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield%)
7. L_4H + $(Ph_3Sn)_2O$ (2:1)	Refluxing in dry benzene for 8 hours product crystallised from benzene- pet. ether mixture.	Ph_3SnL_4 (140°, 35)
8. L_4H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 20 hours in dry benzene, product crystallised from benzene- pet. ether mixture.	Bu_3SnL_4 (90°, 30)
9. L_5H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 6 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Ph_3SnL_5 (102°, 30)
10. L_5H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 22 hours in dry benzene, product crystallised from benzene- pet. ether mixture.	Bu_3SnL_5 (73°, 20)
11. L_6H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 12 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Ph_3SnL_6 (120°, 30)
12. L_6H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 28 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Bu_3SnL_6 (83°, 20)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p. °C, yield,%)
13. L_7H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 10 hours in dry benzene, product crystallised from benzene- pet. ether mixture.	Ph_3SnL_7 (114°, 60)
14. L_7H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 24 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Bu_3SnL_7 (79°, 25)
15. L_8H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 8 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	Ph_3SnL_8 (107°, 80)
16. L_8H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 30 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Bu_3SnL_8 (66°, 20)
17. L_9H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 8 hours in dry benzene, product crystallised from benzene-pet. other mixture.	Ph_3SnL_9 (73°, 70)

Contd..

Table - 2 (Contd..)

Reactants (mole ratio)	Condition used	Product (m.p.°C, yield%)
18. L_{10} + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 10 hours in dry benzene, product crystallised from benzene - pet. ether mixture.	Ph_3SnL_{10} (85°, 85)
19. L_{11} + Ph_3SnOH (1:1)	Stirring at RT for 24 hours, product crystallised from benzene - pet. ether mixture.	Ph_3SnL_{11} (70°C, 50)

* = Decomposition point.

IIID. Analytical Data

Analytical data on the organotin derivated 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) (%) C	H	N	Sn
1. $C_{32}H_{26}O_4N_2Sn$ (Ph_3SnL_1)	62.32 (62.05)	4.31 (4.26)	4.56 (4.53)	19.19 (19.12)
2. $C_{26}H_{38}O_4N_2Sn$ (Bu_3SnL_1)	55.35 (55.71)	6.73 (6.78)	5.03 (5.00)	20.98 (21.16)
3. $C_{50}H_{40}O_5N_2Sn_2$ [$(Ph_3Sn)_2L_2$]	60.20 (60.3)	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)	3.28 (3.23)	27.12 (27.43)
5. $C_{33}H_{28}O_5N_2Sn$ (Ph_3SnL_3)	61.40 (61.77)	4.26 (4.30)	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)	19.92 (20.09)
7. $C_{32}H_{25}O_4N_2SnCl$ (Ph_3SnL_4)	57.63 (58.01)	3.53 (3.81)	4.28 (4.27)	18.20 (18.11)

Contd..

Table - 3 (Contd..)

Formula	Found (Calculated) (%) C	H	N	Sn
8. $C_{26}H_{37}O_4N_2SnCl$	51.61	6.32	4.5	19.23
(Bu_3SnL_4)	(52.40)	(6.22)	(4.70)	(19.94)
9. $C_{32}H_{25}O_4N_2SnF$	59.02	3.72	4.40	18.29
(Ph_3SnL_5)	(60.10)	(3.91)	(4.38)	(18.58)
10. $C_{26}H_{37}O_4N_2SnF$	54.34	6.43	4.73	20.25
(Bu_3SnL_5)	(54.00)	(6.39)	(4.84)	(20.51)
11. $C_{32}H_{25}O_6N_3Sn$	57.29	3.67	6.28	17.71
(Ph_3SnL_6)	(57.68)	(3.78)	(6.30)	(17.83)
12. $C_{26}H_{37}O_6N_3Sn$	51.29	6.31	6.43	19.21
(Bu_3SnL_6)	(51.60)	(6.10)	(6.90)	(19.59)
13. $C_{33}H_{25}O_5N_2Sn$	61.26	4.31	4.23	17.98
(Ph_3SnL_7)	(61.77)	(4.50)	(4.36)	(18.24)
14. $C_{27}H_{40}O_5N_2Sn$	54.89	6.18	4.31	19.64
(Bu_3SnL_7)	(54.85)	(6.77)	(4.74)	(20.09)
15. $C_{32}H_{26}O_5N_2Sn$	59.10	4.14	4.31	17.98
(Ph_3SnL_8)	(60.31)	(4.08)	(4.39)	(18.64)

Contd..

Table - 3 (Contd..)

Formula	Found (Calculated) (%)			Sn
	C	H	N	
16. $C_{26}H_{38}O_5N_2Sn$	54.62	6.38	4.81	20.16
(Bu_3SnL_8)	(54.10)	(6.63)	(4.85)	(20.58)
17. $C_{33}H_{27}O_4N_2SnCl$	58.89	4.00	4.21	17.51
(Ph_3SnL_9)	(59.17)	(4.03)	(4.18)	(17.73)
18. $C_{33}H_{27}O_4N_2SnCl$	59.03	4.16	4.16	17.82
(Ph_3SnL_{10})	(59.17)	(4.03)	(4.18)	(17.73)
19. $C_{34}H_{30}O_5N_2Sn$	61.22	4.43	4.27	17.76
(Ph_3SnL_{11})	(61.38)	(4.51)	(4.21)	(17.85)

IIIB. 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 $\nu_{as}(COO)$, $\nu_s(COO)$, $\nu(Sn-O)$ and $\nu(N = N)$. Not all of these modes could be identified

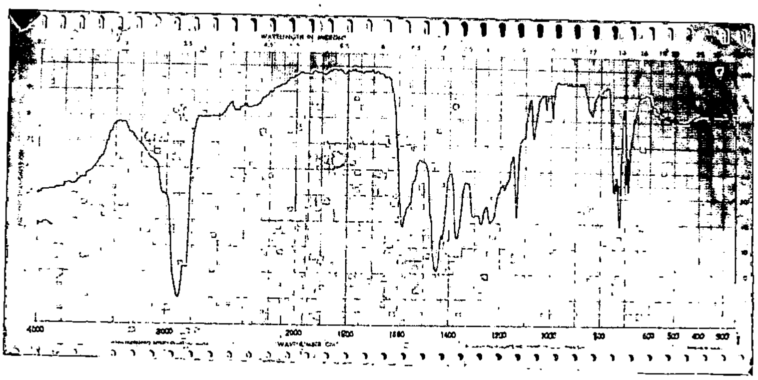


Fig. 1 IR spectra of $(Ph_3Sn)_2P_2$ in Nujol.

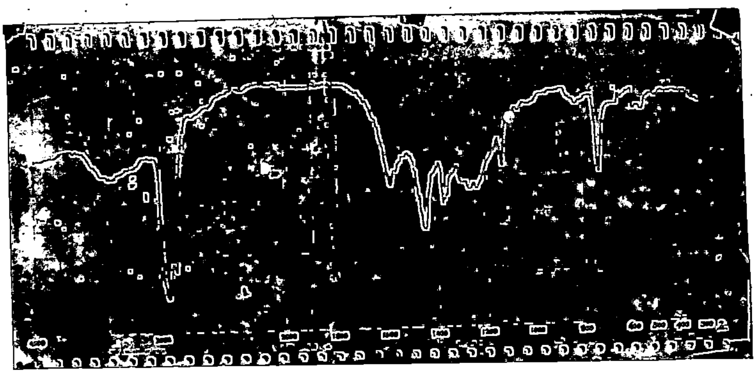


Fig. 2 IR spectra of $(Bu_3Sn)_2P_2$ in Nujol.

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) 1550 - 1700 cm^{-1} : In this region ν_{as}(OCO) is expected (1,3,4,8) and all the compounds are characterised by the presence of a number of medium to strong intensity bands in this region. Assymetric 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 ν_{as}(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 N = N stretch and symmetric OCO stretch are expected to occur in this region.

(i) N = N stretch: The idea of correlating an IR band with N = N stretch in azo dyes has been attractive one. However, substitution on the azo group in dyes are generally fairly symmetrical. N = N stretch is, therefore, likely to be weak. Although the vibration has been reported to occur at 1400-1450 cm^{-1} (5). Miller has emphasised the absence of any diagnostically useful band in the region in azo dyes (6).

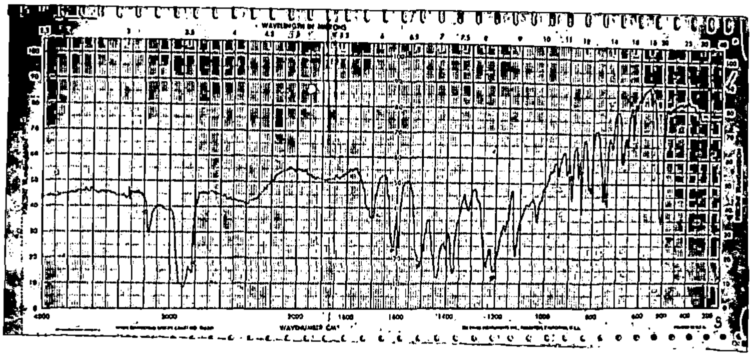


Fig. 3 IR spectra of L_1H in Nujol.

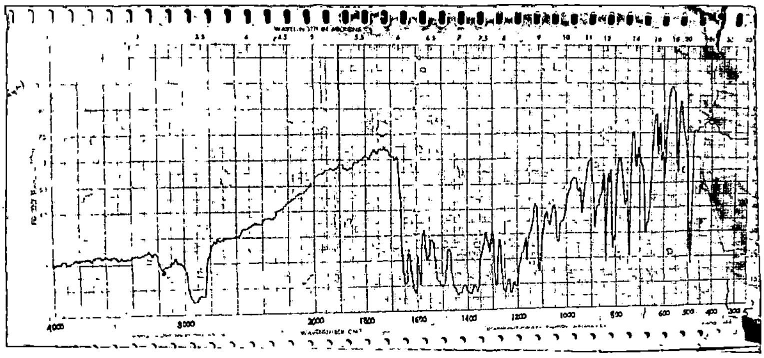


Fig. 4 IR spectra of Bu_3SnL_1 in Nujol.

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

(ii) symmetric COC 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 COC stretch in the present compounds with any degree of certainty. Because of this, symmetric COC stretch has not been considered in the present discussion.

(c) <u>450-600 cm^{-1}</u>. Both ν(Sn-C) and ν(Sn-O) are expected in this region (1,13,3,4,8). Both ν(Sn-C) and ν(Sn-O) are probably very weak in these compounds since comparison with ligand spectra showed no new bands attributable to Sn-C 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 N $\longrightarrow$ Sn co-ordination bond is expected to occur (1,9,10), could not be explored. As such presence or absence of N $\rightarrow$ Sn co-ordination had to be deduced from other evidences to be discussed in the next chapter.

The absorption associated with Aryl -O-CH_2COOH moiety are, however, easily identifiable because of their intensity. Aryl-O-CH_2 vibrations generally lead to two easily identifiable absorption bands at 1310 - 1210 and 1080 - 1010 cm^{-1} (7). The former may be looked upon as an aromatic

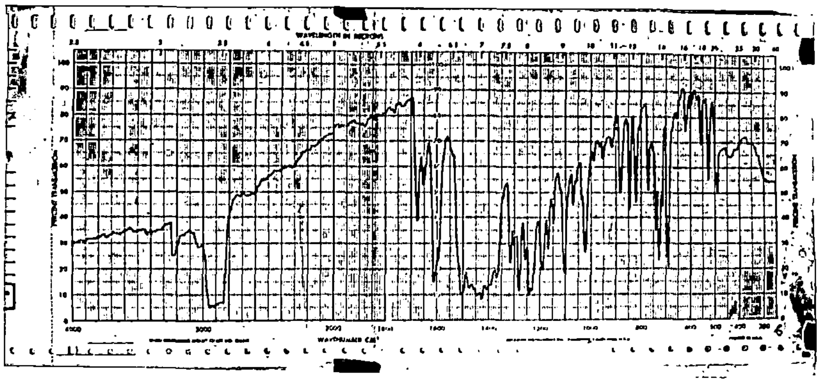


Fig. 5 IR spectra of Ph$_3$SnL$_3$ in Nujol.

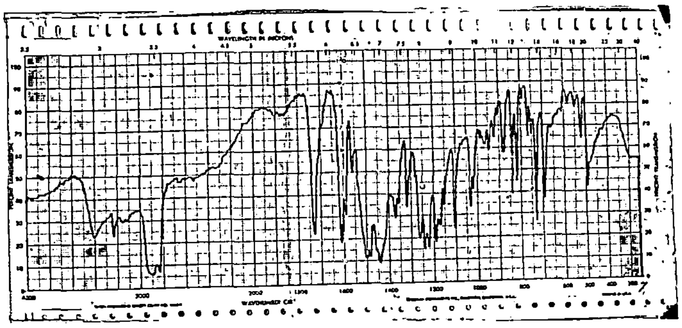


Fig. 6 IR spectra of L$_3$H in Nujol.

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-C stretch, the vibration being similar to the asymmetric C – C – 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 azo) 5-hydroxy phenoxy acetic acids and their organotin derivatives in Nujol.

Compound	Frequencies (in cm^{-1}) of :		
	COO (as)	Aryl – OCH_3	$O-CH_2COOH$
1. L_1H	1700	1240	1120
2. Ph_3SnL_1	1655 (1660)[a]	1220	1100
3. Bu_3SnL_1	1645 (1660)[a]	1225	1110
4. L_2H	1680	1230	1150
5. $(Ph_3Sn)_2L_2$	1560[b]	1220	1135
6. $(Bu_3Sn)_2L_2$	1560[b]	1230	1130
7. L_3H	1730	1240	1100

Contd..

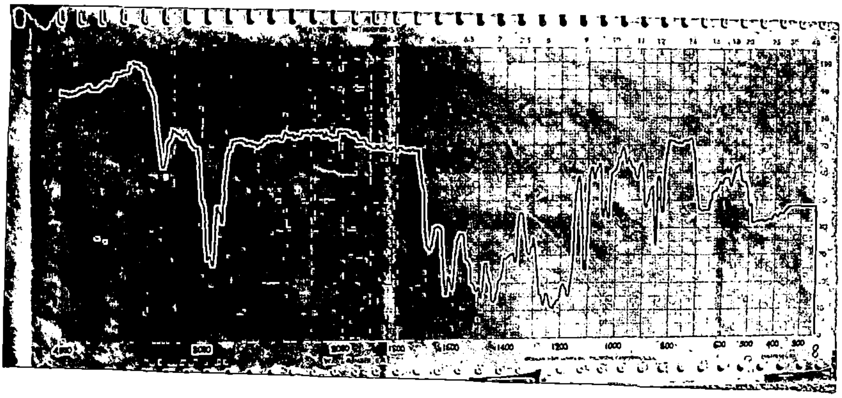


Fig. 7 IR spectra of Eug$_2$Mg in Chloroform.

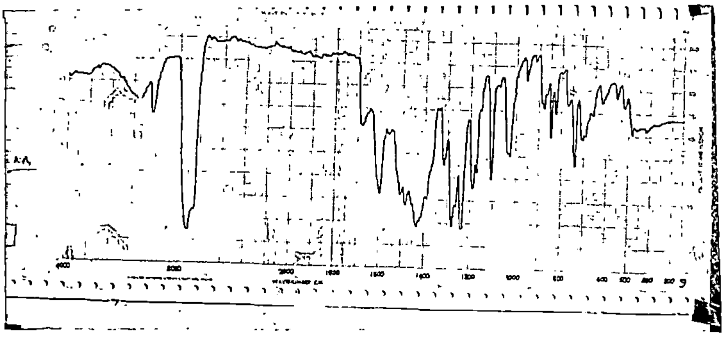


Fig. 8 IR spectra of Eug$_2$Mg in Nujol.

Table – 4 (Contd..)

Compound	Frequencies (in cm^{-1}) of:		
	COO (as)	Aryl – OCH$_2$	O-CH$_2$COOH
8. Ph_3SnL_3	1660	1220	1110
9. Bu_3SnL_3	1660	1230	–
10. L_4H	1730	1240	1130
11. Ph_3SnL_4	1580^b	1230	1100
12. Bu_3SnL_4	1590^b	1225	1110
13. L_5H	1730	1240	1130
14. Ph_3SnL_5	1580^b	1240	1110
15. Bu_3SnL_5	1600^b	1230	1120
16. L_6H	1725	1240	1130
17. Ph_3SnL_6	1670	1220	1110
18. Bu_3SnL_6	1660	1220	1110
19. L_7H	1710	1250	1130
20. Ph_3SnL_7	1660	1250	1120
21. Bu_3SnL_7	1660	1240	1110
22. L_8H	1710	1240	1140
23. Ph_3SnL_8	1660	–	–
24. Bu_3SnL_8	1650	1240	1140
25. L_9H	1750	1260	1140
26. Ph_3SnL_9	1570^b	1250	1130

a) In chloroform solution

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

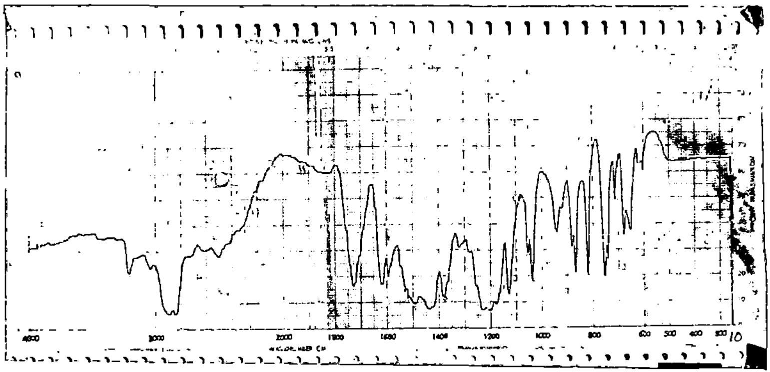


Fig. 9 IR spectra of L_4H in nujol.

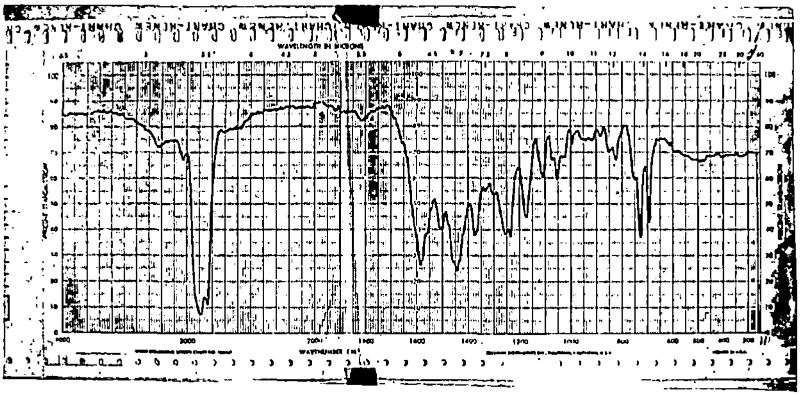


Fig. 10 IR spectra of Ph_3SnL_4 in nujol.

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 diazo moiety (L_2H, L_4H, L_5H, and L_9H), the ν_{as}(COO) in the organotin derivatives occur in the range 1645 - 1630 cm^{-1} both in the solid state (Nujol mole) as in chloroform solution. Unlike simple organotin carboxylates such as, formate, acetate etc., where ν_{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-CH$_2$ frequencies are also generally lowered to some extent in the organotin derivatives. This may be taken as an evidence in favour of O ⟶ Sn co-ordination.

Potentially tetradentate ligand, such as, L_2H, L_4H, L_5H and L_9H, are characterized by organotin derivatives in which the ν_{as}(COO) is lowered to 1620 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 a α-position will not be conductive to the formation polymeric structure involving -COO - bridge. It therefore, appears that the most probable explanation for such lowering

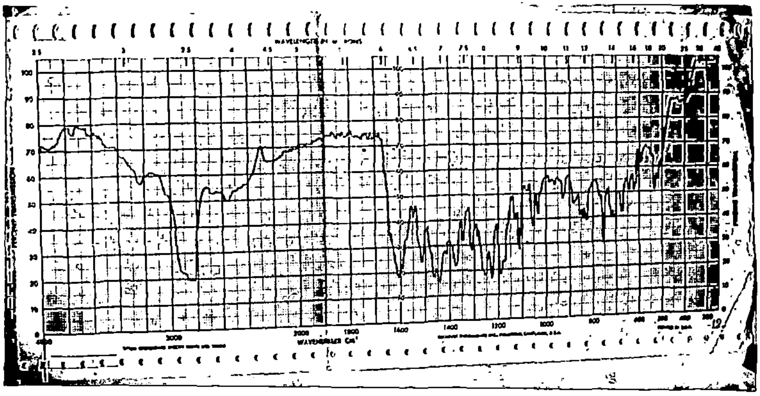


Fig. 11 IR spectra of Bu_2SnL_2 in Nujol.

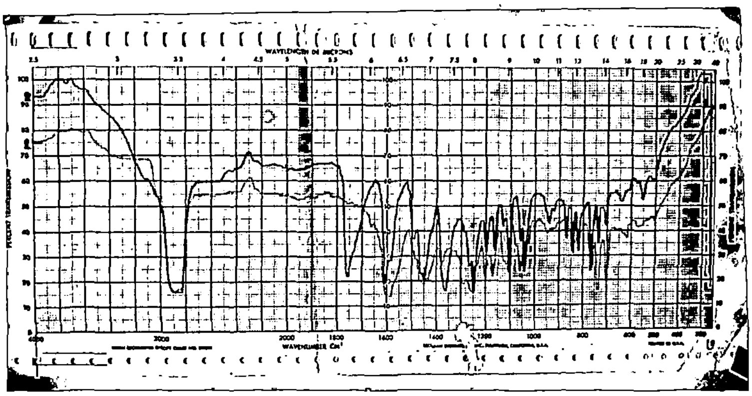
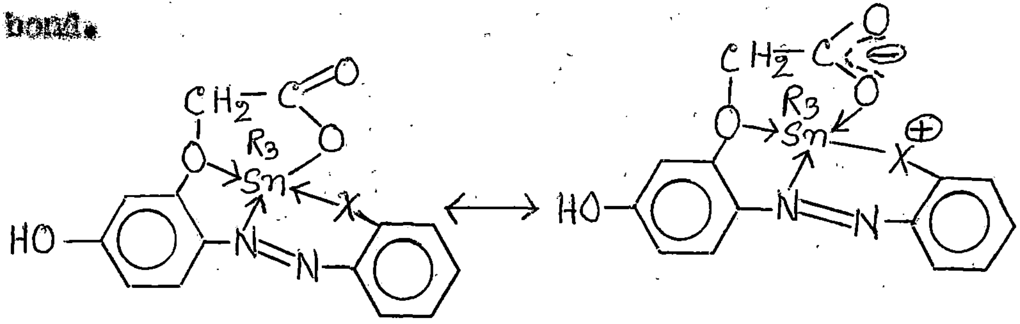


Fig. 12 IR spectra in Nujol of

1. Ph_2SnL_2 2. LH.

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



(XI

Such a resonance is not unreasonable since the formal +ve charge on the donor substituent X will be stabilised 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.

IIIC. Experimental

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

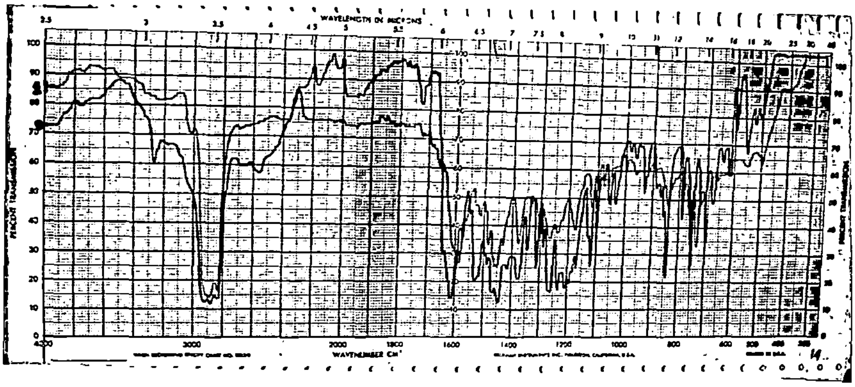


Fig. 13 IR spectra in Nujol of

1. Ph_3SnLi 2. Bu_3SnLi

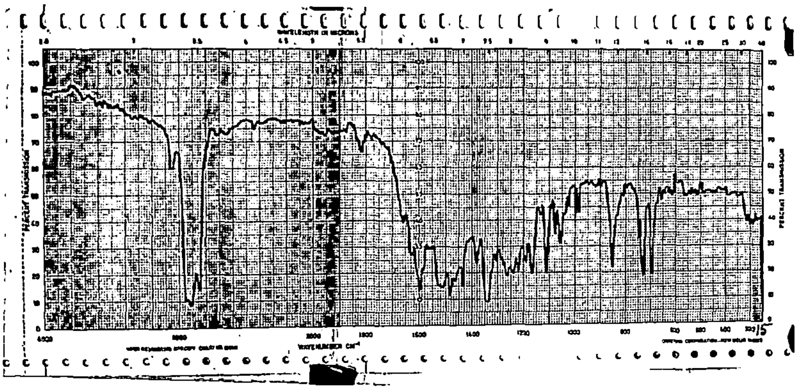


Fig. 14 IR spectra of Bu_3SnLi in Nujol.

chloride was prepared from tetraphenyl tin by the reaction of stannic chloride (13). Triphenyl tin ether (m.p. 122 - 124°C) prepared by the reaction of triphenyl tin chloride and sodium hydroxide (14). Tributyl tin chloride b.p. 152°/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 m-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, m-hydroxy phenoxy acetic acid of m.p. 155°C was obtained.

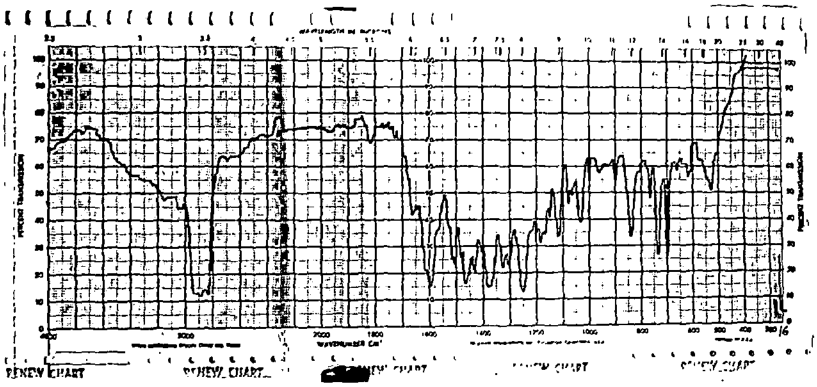


Fig. 15 IR spectra of Ph$_3$SnL$_3$ in Nujol.

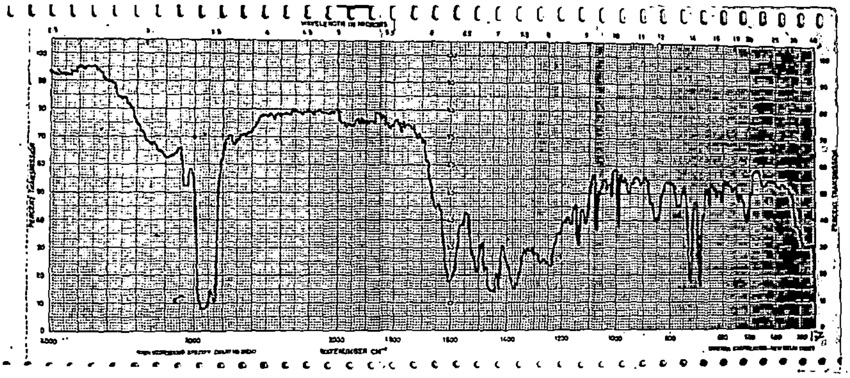


Fig. 16 IR spectra of Bu$_3$SnL$_3$ in Nujol.

IR : ν_{as}(COO) 1710 cm^{-1}

Yield : 65%

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

1. Preparation of L_2H

11 gm. O-aminophenol was diazotised by the usual procedure (11). 16.8 gm HPA was dissolved in 50 ml. of 20% 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 L_2H. decomposition point (D.P.) 200°C.

IR : ν_{as}(COO) 1680 cm^{-1}

Yield: 40%

2. Preparation of L_1H

By following the same procedure and taking the same quantity of other chemicals as described in 1, but using 9.3 gm. aniline as the diazotised component, brick red L_1H, m.p. 205°C was obtained.

IR: ν_{as}(COO) 1700 cm^{-1}

3. Preparation of L_3H

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 L_3H, m.p. 197° C.

IR : $\nu_{as}(COO)$ 1730 cm^{-1}

Yield : 60%

4. Preparation of L_4H

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 L_4H of m.p. 187° C.

IR : $\nu_{as}(COO)$ 1730 cm^{-1}

Yield : 80%

5. The preparation of L_5H

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_5H of m.p. 195°C.

IR : ν_{as}(COO) 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°C in an ice bath and diazotised by the usual method (11). 9 gm. HPA was dissolved in 30 ml. of 30% sodium hydroxide and was cooled to 5°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°C.

IR : ν_{as}(COO) 1725 cm^{-1}

Yield : 40%

7. The preparation of L_7H

By following the similar method and taking the same amount of all other materials as described in 1, but using 12.3 gm. p-anisidine as the component for diazotisation, a chocolate brown solid obtained which after recrystallisation from acetone-pet. ether mixture afforded the dye L_7H of m.p. 136°C.

IR : ν_{as}(COO) 1710 cm^{-1}

Yield : 50%

8. The preparation of L_8H

By following the previous procedure and taking all other materials in the same amount as directed in 1, but using 10.9 gm. m-amino phenol as the component for diazotisation, a brown solid obtained which on recrystallisation from acetone-pet. ether mixture afforded the reddish brown dye L_8H of m.p. 200°C.

IR : ν_{as}(COO) 1710 cm^{-1}

Yield : 70%

9. The preparation of L_9H.
(The methoxy derivative of L_4H)

6 gm of L_4H 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} (COO) 1750 cm^{-1}

Yield : 80%

10. Preparation of L_{10}

1 gm. of L_4H, was dissolved in absolute methanol and cooled. To this was added the ethereal solution of 0.2 gm. diazomethane. After evaporation of ether the oily residue was extracted with ether and the ethereal solution was washed with 30% sodium bicarbonate solution. After evaporation of ether, the brownish yellow ester L_{10} (smell like green mango) was obtained.

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

Yield : 40%

11. Preparation of L_{11}

By following the similar procedure and taking the same amount of all other materials as described in 10, but using 1 gm L_3H instead of L_4H, the deep red ester L_{11} was obtained.

IR : $\nu_{as}(COO)$ 1700 cm^{-1}

Yield: 40%

(ii) Reactions for the preparations of organotin derivatives:

1A. Reaction of triphenyl tin chloride with Na-salt of L_1H

A mixture of 1 gm. of Na-salt of L_1H and 1.4 gm. of triphenyl tin chloride in 200 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. 181°C separated which after several recrystallisation from benzene-pet. ether mixture afforded the bright orange product of m.p. 186°C, yield 60%. The percentage of

	C	H	N	Sn
Found:	62.42	4.21	4.46	19.32
Calculated for $C_{32}H_{26}O_4N_2Sn$:	62.95	4.26	4.50	19.12

IR spectrum: $\nu_{as}(COO)$ 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°C, separated. The product was purified by recrystallising from benzene-pet. ether mixture. The yield of the purified product, m.p. 164°C, was about 80%. The percentage of

	C	H	N	Sn
Found:	62.32	4.31	4.56	19.18
Calculated for				
$C_{32}H_{26}O_4N_2Sn$:	62.95	4.26	4.59	19.12

IR spectrum : $\nu_{as}(COO)$ 1665 cm^{-1}

2A. Reaction of tributyl tin chloride with Na - salt of L_1H

A mixture of 1 gm. Na-salt of L_1H and 1.8 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°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

	C	H	N	Sn
Found:	55.66	6.73	5.00	20.96
Calculated for $C_{26}H_{38}O_4N_2Sn$:	55.71	6.73	5.00	21.16

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

2B. Reaction of bis-(tributyl tin) oxide with L_1H

A mixture of 1 gm. L_1H, 1.1 gm bis-(tributyl tin)oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. benzene was refluxed for 28 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

	C	H	N	Sn
Found:	55.46	6.70	5.1	21.58
Calculated for $C_{26}H_{38}O_4N_2Sn$:	55.71	6.73	5.00	21.16

IR spectrum: $\nu_{as}(COO)$ 1643 cm^{-1}

3A. Reaction of Na-salt of L$_2$H 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°C was obtained.

%	C	H	N	Sn
Found:	60.2	4.1	2.76	24.1
Calculated for				
$C_{30}H_{20}O_6N_2Sn_2$	60.8	4.06	2.84	24.09

IR spectrum: $\nu_{as}(COO)$ 1560 cm^{-1}

3B. Reaction of Bis-(triphenyl tin)oxide with L$_2$H

A mixture of 1 gm. L$_2$H 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. 161°C was obtained. The percentage of

	C	H	N	Sn
Found :	60.1	3.76	2.72	24.00
Calculated for $C_{50}H_{40}O_{5}N_{2}Sn_{2}$:	60.8	4.06	2.84	24.09

IR spectrum : $\nu_{as}(COO)$ 1560 cm^{-1}

4A. Reaction of tributyl tin chloride with Na-salt of L_2H

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 crystallisation from benzene pet. ether mixture, afforded the deep violet organotin derivative (0.6 gm) of D.P. 88°C. The percentage of

	C	H	N	Sn
Found:	52.72	7.20	3.12	27.61
Calculated for				
$C_{38}H_{64}O_4N_2Sn_2$:	52.69	7.39	3.23	27.43

IR spectrum: $\nu_{as}(COO)$ 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 23 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 m.p. 88°C was obtained. The percentage of

	C	H	N	Sn
Found:	52.40	7.19	3.28	27.12
Calculated for				
$C_{38}H_{64}O_4N_2Sn_2$:	52.49	7.39	3.23	27.43

IR spectrum: $\nu_{as}(COO)$ 1500 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

	C	H	N	Sn
Found:	61.40	4.26	4.22	18.29
Calculated for				
$C_{33}H_{23}O_5N_2Sn$	61.77	4.36	4.36	18.24

IR spectrum : $\nu_{as}(COO)$ 1660 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 30 hours and then after cooling was filtered. The filtrate was concentrated and to it was added pet. ether when a red solid (1.6 gm, m.p. 131°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

	C	H	N	Sn
Found :	54.34	6.74	4.64	19.88
Calculated for $C_{27}H_{40}O_5N_2Sn$:	54.85	6.77	4.74	20.09

IR spectrum: $\nu_{as}(OCO)$ 1630 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 8 hours and then was cooled, filtered off. The filtrate was concentrated and when pet. ether was added to it, an orange yellow solid (1.9 gm), m.p. 130°C, separated. After recrystallisation from benzene-pet. ether mixture, the desired organotin derivative (1.8 gm), m.p. 160°C, was obtained. The percentage of

	C	H	N	Sn
Found :	57.63	3.85	4.28	18.20
Calculated for $C_{32}H_{25}O_4N_2SnCl$:	58.61	3.81	4.27	18.11

IR spectrum : $\nu_{as}(OCO)$ 1580 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°C, was deposited on the wall of the container (having the gummy mass at the bottom). The solid, after recrystallisation from benzene-pet. ether mixture, afforded the desired organotin compound (0.6 gm) of m.p. 80°C. The percentage of

	C	H	N	Sn
Found:	51.6	6.32	4.5	19.20
Calculated for $C_{26}H_{37}O_4N_2SnCl$:	52.4	6.22	4.7	19.94

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

9. Reaction of bis-(triphenyl tin)oxide with L_5H

A mixture of 1 gm L_5H, 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

	C	H	N	Sn
Found:	59.02	3.72	4.40	18.29
Calculated for				
$C_{32}H_{25}O_4N_2SnF$:	60.1	3.91	4.38	18.58

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

10. Reaction of bis-(tributyl tin)oxide with L$_6$H

A mixture of 1 gm L$_6$H, 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. When 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. 75°C separated. The percentage of

	C	H	N	Sn
Found :	54.34	6.45	4.78	20.26
Calculated for				
$C_{26}H_{37}O_4N_2SnF$:	54.9	6.39	4.84	20.81

IR spectrum : $\nu_{as}(OCO)$ 1600 cm^{-1}

11. Reaction of bis-(triphenyl tin)oxide with L_6H

A mixture of 1 gm. L_6H, 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°C, separated which after recrystallisation from benzene-pet. ether mixture yielded the brownish-orange organotin carboxylate (0.6 gm) of m.p. 120°C. The percentage of

	C	H	N	Sn
Found:	57.39	3.67	6.28	17.71
Calculated for				
$C_{32}H_{25}O_6N_3Sn$:	57.68	3.75	6.3	17.83

IR spectrum : $\nu_{as}(OCO)$ 1670 cm^{-1}

12. 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 20 hours, when pet. ether was added to the concentrated benzene solution, an orange solid (0.6 gm) m.p. 84°C obtained. After several crystallisation from benzene-pet. ether mixture, the desired tributyl tin derivative (0.4 gm) m.p. 88°C, was obtained. The percentage of

	C	H	N	Sn
Found:	51.21	6.31	6.43	19.21
Calculated for				
$C_{26}H_{37}O_6N_3Sn$:	51.50	6.10	6.90	19.59

IR spectrum : $\nu_{as}(OCO)$ 1660 cm^{-1}

13. 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 (1.9 gm), m.p. 112°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°C. The percentage of

	C	H	N	Sn
Found:	61.26	4.31	4.23	17.93
Calculated for				
$C_{33}H_{28}O_5N_2Sn$:	61.77	4.30	4.36	18.24

IR spectrum : ν_{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 pet. ether was added to it when a gummy mass separated. One keeping the solution for 4 days at R.T., an reddish orange solid (0.7 gm), m.p. 73°C, deposited on the wall of the container which was recrystallised from benzene-pet. ether mixture resulting in the formation of the orange crystals of the tributyl tin carboxylate (0.5 gm), m.p. 79°C. The percentage of

	C	H	N	Sn
Found:	54.39	6.13	4.61	19.64
Calculated for				
$C_{27}H_{40}O_5N_2Sn$:	54.83	6.77	4.74	20.09

IR spectrum : ν_{as}(OCO) 1600 cm^{-1}

15. Reaction of bis-(triphenyl tin) oxide with L_8H

A mixture of 1 gm. L_8H, 1.2 gm. bis-(triphenyl tin) oxide and 0.5 gm. of anhydrous sodium sulphate in 200 ml. benzene was refluxed for 8 hours. The reaction mixture was then cooled and filtered. On addition of pet. ether to the concentrated solution, an orange solid (1.6 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

	C	H	N	Sn
Found :	59.10	4.14	4.31	17.98
Calculated for $C_{32}H_{26}O_5N_2Sn$:	60.31	4.08	4.39	18.64

IR spectrum: $\gamma_{as}(COO)$ 1660 cm^{-1}

16. Reaction of bis-(tributyl tin) oxide with L_8H

A mixture of 1 gm. L_8H, 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. 65°C. The percentage of

	C	H	N	Sn
Found:	54.62	6.39	4.81	20.16
Calculated for				
$C_{26}H_{33}O_5N_2Sn$:	54.1	6.53	4.85	20.58

IR spectrum : $\nu_{as}(COO)$ 1600 cm^{-1}

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

A mixture of 1 gm L_2H, 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 recrystallisation from benzene-pet. ether mixture, afforded the triphenyl tin carboxylate (1.4 gm), m.p. 78°C. The percentage of

	C	H	N	Sn
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: $\nu_{as}(COO)$ 1570 cm^{-1}

18. Reaction of bis-(triphenyl tin)oxide with L_{10}

A mixture of 1 gm. L_{10}, 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. 80°C. The percentage of

	C	H	N	Sn
Found:	59.03	4.14	4.10	17.82
Calculated for $C_{33}H_{27}O_4N_2SnCl$:	59.17	4.03	4.18	17.73

IR spectrum : $\nu_{as}(COO)$ 1755 cm^{-1}

19. Reaction of triphenyl tin hydroxide with L_{11}

A mixture of 1 gm. L_{11}, 1.2 gm triphenyl tin hydroxide 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 (0.8 gm), m.p. 65°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

	C	H	N	Sn
Found:	61.22	4.48	4.27	17.76
Calculated for $C_{34}H_{30}O_5N_2Sn$:	61.38	4.51	4.21	17.85

IR spectrum : ν_{as}(COO) 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 (E.Merck).

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