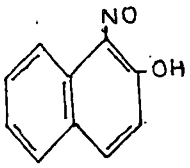
CHAPTER - III

Reactions of triorgano tin compounds with 1-nitroso-2-napthol, potassium 1-nitroso-2-napthoxide, diacetyl mono oxime, - benzil mono oxime and benzoin oxime

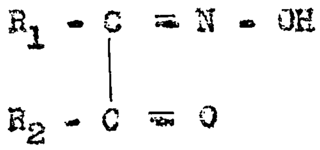
Introduction :

III A. Considerable amount of work on the action of chelating agents like 8-hydroxy quinoline (1-5), carboxylates (6), dithiocarbamate (7), dithiophosphinate (8), tropolone (9), dithiozone (10 - 11), 1,10 phenanthroline and 22′,bipyridine (12 - 14), acetyl acetone and picolinic acid (15 - 17), 2-thenoyl trifluoro and p -fluoro benzoyl acetone (18), thiocyanate (5) etc. On organotin compounds has been reported in the literature. Both monoprotic and diprotic chelating agents are known to react with phenyl tin compounds forming a number of organotin complexes through phenyl-tin cleavage. A number of organotin derivatives of oximes and hydroxylamines formed through the replacement of hydroxyl hydrogen atom has also been reported (19 - 31).

Since the present study is primarily concerned with the reactions of organotin halides and carboxylates with 1-nitroso-2 napthol (I) and Keto - oximes of the type II, all of which



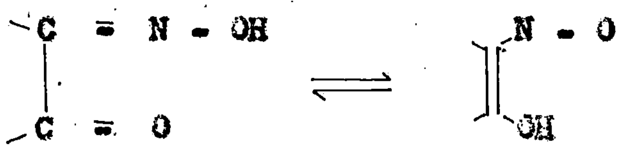
I



$$\begin{array}{l} R_1 - C = N - OH \\ \qquad\;\; | \\ R_2 - C = O \end{array}$$

II

can undergo, at least in principle, tautomerism of the type III, it would be desirable to briefly



III

review the nature and type of organotin hydroxylamine and oxime derivatives first.

B. Organotin hydroxylamine and oxime derivatives:

This topic has been recently reviewed by Mehrotra etal (19).

Like silicon and germanium, tin forms a number of organometallic derivatives with hydroxylamines and oximes through the replacement of the hydroxyl hydrogen. These compounds are important industrially because of their uses as bactericides, fungicides, insecticides and herbicides (21 -22, 24 - 28, 31).

(a) Methods of preparation : Organotin oximates are generally prepared by one of the following methods :

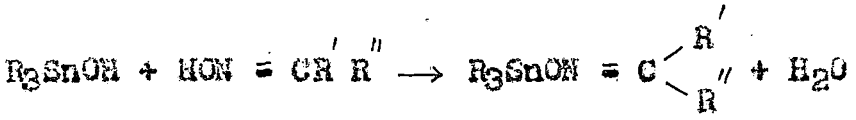
(i) By the reaction of the sodium or lithium salts of oximes with organotin halides (20 - 22) :

$$R_{4-n}SnCl_n + nNa(Li)ON = CR'R'' \longrightarrow R_{4-n}Sn(ON = CR'R'')_n + n\,NaCl(or\ LiCl) \qquad (1)$$

(ii) By the reaction of hexaorgano stannoxanes with oximes (20 - 21, 23 - 29) :

$$(R_3Sn)_2O + 2HON = CR'R'' \longrightarrow 2R_3SnON = CR'R'' + H_2O \qquad (2)$$

(iii) By the reaction of triorganotin hydroxides with oximes (20, 23) :



$$R_3SnOH + HON = CR'R'' \longrightarrow R_3SnON = C\begin{matrix} \diagup R' \\ \diagdown R'' \end{matrix} + H_2O \qquad (3)$$

Hydroxylamine derivatives also have been prepared (30) by the methods II and III using hydroxylamine instead of the oxime.

(IV) By reacting alkyl tin alkoxides with oximes (20,23 - 24, 29, 31) :

$$R_{4-n}\ Sn(OR')_n + nHON = CR''R''' \rightarrow R_{4-n}\ Sn(ON = CR''R''')_n + nR'OH \qquad (4)$$

(V) Organotin derivatives of a dicyano formaldehyde oxime have been prepared by the following reaction (32) :

$$R_2Sncl_2 + 2AgON = C(CN)_2 \rightarrow R_2Sn\left[ON = C(CN)_2\right]_2 + 2Agcl \qquad (5)$$

(b) General Properties :

(i) Organotin derivatives of oxime and hydroxylamine are generally volatile and can be distilled unchanged except the types $R_2Sn(OR')(ONE^{t}_{2})$ and $R_2Sn(ONE^{t}_{2})_2$.

(ii) Oximates of tin are readily hydrolysed by water to give parent oxime quantitatively (20,29).

$$R_{4-n}\ Sn(On = CR'R'')_n + nH_2O \rightarrow R_{4-n}\ Sn(OH)_n + nR'R''C = NOH \qquad (6)$$

(iii) These compounds react with acyl or benzoyl halides forming organotin halides and O-acyl or O-benzoyl oxime (29).

$$R_{4-n}Sn(ON=CR'R'')_n + nR'''COX \rightarrow R_{4-n}SnX_n + nR'R''C-NO.COR''' \qquad (7)$$

(iv) Exothermic cleavage of Sn - O bond in these compounds occurs with organo germenium and silicon chloride (20,34-36).

$$R_3SnON=CR'R'' + R_3'''MCl \rightarrow R_3SnCl + R_3'''MON=CR'R'' \qquad (8)$$

$$[M = Si \text{ or } Ge]$$

C. Organotin derivatives of N - benzoyl hydroxylamines :

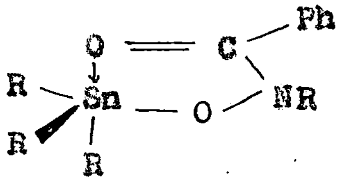
In addition to the organotin hydroxylamines a few O-triorganotin N-benzoyl hydroxylamines have also been reported (30) : These are :

$R_3SnONHCOPh$ (R = Me, n - Pr)

$R_3SnONPhCOPh$ (R = Me, n - Pr, Ph)

Attempts to prepare $Ph_3SnONHCOPh$ from Ph_3SnOH and N-benzoyl hydroxylamine results in $SnPh_4$. However the ionic species NE^{+} ($Ph_3\overline{SnONPhO}^{-}$) has been reported (33).

All these compounds are inert to hydrolysis and stable (33), the increased stability compared to simple oximates is assigned to the increase in co-ordination number of tin via intramolecular co-ordination of CO group to the metal as follows :



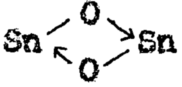
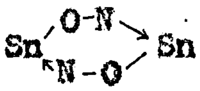
(IV)

D. Structural feature :

Structural studies on organotin hydroxylamines and oximes are limited to only a few derivatives and the conclusions derived are mostly tentative. A lowering of ν(CN) by 20 - 50 cm^{-1} is observed for the oximates of tin which is assigned to be due to mass effect (20).

On the basis of comparative spectral data on trimethyl tin acetoximate $(CH_3)_3SnON = C(CH_3)_2$ and cyclohexanone oximate

$(CH_3)_3SnON=$  in the range of 600 - 300 cm^{-1}, Harrison and Zuckerman (20,30) concluded that the latter compound tended to associate unlike the former or the other higher alkyl and aryl tin analogues. The quadrupole splitting data in the Mossbauer spectra also indicated a higher co-ordination number for tin in trimethyl tin cyclohexanone - oximate

Mass spectral study of trimethyl tin cyclohexanone-oximate (20,33) supports a structure having the dimeric units with cyclic  bridge rather than the  ring. The tendency for oligomerisation is not yet understood in contrast to acetoximate although the steric requirement is probably more demanding in the former.

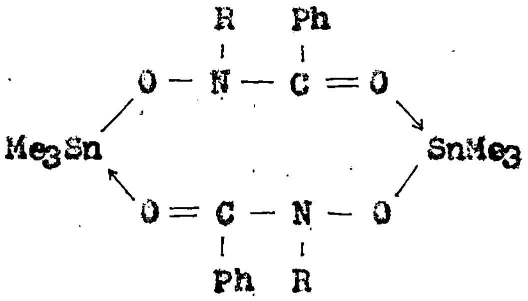
Diorganotin diethyl hydroxylamines of the type $Bu_2Sn(OR)(ONE^t)_2$ (R = E^t, iPr) are reported to give molecular association ~ 3·0 in boiling benzene. The association of these derivatives is thought to be more likely through the SnONSnON ring. The presence of Sn - O - N bond has been established in compounds of the type R_{4-n} Sn $[ON = C(CN)_2]n$ (32) by IR spectral study (37).

Unlike the simple oximates N-phenyl N-benzoyl hydroxylamine derivatives $R_3SnONPhCOPh$ are monomeric in dilute chloroform solution, though O - (trimethyl stannyl) N-benzoyl hydroxylamine

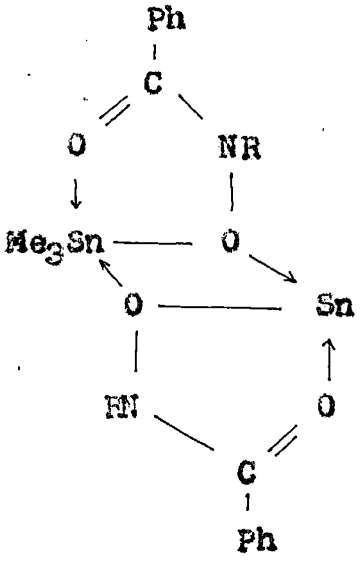
$(CH_3)_3SnONHCOPh$ shows some association via hydrogen bonding.

The crystal structure of $Ph_3SnONPhCOPh$ has been determined (38). The compound possesses a trigonal bipyramidal arrangement of the group around tin, with two equatorial and one axial Ph group. The hydroxylamine residue is covalently bonded at equatorial site and the CO group is co-ordinated via axial site. The structure is consistent with the lowering of $C=0$ stretching frequency from 1620 cm^{-1} in the parent hydroxylamine to 1540 cm^{-1} in the O-triphenyl derivatives.

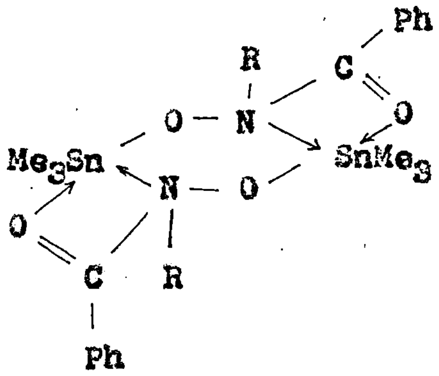
Though $Ph_3SnONPhCOPh$ is monomeric, the corresponding methyl derivative is associated in the solid state into dimeric species which may have the following structures :



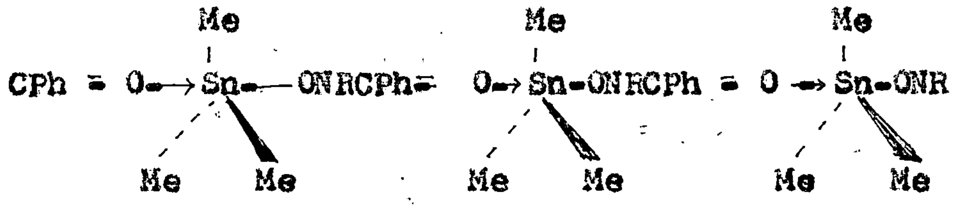
(A)



(B)



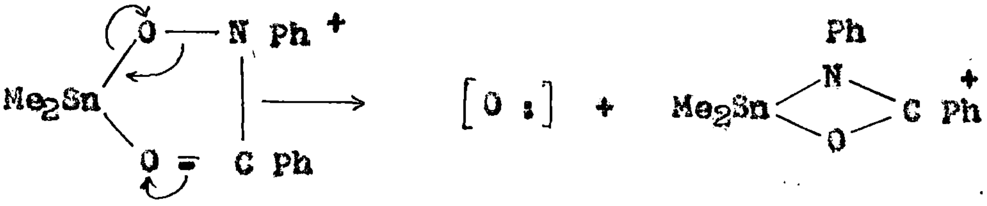
(C)



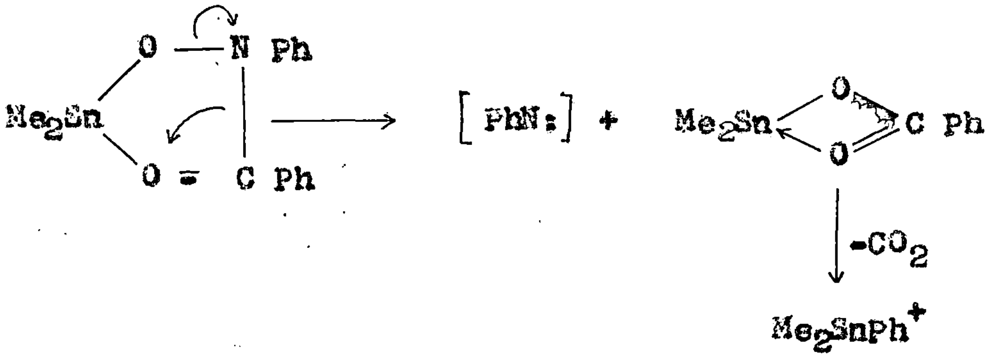
(D)

Though the experimental data can not be used to distinguish between A and C, structure involving dimerization via the formation of distannoxane ring is prevalent in the organotin chemistry (39). Similar co-ordination dimerization equilibria in solution have been found for 1,3 disubstituted distannoxane (40) and dialkyl tin alkoxide halide (41).

The mass spectra (33) for $Me_3SnONHCOPh$ and $Me_3SnONPhCOPh$ indicates the association. High resolution mass measurement have confirmed the presence of Sn-O-Sn backbone. Mass spectral study again suggests the novel ring contraction reaction involving elimination of oxygen from the cation $Me_2SnONPhCOPh^+$ and phenyl nitrene from $Me_2SnONPhCOPh$:



(9)



(10)

The latter decarboxylation process is well known in the organometallic chemistry (42).

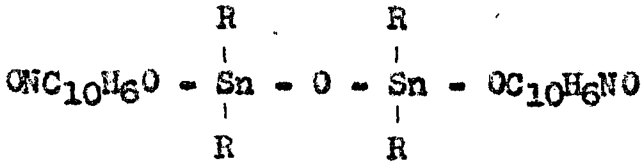
IR spectra (33) of these compounds show a lowering of ν(C = 0) stretching frequency from 1620 cm^{-1} in the parent hydroxylamine HONPhCOPh to 1540 - 1557 cm^{-1} in the compounds of the type $R_3SnONPhCOPh$.

The hydroxylamine HONHCOPh gives two bands for ν(C = 0), 1679 cm^{-1} and 1658 cm^{-1}. In this case also similar lowering to 1570 cm^{-1} - 1540 cm^{-1} are found for the compounds of the type $R_3SnONHCOPh$. These types of compounds again exhibit broad NH stretching frequency at 3200 cm^{-1}. All the compounds show ν(N-O) stretching frequency from 900 cm^{-1} to 940 cm^{-1} along with the parent hydroxylamines.

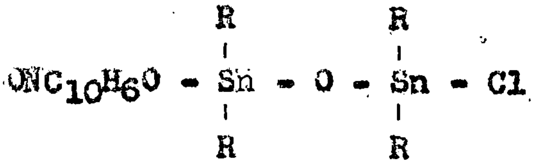
The trimethyl derivatives are expected to show two bands for antisymmetric and symmetric stretching frequencies in the region 500 - 600 cm^{-1}. In this region both $Me_3SnONPhCOPh$ and $Me_3SnONHCOPh$ exhibit three bands. For $Me_3SnONPhCOPh$ the band at 508 cm^{-1} is clearly resolved into 507 and 497 cm^{-1}. For $Me_3SnONHCOPh$ similar splitting is observed.

E. Objective and scope of the present work :

Despite the attention given to hydroxylamine, oxime and related ligands, nitrosonapthols, e.g. 1-nitroso 2-napthol and Keto oximes e.g. diacetyl monooxime, have received comparatively little attention though all these compounds may act like oxime due to tautomerism discussed earlier. The first reported work on the action of 1-nitroso-2-napthol on organotin compounds appears to be due to Okawara etal (43). Okawara etal have found that dimethyl and diethyltin chlorides react with 1-nitroso-2-napthol in methanol in the presence of ammonia to from tetra alkyl 1,3 bis (1-nitroso-2-napthoxy) distannoxanes. However with di n-propyl and di n-butyl tin dichlorides corresponding tetra-alkyl 1-(1-nitroso-2-napthoxy)-3 chloro distannoxanes were obtained.



$$ONC_{10}H_6O - \overset{R}{\underset{R}{Sn}} - O - \overset{R}{\underset{R}{Sn}} - OC_{10}H_6NO \qquad [R - CH_3-, C_2H_5 -]$$



$$ONC_{10}H_6O - \overset{R}{\underset{R}{Sn}} - O - \overset{R}{\underset{R}{Sn}} - Cl \qquad \begin{bmatrix} R - nC_3H_7-, \\ nC_4H_{10}- \end{bmatrix}$$

No monotin derivatives were however obtained from these reactions.

Recently Mehrotra etal (44) have described the preparation of a few mono-tin derivatives of 1-nitroso-2-napthoxide through the reactions of dialkyltin diisopropoxides with 1-nitroso-2 napthol in the molar ratio of 1 : 1 and 1 : 2 in dry benzene solution. Two types of compounds, viz.,

(i) $R_2Sn\ (OC_{10}H_6NO)\ O\text{-}isoPr$

(ii) $R_2Sn\ (OC_{10}H_6NO)_2$

have been reported as the products. It is worth mentioning at this point that we have failed to prepare any mono-tin derivative in our study with 1-nitroso-2-napthol and related systems using reaction conditions where 8-hydroxyquinoline, hydroxylamine and oxime give well define mono tin derivatives. In fact the present study which began before the publication of report by Mehrota etal (44) was aimed at the synthesis of monotin derivatives of 1-nitroso-2-napthol.

The failure to obtain mono-tin derivatives of 1-nitroso-2-napthol under conditions where apparently similar ligands yield the desired products, prompted us to undertake a systematic study on the reactions of 1-nitroso-2-napthol, diacetyl mono oxime, alpha-benzil oxime etc. on a variety of organotin compounds, viz., triorganotin halides, carboxylates and hexaorganotin distannoxane etc., under different conditions with a view to understanding the peculiar behaviour of this group of ligands.

Results and discussion :

1. Summary of the results on reactions studied :

The conditions of reactions and the products together with possible structure formed in different reactions are given in the table I, II and III. Because of extremely low solubility of most of the products in all common solvents the formulae and structures given in tables have been inferred from elemental analysis and IR spectra together with UV - visible spectra where possible.

Table I : The reactions of triorganotin compounds with 1-nitroso-2-napthol.

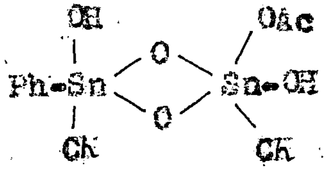
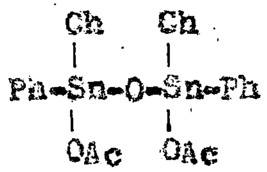
Tri organo tin compounds	Mole ratio Triorgano tin compounds / Ligands	Concidition used	Nature of the Products			Analysis found (Calculated for)%				The products and their probable structures
			Colour	mp/ Decomposition point°C	Solubility	C	H	N	Sn	
Ph_3SnOAC	1 : 1 (a slight excess of the ligand was used)	Refluxed for 7 hours in benzene	A) White	>360°	Insoluble in all common solvents, sparingly soluble in hot $CHCl_3$	35.09 (35.47)	2.95 (2.96)		42.83 (43.85)	Ph-Sn(OAc)-O-Sn(Ph)(OAc
			B) Red	>360°	Sparingly soluble in all common solvents, sparingly in pyridine	43.71 (52.8)	3.32 (3.06)	3.57 (3.56)	30.5 (30.2)	
			C) Violet	>360°	Springly to moderately soluble in common solvents	50.47 (49.7)	3.42 (3.23)	3.36 (2.22)	26.92 (27.35)	 $Ph-\underset{OAc}{\overset{Ch}{Sn}}-O-\underset{OAc}{\overset{Ch}{Sn}}-Ph$

Table- 1 Contd.

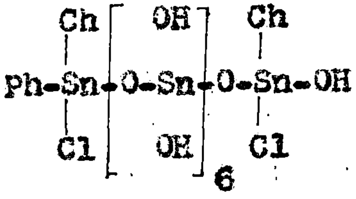
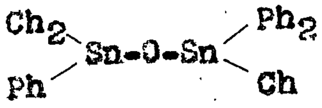
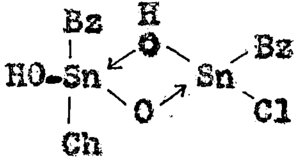
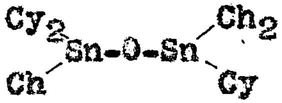
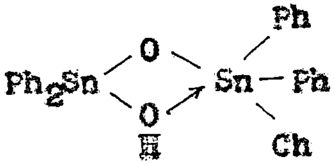
Tri organo tin compounds	Mole ratio Triorgano tin compounds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					The products and their probable structures
			Colour	mp/ Decomposition point °C	Solubility	C	H	N	Cl	Sn	
			D)Green	>360°	Sparingly soluble in common solvents.	Formed in small amounts, could not be purified and characterised					
			E)Yellow	>360°	Sparingly soluble in common solvents	as above					
Ph_3SnCl	1 : 1 a slight excess of the ligand was used.	Refluxed for 7 houss in benzene	Greenish black	>360°	Insoluble in common solvents, soluble in DMF.	16.82 (17.59)	1.77 (1.62)	1.83 (1.83)	4.17 (4.00)	52.86 (52.52)	 $Ph-Sn(Ch)(Cl)-[O-Sn(OH)_2]_6-O-Sn(Ch)(Cl)-OH$
			B)Green	>360°	Sparingly soluble in common solvents	58.72 (57.6)	3.03 (3.3)	4.48 (4.2)		24.00 (23.7)	

Table-1 Contd.

Tri organo tin compounds	Mole ratio Triorgano tin compounds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					The products and their probable structures
			Colour	mp/ Decomposition point °C	Solubility	C	H	N	Cl	Sn	
			C)Yellow	$>360^{\circ}$	Fairly soluble in benzene and alcohol	50.01 (50.62)	3.02 (2.75)	5.19 (5.14)		22.3 (21.77)	$PhSnch_2(Cl)$. $Sn(Ch_2)$ (Cl) OH
											Or
						(49.79)	(2.89)	(5.05)		(21.42)	$PhSnch_2(Cl)$. $Sn(Ch_2)$ Cl OH, H_2O

[Ph = C_6H_5 ; OAc = $-OCOCH_3$; Ch = $-C_{10}H_6NO_2$]

Table-1 Contd.

Tri organo tin compounds	Mole tatio Triorgano tin compounds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					The products and their probable structures
			Colour	mp/ Decomposition point °C	Solubility	C	H	N	Cl	Sn	
Bz_3Sncl	1 : 1	Refluxed for 7 hours in benzene	Greenish yellow	230°	Sparingly soluble in common solvents	42.52 (43.1)	3.42 (3.29)	1.94 (2.09)		34.82 (35.4)	
Cy_3SnBr	1 : 1	Refluxed for 7 hours in benzene	Green	> 360°	Sparingly soluble in common solvents	57.31 (56.58)	4.3 (5.00)	4.8 (4.1)		22.62 (23.28)	
$(Ph_3Sn)_2O$	1 : 1 (A slight excess of ligand was used.	Refluxed in benzene for 7 hours	Yellow	160°d	Moderately soluble in common solvents	55.34 (54.37)	4.04 (3.60)	1.96 (1.87)		30.7 (31.64)	

Bz - $C_6H_5CH_2$; Cy - Ch - $C_{10}H_6NO_2$-

Table II : Reactions of triorganotin halides with potassium 1-nitroso-2-napthoxide.

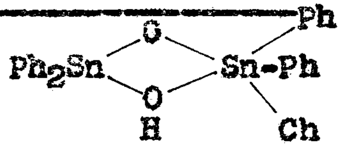
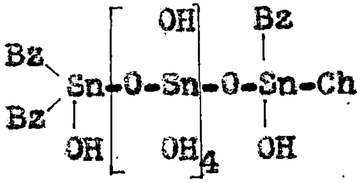
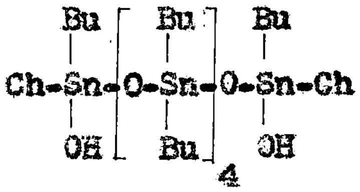
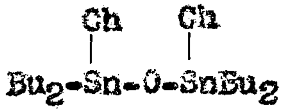
Tri organo tin compounds	Mole ratio Triorgano tin compounds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					The products and their probable structures
			Colour	mp/ Decomposition point ^{o}C	Solubility	C	H	N	Cl	Sn	
Ph$_3$SnCl	1 : 1	Refluxes for 2 hours in Methanol	Yellow	160^{od}	Moderately soluble in common solvents	53.87 (54.37)	3.68 (3.60)			30.92 (31.64)	
B$_{z3}$SnCl	1 : 1 (a slight excess of ligand was used)	Refluxed for 2 hours in methanol	Green	$>360^{o}$	Insoluble in common solvents sparingly soluble in pyridine	26.71 (26.44)	2,67 (2.63)	1.03 (0.99)		49.24 (50.6)	

Table-2 Contd.

Tri organo tin compounds	Mole ratio Triorgano tin compounds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					Thr products and their probable structures
			Colour	Mp/ Decomposition point °C	Solubility	C	H	N	Cl	Sn	
Bu $SnCl_3$	1 : 1	Refluxed for 2 hours in methanol	A)Green	>360°	moderately soluble in common solvents	41.85 (41.37)	6.32 (5.98)			39.61 (40.92)	
			B)Brown	238-40°	Sparingly soluble in common solvents	53.84 (52.2)	5.98 (5.8)	3.13 (3.36)		28.2 (28.3)	

[Ch = $C_{10}H_6NO_2$- , Bu = C_4H_9-]

Table-III : Reactions of triorganotin compounds with diacetyl monoxime, α- benzil oxime, benzoin oxime.

Triorganotin compounds	Legands	Mole ratio triorganotin compounds / ligands	Nature of the Products			Analysis found(Calculated for)%				Products and their probable structures.
			Colour	m.p/ Decomposition point °C	Solubility	C	H	N	Sn	
Ph_3SnOAc	Diacetyl mono-oxime	1 : 1 Refluxed for 7 hours in benzene	A)While	$>360^\circ$	Insoluble in common solvents, sparingly soluble in hot $CHCl_3$				43.3 (43.85)	Ph-Sn(OAc)-O-Sn(Ph)(OAc)-O- Identified on the basis of spectral identity with the white compound, obtained in the reaction of Ph_3SnOAc with 1-nitroso-2-napthol.
			B)Yellow	Not characterised						
Ph SnOAc	2-nitroso-1-napthol	1 : 1 Refluxed for 7 hours in benzene	White	360°	Insoluble in common solvents sparingly soluble in hot $CHCl_3$				42.2 (43.85)	Ph-Sn(OAc)-O-Sn(Ph)(OAc)-O- Identified as in above

Table-III Contd

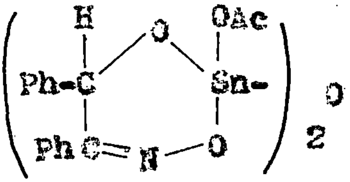
Triorgano tin compounds	Legands	Mole ratio triorganotin compounds / ligands	Nature of the Products			Analysis found(Calculated for)%				Products and their probable structures.
			Colour	m.p/ Dcomposition point °C	Solubility	C	H	N	Sn	
Ph_3SnOAc	α-benzil oxime	1 : 1 (a slight excess of ligand was used Refluxed for 7 hours in C_6H_6	White	〉360°	Same				42.82 (43.85)	Ph-Sn(OAc)-O-Sn (Ph) (OAc)O- identified as in above
Ph_3SnOAc	Benzoin oxime (cupron)	1 : 2.4	White	232°	Soluble in common solvents	45.06 (45.75)	3.70 (3.57)		27.98 (28.28)	

Table-III Contd.

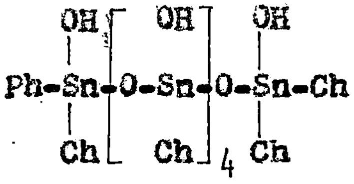
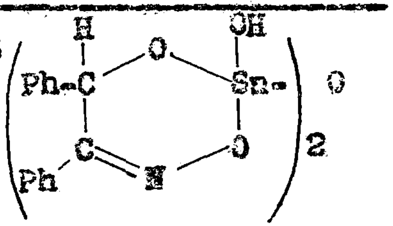
Triorgano tin compounds	Legands	Mole ratio triorganotin compounds / ligands	Nature of the Products			Analysis found(Calculated for)%				Products and their probable structures.
			Colour	M.p/ Decomposition point °C	Solubility	C	H	N	Sn	
Ph_3Sncl	Diacetyl mono oxime	1 : 1 (a slight excess of ligand was used) Refluxed for a long time in C_6H_6	White	>360°	Insoluble in common solvents	23.78 (24.41)	3.76 (3.17)	6.09 (5.86)	42.2 (42.62)	 $Ph-\underset{Ch}{\overset{OH}{Sn}}-\left[O-\underset{Ch}{\overset{OH}{Sn}}\right]_4-O-\underset{Ch}{\overset{OH}{Sn}}-Ch$ [Ch = $(CH_3)_2COCNO-$]
Ph_3Sncl	∝ - benzil oxime	1 : 1 (a slight excess of ligand was used Refluxed for a long time in C_6H_6	White	>360°	Polymers of variable composition separated					

Table-III Contd.

Tri organo tin compounds	Legands	Mole ratio triorgano tin compounds / legands condition used	Nature of the products			Analysis found(Calculated for)%				Products and their probable structures.
			Colour	m.p/ Dcomposition point	Solubility	C	H	N	Sn	
Ph_3SnCl	Benzoin oxime		White	250°d	Soluble in common solvents	44.39 (45.56)	3.52 (3.25)		31.85 (32.2)	
Bu_3SnCl	Diacetyl mono oxime	1 : 1	No reaction took place.							
Bu_3SnCl	Benzoin oxime	1 :1.4	No reaction took place							

2. Salient features of the reaction of 1-nitroso-2-napthol and related compounds :

a) General nature of the products :

Though molecular weights could not be determined by cryoscopic or ebullioscopic methods because of the very low solubility of the products in all common organic solvents, analytical data invariably indicated formation of polystannoxanes of varying degree with extensive cleavage of Sn-R bonds. In most cases, a number of products were formed, and only in a few cases a single product was obtained. In this respect 1-nitroso-2-napthol differs rather surprisingly from other chelating agents like 8-hydroxy quinoline (1-6), dithiocarbamate (7), tropolone (9), acetyl acetone and picolinic acid (15-17) etc, which under comparable reaction condition (refluxing in benzene or stirring at room temperature) furnish products according to equations :

$$R_3Sn\,X + NaOx \rightleftharpoons R_3SnOX + NaX \qquad (11)$$

$$R_2Sn\,X_2 + HOx \rightleftharpoons R_2Sn(Ox)X + HX \qquad (12)$$

$$R_2Sn(Ox)X + HOx \rightleftharpoons R_2Sn(Ox)_2 + HX \qquad (13)$$

etc.

$[Ox = C_9H_6(N)O-, X = \text{habogen}]$

Cleavage of Sn-R bond also occurs in many cases (58-61). However the products of such cleavage reactions are generally simple. Thus, R_2SnX_2 when refluxed with oxine in benzene furnishes $Sn(Ox)_2X_2$ formed by cleavage of Sn-R bonds along with $R_2Sn(Ox)_2$. Formation of polymeric products is generally not observed. However with 1-nitroso-2-napthol, no simple products could be isolated, polystannoxanes of varying complexities are always formed and surprisingly no monotin product could be isolated. The products may be devided into following categories :

(i) Distannoxanes : Reactions of 1-nitroso-2-napthol with triphenyl tin acetate, triphenyl tin chloride, tribenzyl tin chloride, tricyclohexyl tin bromide and bis triphenyl tin oxide furnish a distannoxane as one of the products in each cases.

(ii) Polystannoxanes : Infusible and insoluble polymeric products are common in most cases. Though no general trend in their composition could be discerned, analytical data suggest the formation of polymeric chains containing usually six tin atoms. In a number of cases, polymers of variable compositions are formed.

(iii) Stannoic acid derivatives : In a few cases 1-nitroso-2-napthol behaves as a catalyst leading to the cleavage of Sn-R bonds resulting in the formation of stannoic acid derivatives. Thus the reaction of triphenyl tin acetate with 1-nitroso-2-napthol gives a white product which has been definitely identified as phenyl stannoic acetate, $[PhSn(OAc)O]_x$.

Oximes like diacetyl monooxome, α- benzil oxime etc. also react similarly with the formation of polymeric products formed by extensive cleavage of Sn-R bonds. It is interesting to note that diacetyl mono oxime and α-benzil oxime produce phenyl stannoic acetate from triphenyl tin acetate just like 1-nitroso-2-napthol.

b) Colour and electronic spectra of the products :

All products which contain 1-nitroso-2-napthol ligand were coloured. The colour varied from yellow to red and even to intense green in some cases. Since the electronic absorption spectra of 1-nitroso-2-napthol and its derivatives could be interpreted either in terms of the oxime structure or the nitroso napthol structure, the absorption spectra are particularly helpful in the elucidation of the structure of the products. On the basis of electronic absorption spectra, the products could be devided into two categories :

(i) Yellow compounds : In a few cases, e.g., in the reaction of 1-nitroso-2-napthol with $(Ph_3Sn)_2O$ or that of potassium salt with

Ph SnCl, a yellow product was formed which shows almost identical absorption spectra with that of 1-nitroso-2-napthol (Table-IV) suggesting a closely similar structure (to be discussed latter). Methanolic NaOH has the same effect on its spectrum as that of free ligand.

Table - IV

Electronic absorption spectra of 1-nitroso-2-napthol and its organo tin derivatives :

Compound Formula (Colour)	Solvent	λmax in nm
1-nitroso-2 napthol	Methanol	214, 262, 372
	CCl_4	275.5, 377.5
	$CHCl_3$	274.5, 382.0
	C_6H_6	280.0, 379.0
	MeoH/NaoH	293.0, 370.0, 420
	MeoH/NaoH (Concentrated solution)	293.0, 370.0, 420, 590.

Table- IV Contd.

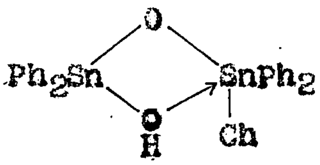
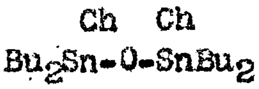
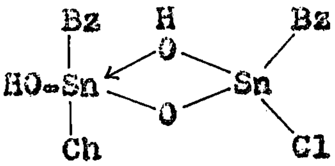
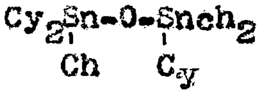
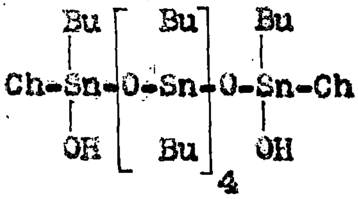
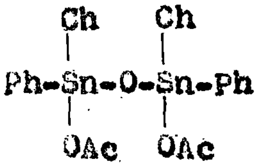
Compound Formula (Colour)	Solvent	λ max in nm
Potassium-1-nitroso-2-napthoxide. (Green)	Methanol	215, 261, 370
	Concentrated solution in Methanol	605
	Methanol	215, 260, 370
	CCl_4	~~225~~ 275, 377
(Yellow)	MeOH/NaOH	260(inflex), 292, 374, 420
 $\overset{Ch}{Bu_2Sn}-O-\overset{Ch}{SnBu_2}$	Methanol	228, 280(Sh),330(Sh)
(Brown).	DMSO	280, 330(Sh)
	Methanol	233, 280, 330
(Greenish Yellow)		

Table-IV Contd.

Compound Formula (Colour)	Solvent	λmax in nm.
 $Cy_2\underset{Ch}{Sn}-O-\underset{Cy}{Snch_2}$	Methanol	255, 272(Sh), 345, 395, 590
	$CHCl_3$	258, 275 , 340, 405, 600
(Green)	CCl_4	260(Sh), 370, 590
	DMSO	270(Sh) 350 580
 $Ch-\overset{Bu}{\underset{OH}{Sn}}-\left[O-\overset{Bu}{\underset{Bu}{Sn}}\right]_4-O-\overset{Bu}{\underset{OH}{Sn}}-Ch$	Methanol	227, 270(Sh), 310(Sh) 380(Sh)570
	CCl_4	270, 320(Sh),415, 615
(Green)		
 $Ph-\overset{Ch}{\underset{OAc}{Sn}}-O-\overset{Ch}{\underset{OAc}{Sn}}-Ph$	Methanol	225, 250(Sh), 340, 570
	$CHCl_3$	350, 570
(Violet)		
$[Ph-Sn(OAc)O-]_x$	$CHCl_3$	252·8, 259, 263·6, 268
(White)		

Ph = $-C_6H_5$; Bu = $-C_4H_9$; Cy = Cyclo $C_6H_{11}-$;

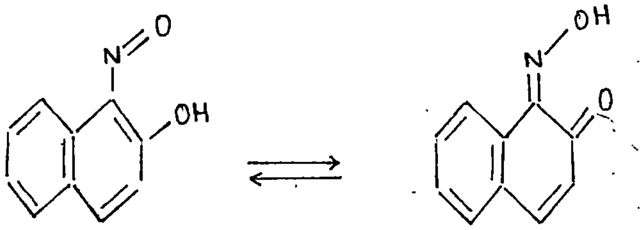
Ch = $-OC_{10}H_6NO$.

(ii) The second category includes products showing a moderately intense long wave length absorption band in 560-625 nm region. These compounds also show an absorption band at 330-350 nm, often as a shoulder of the shorter wave length band near 270-280 nm. In addition, some of the compounds show absorption around 400 nm also. The compounds are generally intensely coloured from red to green and are stable. Unlike the yellow compounds, these compounds show very little effect of methanolic NaOH or polar solvents like DMSO on its spectrum. The increased stability and the large bathochromic shift of the longest wave length band suggests these compounds to contain chelated 1-nitroso-2-napthol group.

3. Structural aspects of the products :

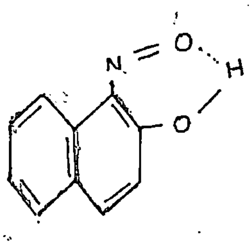
a) General :

Studies using 1-nitroso-2-napthol (43,44) so far implicitly assumed that this compound reacts in the nitroso napthol form. However the situation is not as simple as these studies imply because of the possibility of the following tautomerism :

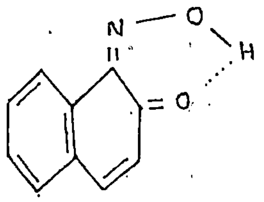


(V) (VI)

Apart from this, another situation in which the hydrogen is internally bonded with both the oxygen atoms giving rise to a delocalised system, as shown below is also possible.



VII



VIII

In order to fully appreciate the reactions of 1-nitroso-2-napthol with organotin compounds and the structural features of the products formed, it is therefore imperative to discuss first the structural aspects of the free ligand both in solution and the solid state.

That 1-nitroso-2-napthol is present predominantly in the oxime form is indicated by its electronic spectrum (figure-1) since :

(i) Napthols and substituted napthols like halo - or amino napthols have no absorption in the visible region. On the other hand both 1:2 and 1:4 napthaquinones are coloured with absorption in 380-420 nm region. The oxime form (VI) is structurally very similar to 1:2 napthaquinone. Indeed the absorption spectra of 1:2 napthaquinone and 1-nitroso-2-napthol are very similar

(Table-V) indicating the presence of the oxime structure.

Table- VI *

Electronic absorption spectra of 1-nitroso-2-napthol and napthaquinones :

Compounds	Solvent	λmax in nm(log ϵ max)			Ref
1-nitroso-2-napthol	EtOH	214	263 (4.08)	372.5(3.70)	45
	CCl_4		275.5(4.1)	377.5(3.78)	
1,2napthaquinone	MeOH		250(4.5)	340(3.5) 400 (3.5)	69a
	$CHCl_3$		250(4.5)	350(3.3) 400 (3.5)	
1,4 napthaquinone	MeOH		250(4.6)	330(3.8)	69 b
	CCl_4		262(4.0)	330(3.5)	69 c

* Ref - 69

a) S. Nagakura and A. Kuboyama, J. Am. chem. Soc., 76 (1954)

b) C. J. P. Spruit Rec. trav. chim., 68 (1949)

c) H. Peters., Anal. chem., 31 (1959)

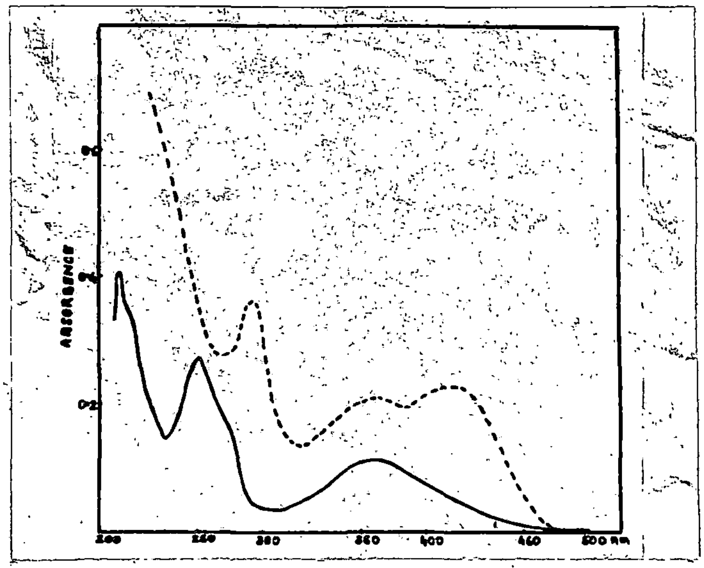


Figure - 1 : Electronic absorption spectra of 1-nitroso-2-napthol in

Methanol; ————————————

Methanol/NaOH : - - - - - - - - - -

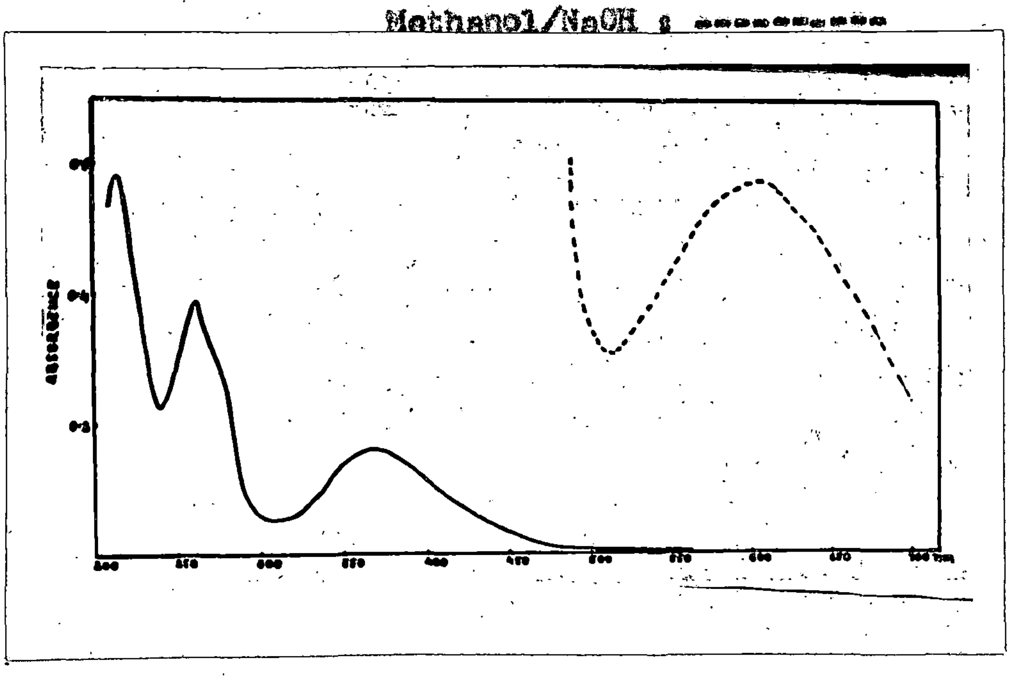


Figure - 2 : Electronic absorption spectra of potassium 1-nitroso-2-napthoxide in

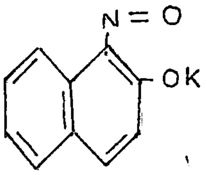
Methanol :————————————

Concentrated solution (methanol)- - - - - - - - - - -

(ii) Nitroso compounds generally possess a weak ($\epsilon \simeq 10-80$) absorption band in 600-750 nm region due to n- π^* transition. This transition imparts a blue to bluish green colour to nitroso derivatives. Absence of any such absorption in the spectrum of 1-nitroso-2-napthol in nonpolar solvents shows the absence of nitroso form.

The same conclusion has been drawn by Burawoy etal (45) from a detailed study of the electronic spectra of a number of quinones, quinone oximes and nitroso compounds.

When sodium or potassium hydroxide is added to a solution of 1-nitroso-2-napthol, a green colour appears. Electronic absorption spectra of such alkaline methanolic solution show a weak and broad absorption at 590-600 nm (figure-1). Potassium 1-nitroso-2-napthoxide in methanol shows an absorption band at 605 nm with $\epsilon_{max} \simeq 60$ (figure-2). The position as well as the molar extinction of this band is characteristic of the presence of nitroso group (45) showing that potassium derivative exists predominantly in the form (IX).



(IX)

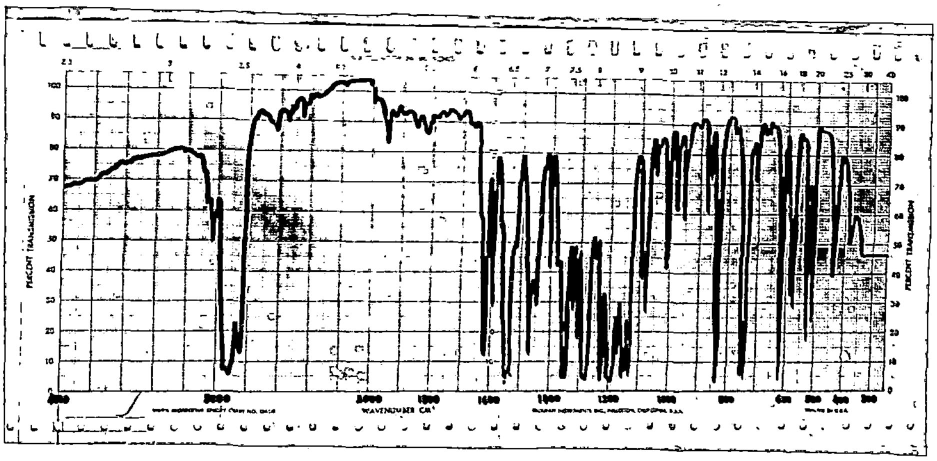


Figure - 3 : Infra red spectrum of potasium 1-nitroso-2-napthoxide

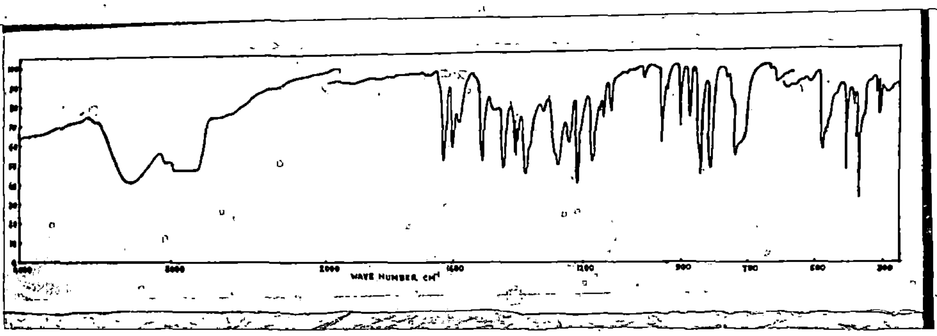


Figure - 4 : Infra red spectrum of 2-napthol

The IR spectra of the potassium derivative (figure-3) shows a~~s~~ broad and strong absorption band at 1550 cm^{-1} (doublet) and 1195 cm^{-1}. The 1195 cm^{-1} band is characteristic of phenolic C-O stretch (lit.62 range 1260 - 1180 cm^{-1}) and 1550 cm^{-1} band can be assigned with reasonable certainty to ν (N = O). Many aromatic nitroso monomers are known to absorb in this region (63-67). In this connection attention may be drawn to the assignment of 1625 cm^{-1} absorption in the IR spectrum of 1-nitroso-2-napthol to ν (N = O) by Mehrot~~g~~ra etal (44). This assignment seems to be completely erroneous because :

(1) The spectrum of 2-napthol shows a similar absorption at about 1625 cm^{-1} (figure-4).

(2) Aromatic nitroso monomers usually absorb at 1513 - 1488 cm^{-1}. While a raising of the ν (N = O) by 30 - 40 cm^{-1} may not be unreasonable if conjugation of the N = O group with the aromatic ring is hindered to some extent by steric or other reasons (aliphatic nitroso compounds absorb at somewhat higher frequencies), 1625 cm^{-1} appears to be too high. Even aliphatic nitroso monomers absorb below this region.

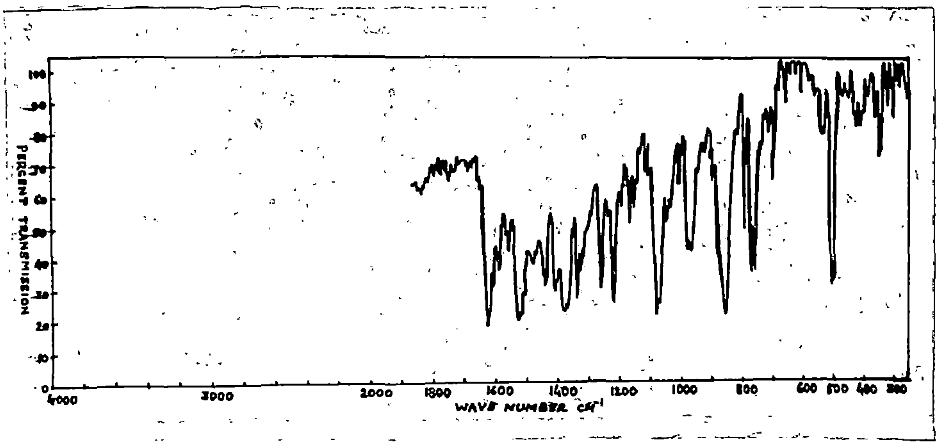


Figure - 5 : Infra red spectrum of 1-nitroso-2-napthol

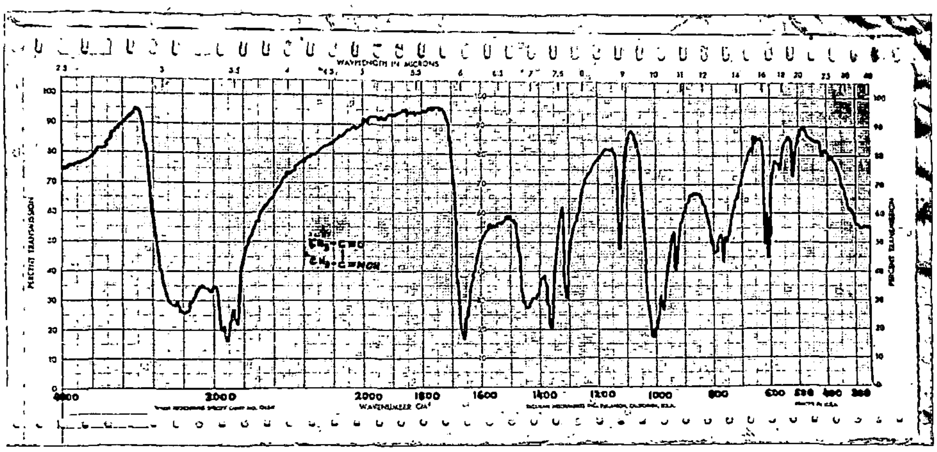
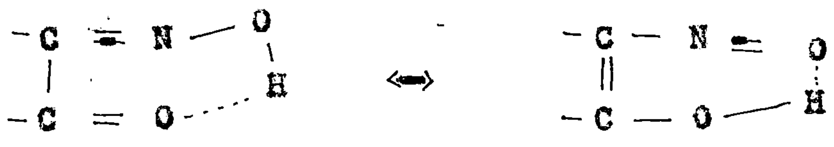


Figure - 6 : Infra red spectrum of diacetyl mono oxime

(3) As already indicated, the electronic absorption spectra of 1-nitroso-2-napthol indicates the absence of free - N = 0 group.

(4) The presence of a broad strong IR absorption band in the spectrum of 1-nitroso-2-napthol (fig-5) at 1070 cm^{-1} is particularly significant. This band is absent in the potassium salt which is shown to contain - N = 0 group by its electronic absorption spectrum. Therefore this band can be assigned to = N - 0 stretch. Although = N - 0 stretch occurs in 960 - 930 cm^{-1} in oximes, however, in 1,2 quinone mono oximes this stretch occurs at higher frequency due to contribution from structure (XI) which increases the N - 0 bond order.



(X) (XI)

Thus diacetyl mono oxime, $CH_3CO.C(CH_3)NOH$ absorps at 1020 cm^{-1} due to ν (= N - 0) (figure-6).

A comparison of the IR absorptions of 2-napthol, 1-nitroso-2-napthol and its potassium derivative in 1700 - 1500 cm^{-1} region together with other characteristic bands given in the table VII is extremely helpful for assignment of the bands as well as structures.

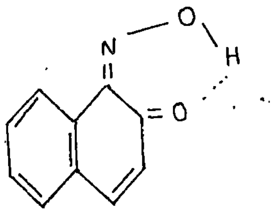
Table - VII

IR absorptions of 2-napthol, 1-nitroso-2-napthol and its potassium derivative in the 1700 - 1500 cm^{-1} region and other important absorptions :

2-napthol	1-nitroso-2-napthol	Potassium 1-nitroso-2-napthoxide	Assignment
1628 (s)	1620 (s)	1620 (s)	Ring
1600 (ms)	1605 (ms)	1595 (ms)	
1580 (ms)	1585 (ms)		
	1555 (w)		$\nu(C \doteq O + C \doteq N)$
		1550	$\nu(N = O)$
		1540	
	1525 (s)		$\nu(C \doteq O + C \doteq N)$
1510 (s)	1508 (ms)	1520 (ms)	Ring
1365 (ms)			$\delta(OH)$
1270 (s,br)		1195 (s,br)	$\nu(C - O)$
	1070 (s)		$\nu(N - O)$

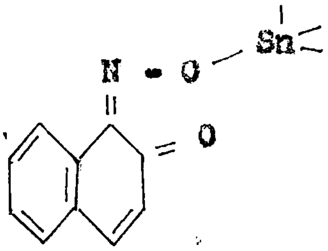
S = Strong ; ms = Medium strong ; w = weak ; br = broad.

The strong absorption in 1630 - 1620 cm^{-1} occurs in all compounds including 2-napthol and as such can not be assigned to ν(C = 0), ν(C = N) or ν(N = 0) which are possible in 1-nitroso-2-napthol and its derivatives. Though only a pair of bands near 1600 cm^{-1} is found in benzene and its derivatives due to ring stretch, substituted anthracene often shows absorption bands in 1640 - 1620 cm^{-1} (62). The 1620 cm^{-1} band in 1-nitroso-2-napthol should therefore be assigned to ring vibration since it occurs in 2-napthol also. The assignment of other absorptions in table VII are evident except for the absorptions at 1555 and 1525 cm^{-1} in 1-nitroso-2-napthol. The raising of the ν(N - 0) by more than 100 cm^{-1} in 1-nitroso-2-napthol compared to the position in simple oximes (960 - 930 cm^{-1}) shows a considerable contribution by structure (XI). The resonance between X and XI is therefore expected to make C = 0 , C - C and C = N bonds nearly equivalent and no pure C = 0 or C = N stretch in the usual region could be expected. Instead, the situation is comparable to metal chelates of 1,3 diketones (68) which absorb near 1580 cm^{-1} since here the two C = 0 and C = C bonds become nearly equivalent. Thus the two bands at 1555 cm^{-1} and 1525 cm^{-1} should be assigned to stretches involving both ν(C = N) and ν(C = 0). The structure of 1-nitroso-2-napthol should therefore be represented as in XII.



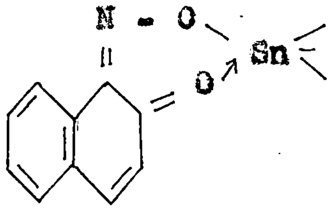
(XII)

Having thus established the oxime structure of 1-nitroso-2-napthol we may now discuss the various possibilities which may result from the substitution of the hydrogen atom by a tin atom. The product may exist either as an uncoordinated oximate~~d~~ (XIII) or chelate (XIV).



(XIII)

Oximate
uncoordinated



(XIV)

Oximate
chelate

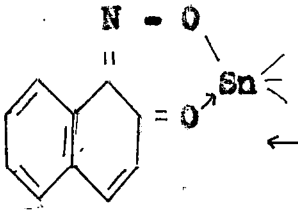
The uncoordinated oximate structure would be expected to show :

(i) an absorption band around 400 - 430 nm similar to 1,2 napthaquinone (57).

(ii) ν (N - O) in IR in the range of 960 - 930 cm^{-1} together with ν (C = O) which is now free and hence expected to be much above

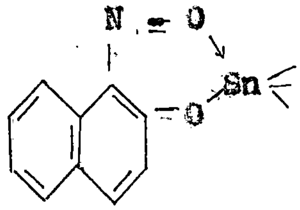
1600 cm^{-1}. Since none of the products show these characteristics, unchelated oximates are not formed.

As in the free ligand chelation would lead to resonance between the structures XV and XVI.



(XV)

$$\longleftrightarrow$$



(XVI

Two IR absorption involving both ν(C = O) and ν(C = N) would be once again expected in the 1600 - 1500 cm^{-1} range.

In the UV - visible spectrum the co-ordination by the O-atom with the tin is expected to cause a large bathochromic shift of the B - and K - bands (45).

All products of the red-green series mentioned earlier show moderately high intensity absorption around 560 - 625 nm which cannot be assigned to $n-\pi^*$ transition of the nitroso group because of the high intensity (of the order of 10^3) ; the intensity of

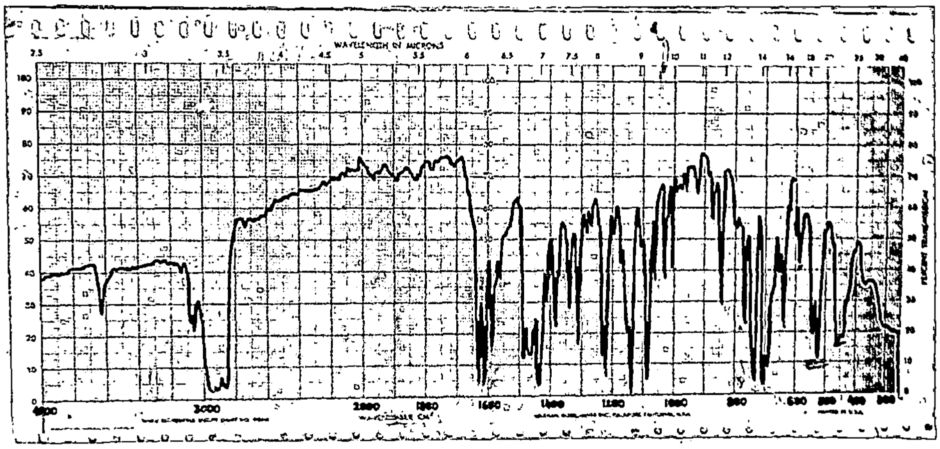


Figure -7: Infra red spectrum of $Ph_4ChSn_2(OH)O$

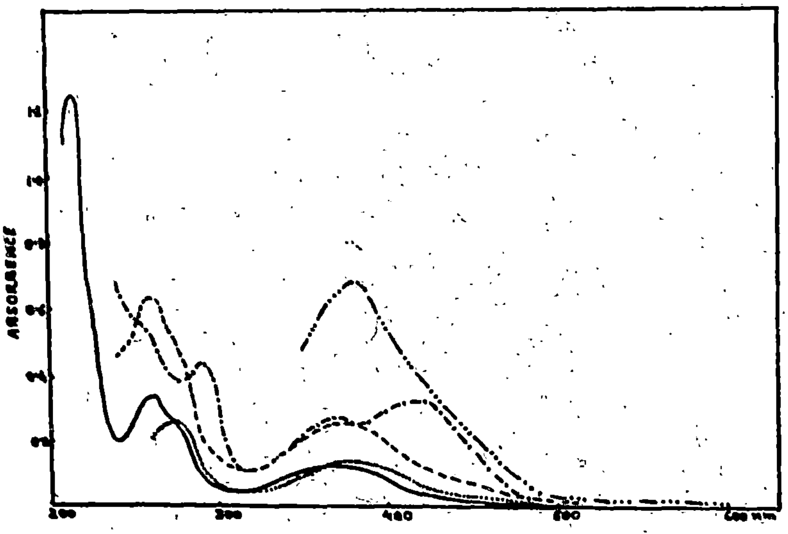


Figure - 8: Electronic absorption spectra of $Ph_4ChSn_2(OH)O$ in

Methanol : ———————— and – – – – – – –

Methanol/NaOH : —·—·—·—·—

CCl_4 : ··················

DMSO : —··—··—··—

nitroso absorption being only 10 - 70 (46).

These products are thus chelated oximates having structure XV. Accordingly the ir spectra shows strong absorption at ~ 1590 cm^{-1} [ν(C = O), coordinated to tin] .

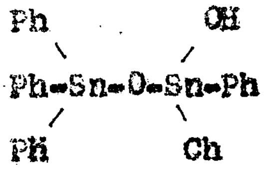
(b) Some selected compounds :

(i) Yellow product formed in the reaction of 1-nitroso-2-napthol with $(ph_3Sn)_2O$ or the reaction of Ph_3SnCl with potassium 1-nitroso-2-napthoxide :

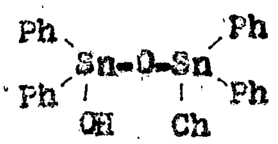
The analytical data on this product suggests a molecular formula of $Ph_4ChSn_2(OH)O$ [Ph = $-C_6H_5$; Ch = $-ON(O)\,C_{10}H_6$]. The presence of a moderately short medium intensity IR band at 3610 cm^{-1} shows the presence of $-OH$ group attached to tin atom (cf. Ph_3SnOH). This is further supported by the presence of absorptions at 580 cm^{-1} due to ν (Sn - O). Presence of another strong absorption at 685 cm^{-1} is indicative of Sn-O - Sn skeleton. The IR spectrum of the compound is shown in figure - 7.

The UV - visible spectrum is very similar to that of free ligand (figure - 8 and table - IV) Thus an oximate structure is indicated. However, absence of any bathochromic shift as well as the comparatively weak stability of the compound as suggested by the effect of polar solvents and methanolic sodium hydroxide on its UV - visible spectrum is indicative of only weak co-ordination.

On the basis of these data the following two structures may be written for this compound.

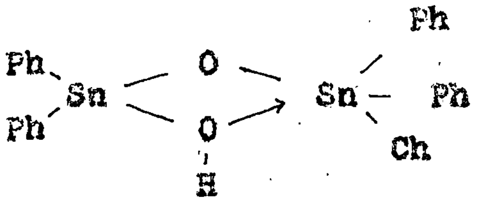


Or



$[Ch = ON(O)C_{10}H_6]$

However, in order to account for the stability of the distannoxanes (it does not lead to higher polystannoxanes by elimination of water) the structure (XVII) in which - OH is co-ordinated to another tin atom (preferably the atom containing the ligand since this tin atom will be more electron attracting due to its being bonded to two oxygen atoms) is more preferable.



(XVII)

$Ph = -C_6H_5$

$Ch = -ON(O)C_{10}H_6$

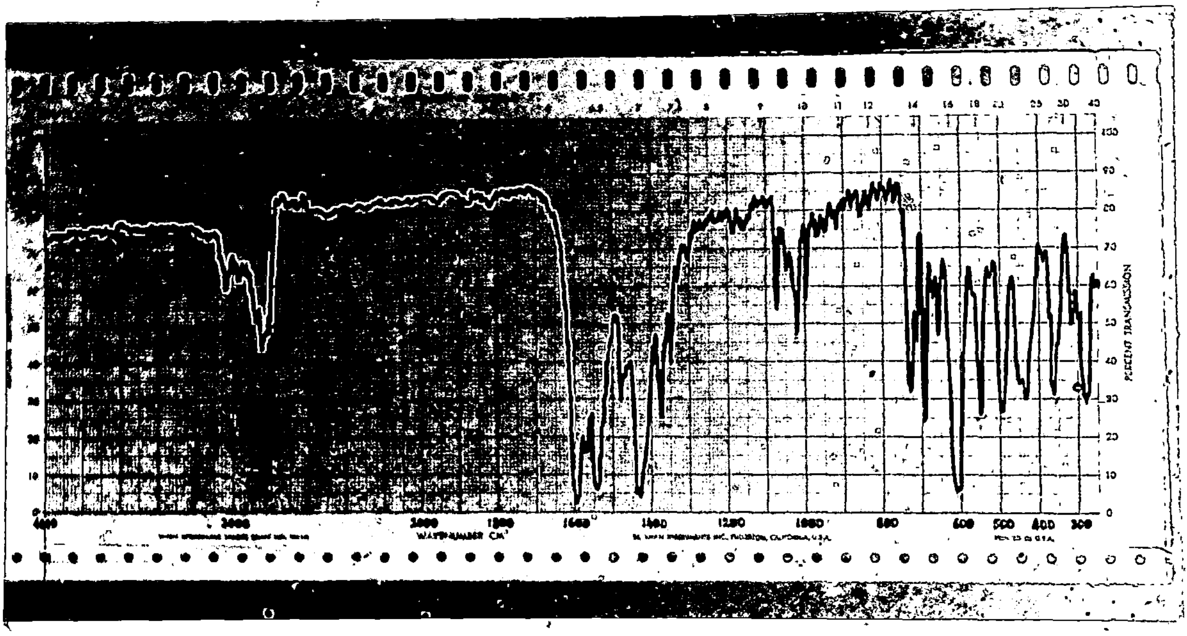


Figure - 9 : Infra red spectrum of $-O-(Ph)Sn(OAc)-O\ Sn(Ph)(OAc)-$

(ii) White polymer obtained from the reaction of 1-nitroso-2-napthol or 2-nitroso-1-napthol or diacetyl mono oxime or alpha-benzil oxime with triphenyl tin acetate :

Reactions of triphenyl tin acetate with nitroso napthols or Keto-oximes like diacetyl mono oxime and α-benzil oxime furnish a white compound which could be formulated as a polymer

$$- O - (C_6H_5)Sn(OAc)-O-Sn(C_6H_5)(OAc) -$$

(XVIII)

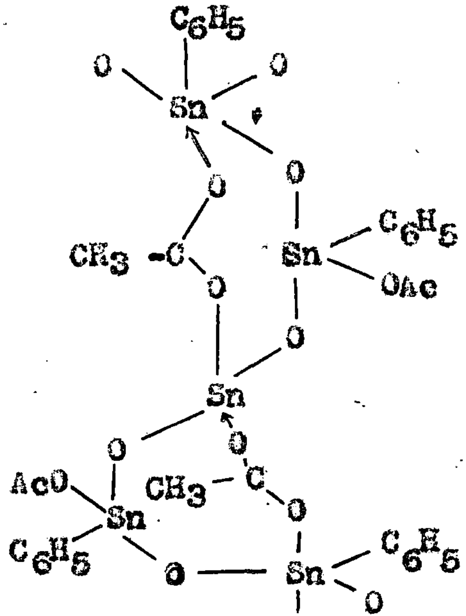
where OAc is $-OCOCH_3$. The structure has been established on the basis of spectral study and elemental analysis and its reaction with oxine.

The UV spectrum of the compound shows several absorption peaks in 230 - 270 nm region (solvent ; chloroform) which correspond very closely to absorption arising due to benzene ring which are perturbed only slightly in phenyl - tin system.

IR spectrum of the compound is shown in the figure - 9. The compound shows all the usual benzene ring vibrationand in particular has a moderately strong band at 1077 cm^{-1}. This band is assigned to a C - H in plane deformation mode and has been shown to be characteristic of phenyl - tin group (52). The strong absorption at 727 cm^{-1} is assigned to out of plane C - H vibration of phenyl ring.

The presence of strong absorption around 617 cm^{-1} can be assigned to (Sn-O-Sn). All polystannoxanes are known to absorb in this region (53). The strong band around 1600 cm^{-1} and 1550 cm^{-1} must be assigned to νas (-COO) as no other group in the system is expected to show such strong absorption in this region. The two values of νas (-OCO) indicates bridged acetate group, though possibility of ionic acetate group (51) can not be completely excluded.

The presence of $C_6H_5Sn(O)OAc$ group has also been supported by its reaction with oxine. In order to account for all these observations and analytical data a helical structure (XIX) where every third tin atom is bridged by acetate group is tentatively suggested.

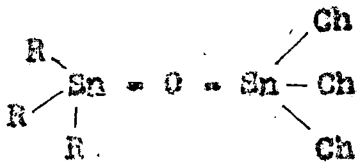


(XIX)

(iii) Distannoxanes of the type $R_3Ch_3Sn_2O$:

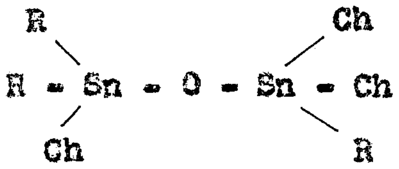
$[Ch = C_{10}H_6 No_2]$

Reactions of 1-nitroso-2-napthol with Ph_3Sncl or (cyclo-$C_6H_{11})_3$ SnBr furnish deep green compounds which could be formulated as $R_3Ch_3Sn_2O$ where R is either Ph or cyclo- C_6H_{11}. Of the two possibilities XX and XXI



(XX)

Or



(XXI)

the later is to be preferred since UV - visible spectrum shows the presence of two absorption bands at 395 nm (similar to free ligand) and 590 - 610 nm indicating presence of two nonequivalent type of ligands.

(IV) Product of the reaction of benzoin oxime (cupron) with triphenyl tin acetate :

The reaction of triphenyl tin acetate with benzoin oxime furnishes

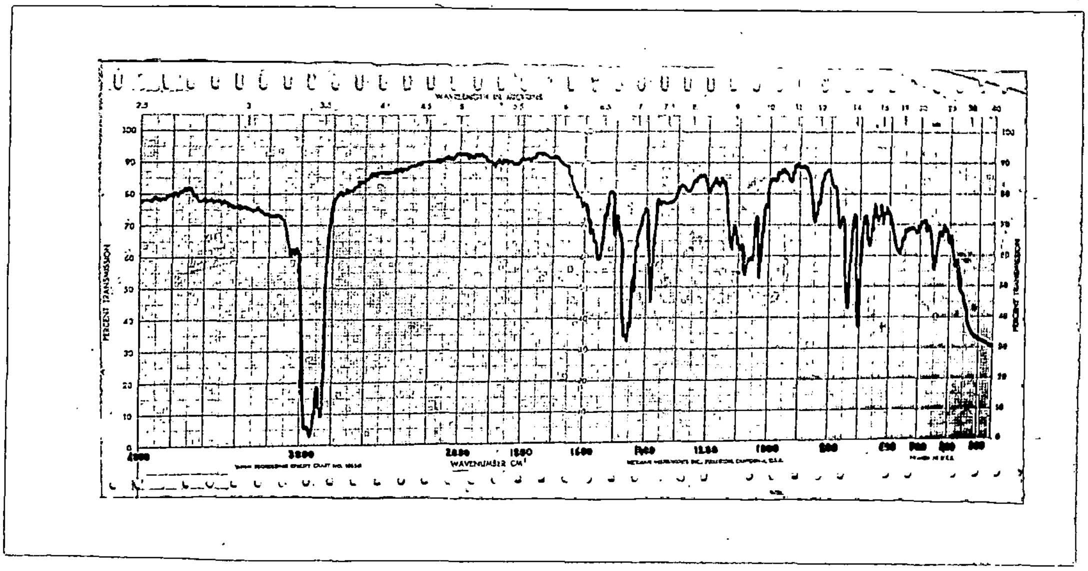


Figure - 10 : Infra red spectrum of XXII

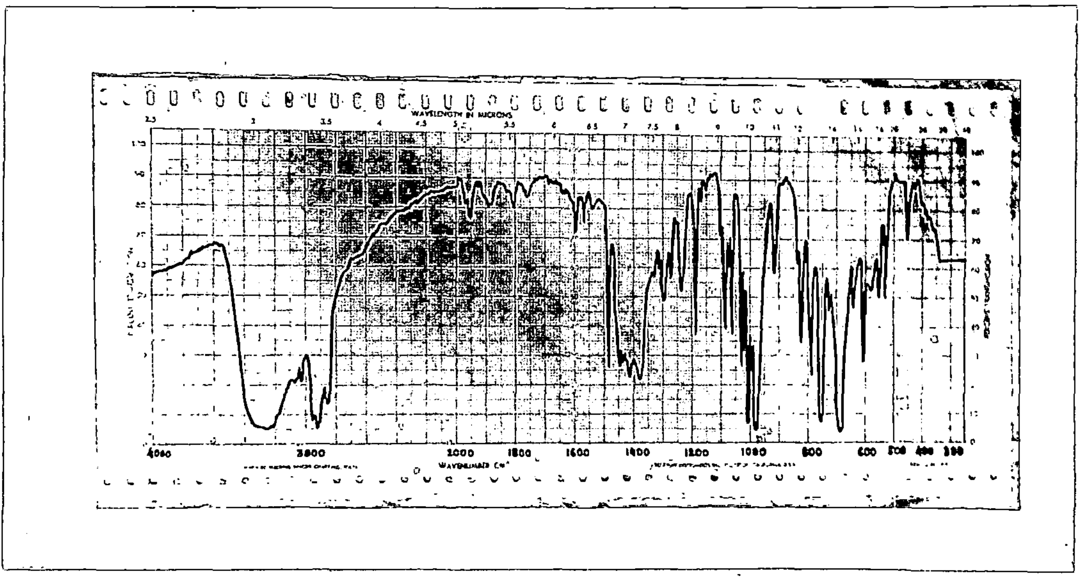
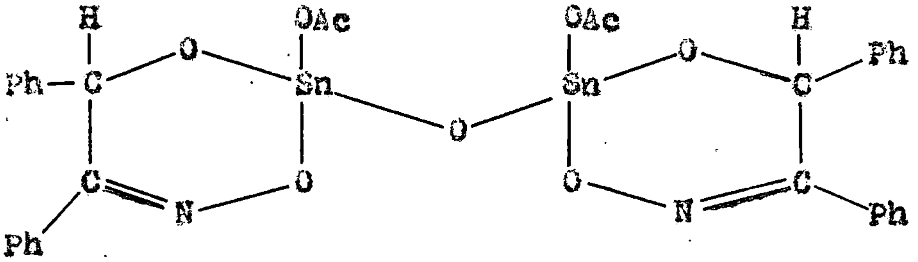


Figure - 11 : Infra red spectrum of benzoin oxime a white compound (m.p 232°). The IR spectrum of the compound shown in figure 10 shows absence of any absorption due to -OH group indicating that the ligand uses both the oxime and hydroxyl H - atoms for salt formation. Presence of COO group is indicated by the absorption at 1555 cm^{-1} due to νas (OCO). As in 1-nitroso-2-napthol derivatives, a strong absorption at 1075 cm^{-1}, ascribable to ν(N - O) is observed. In addition, comparison with the spectrum of the free ligand (fig - 11) shows the presence of a new absorption at 768 cm^{-1}. This band can be assigned to νas (Sn - OSn). Together with the analytical data, these evidences suggest the following structure for this product.



[OAc = - $OCOCH_3$]

(XXII)

It is interesting to note that no absorption due to C - N stretch could be observed either in the free ligand or in the tin complex.

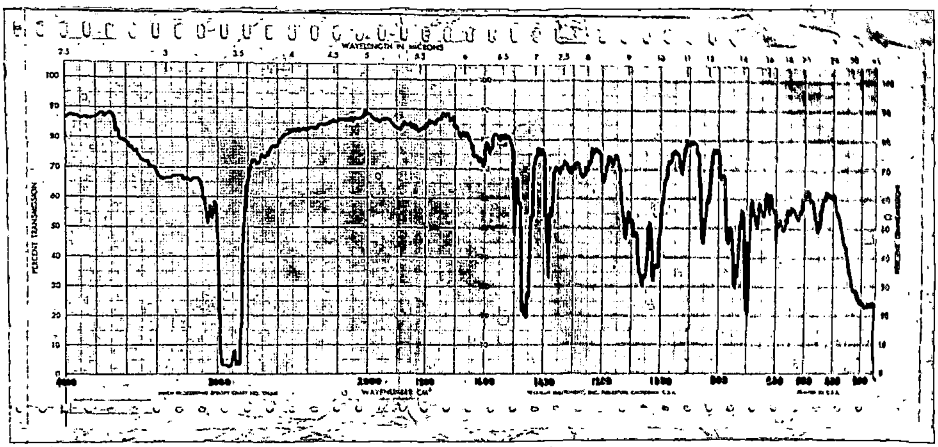
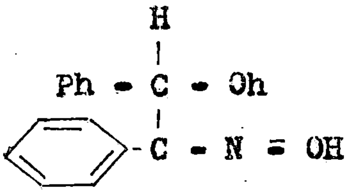
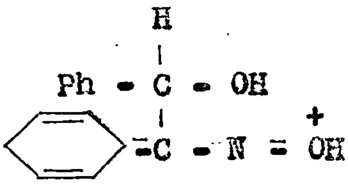


Figure - 12 : Infra red spectrum of XXV

Though no definite reason could be given for this, it may be due to resonance of the type XXIII - XXIV etc. Which may lower it



(XXIII)

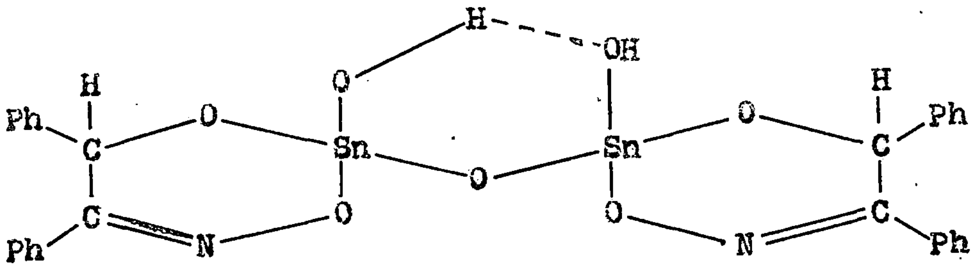


(XXIV)

(V) Product of the reaction of benzoin oxime (cupron) with triphenyl tin chloride :

The reaction of Ph_3SnCl with benzoin oxime furnishes a while compound (m.p.>250°).

The IR spectrum of the product (figure -12) is very similar to that of XXII except for the broad absorption at 3380 cm^{-1} due to hydrogen-bonded hydroxyl group and the absence of the ν (OCO) absorption at 1555 cm^{-1} observed in XXII. Analytical data and the similarity of the spectrum with that of XXII suggest the following structure for this product :



(XXV)

As shown in XXV, the steric disposition of the two OH groups are very favourable for H-bonding, thus accounting for the broad absorption at 3380 cm^{-1}.

(VI) Polystannoxanes :

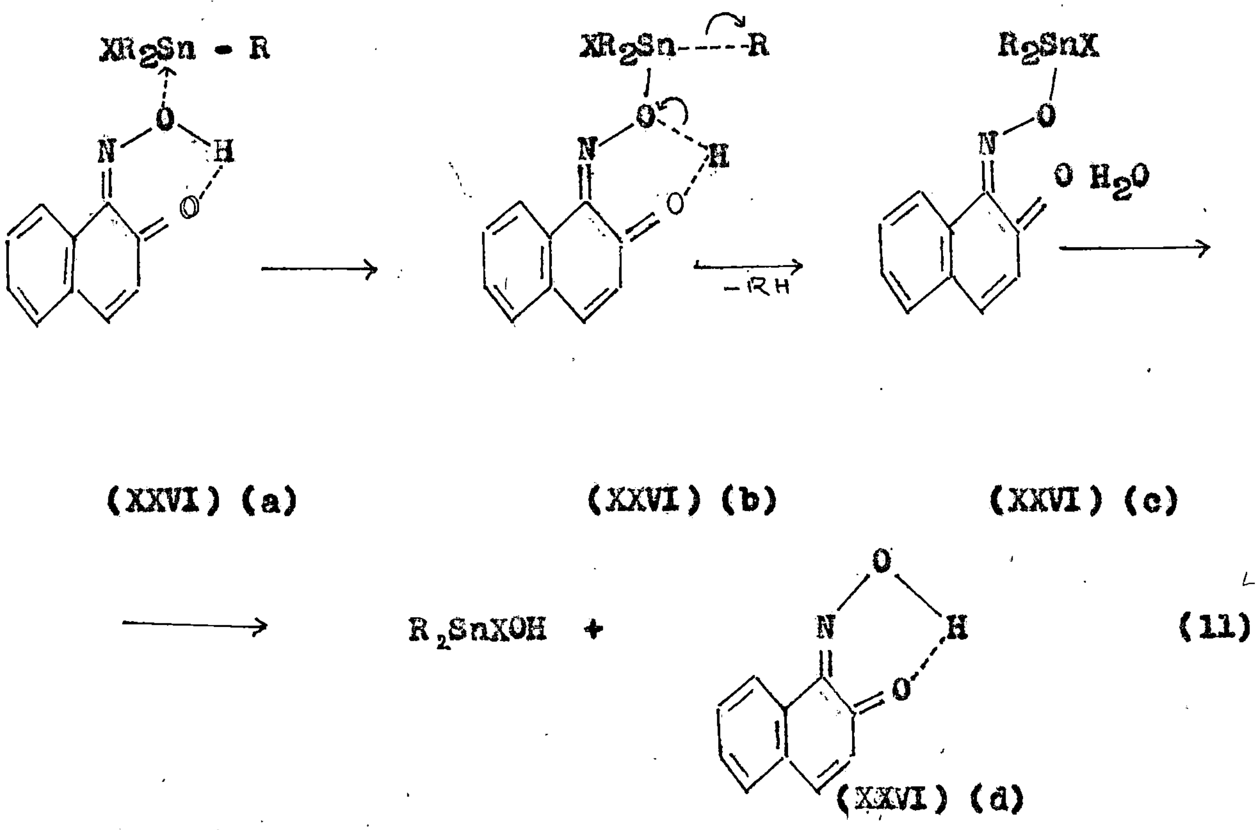
Polystannoxanes formed in the reactions studied do not fall into any general type and as such their probable structures have been discussed under the corresponding reactions separately.

4. Probable mechanism .

The products of the reactions are so varied and complex that no definite suggestions regarding probable mechanism is possible in the present systems.

Since the reaction of Potassium 1-nitroso-2-napthoxide (KCh) with Ph_3SnCl does not furnish the expected simple product, viz., Ph_3Snch, but leads to cleavage of Sn - Ph [illegible] bond, a nucleophilic attack at the tin atom which lowers the effective electronegativity of the tin atom and thereby increases the $>\overset{\delta+}{Sn} - \overset{\delta-}{C}<$ bond polarity is suggested. Probably the electron transfer from the ligand to the tin atom in the initial step of the reaction is of such a magnitude that the carbanion character of the carbon atom of Sn - C bond is increased to an extent where it becomes labile.

As already shown 1-nitroso-2-napthol exists in the oxime form with strong internal hydrogen-bonding with the carbonyl oxygen. As such the lone pair on the oxime oxygen would be more readily available for nucleophilic attack. The reaction therefore proceeds most probably through an initial nucleophilic attack by the ligand as shown in XXVI (a). A slight



(XXVI) (a) (XXVI) (b) (XXVI) (c)

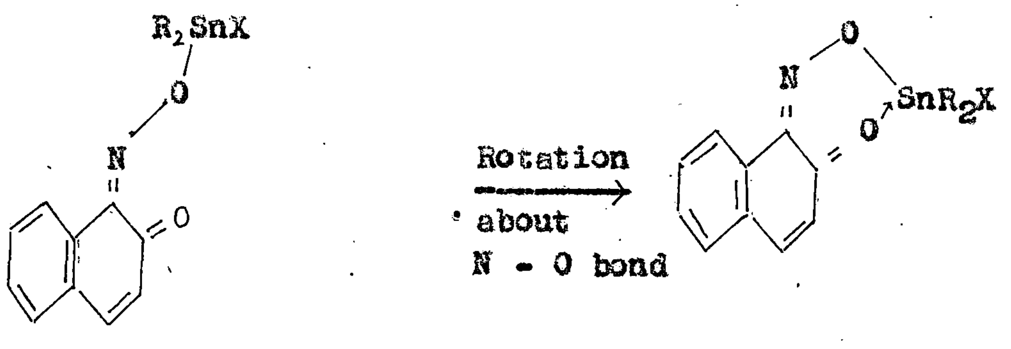
R_2SnXOH +

(XXVI) (d)

(11)

electronic rearrangement then leads to cleavage of the R group [XXVI (b,c)] . Because of the steric requirements of the approach of the ligand co-ordination by the carbonyl oxygen is not possible as soon as the R - group leaves. However, because of the presence of two highly electronegative atoms attached to the tin atom (Sn - O and Sn-X), the tin atom would have very high Lewis acdity, so that co-ordination by water present in the system (moisture could not be rigorously avoided in our systems) may take place rather easily. Unlike the carbonyl oxygen of the ligand which can co-ordinate only after the departure of R group followed by a steric rearrangement (rotation about the N - O bond would bring the tin atom to a proper position for co-ordination as shown below).

Co-ordination



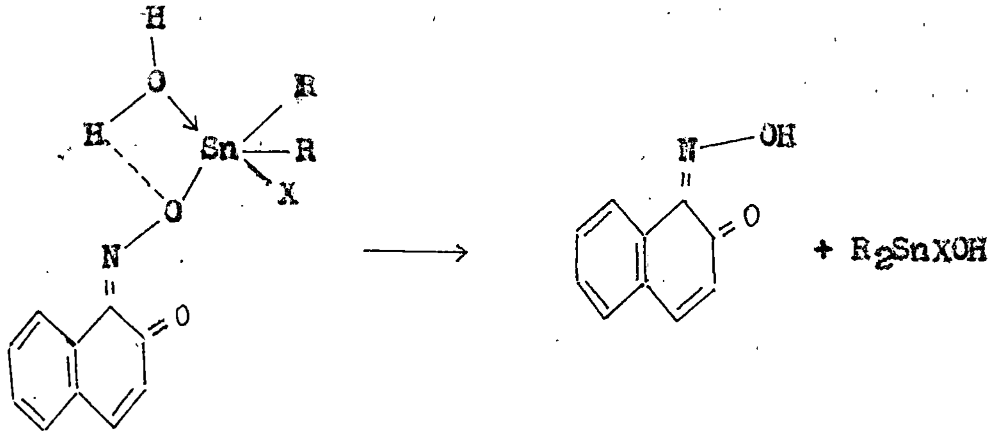
(12)

XXVII (a)

XXVII (b)

Initially formed derivative, co-ordination with carbonyl oxygen not possible.

by H_2O is not hindered by any special steric requirement, so that it may take place even during the stage when cleavage of R group is taking place.



XXVIII

(13)

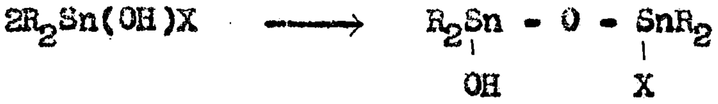
It is evident from XXVIII, because of its very favourable steric disposition the H-atom of the co-ordinated water molecule can interact strongly with the NO group. This would not only hinder the rotation about the N - O bond necessary for chelation, but slight electronic rearrangement as shown may lead to very facile hydrolysis leading to the formation of R_2SnXOH. This compound may then react further with another molecule of 1-nitroso-2-napthol and lead to further cleavage of Sn-R bonds. Or alternatively it may undergo condensation reaction with another organotin molecule either through the elimination of HX or H_2O molecule as shown below :

$$R_3SnX + Hch \longrightarrow R_2SnchX + RH \qquad (14)$$

$$R_2SnchX \xrightarrow{H_2O} R_2Sn(OH)X + Hch \qquad (15)$$

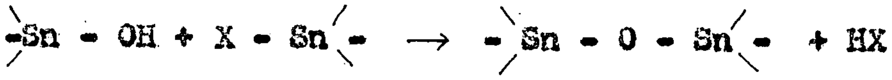
$$R_2Sn(OH)X \xrightarrow{Hch} RSn(OH)Xch + Rh \qquad (16)$$

$$RSn(OH)Xch \xrightarrow{H_2O} RSnX(OH)_2 + Hch \qquad (17)$$

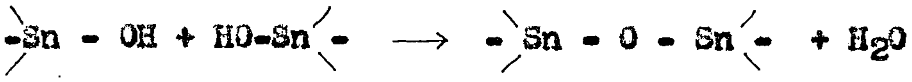


$$2R_2Sn(OH)X \longrightarrow \underset{OH}{R_2Sn} - O - \underset{X}{SnR_2}$$

(18)



(19)



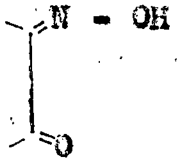
(20)

etc.

Even the distannoxanes formed may react further with the ligand leading to more complex molecules. In some cases the ligand may act virtually as a catalyst for the cleavage of Sn - R bonds by water. The formation of phenyl stannoic acetate in the reaction of Ph_3SnOAc with 1-nitroso-2-napthol, 2-nitroso-1-napthol or diacetyl mono oxime provides such an example.

Though the ease of cleavage of the Sn - R bonds by 1-nitroso-2-napthol or more generally speaking 1,2 diketo mono oximes could be explained by the above scheme, the end product could not be predicted. At this stage it may only be said that the cleavage till a stable product, i.e., stable towards nucleophilic attack by water, is formed.

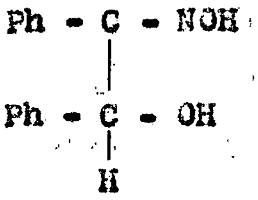
Though the above mechanism has been discussed with 1-nitroso-2-napthol, the arguments apply to all ligands containing the structural unit XXIX, i.e, to all 1,2 diketo mono oximes.



(XXIX)

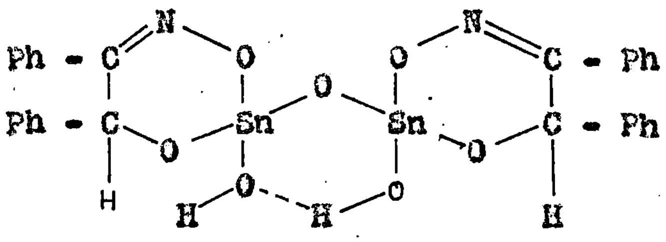
It is therefore not surprising to see that both diacetyl mono oxime $CH_3CO.C(=NOH).CH_3$ and α benzil oxime lead to same type of polymeric products when reacted with triphenyl tin acetate and triphenyl tin chloride.

In order to find out whether the Keto group in XXIX and the consequent conjugation extending over the entire molecule is essential for unusual reactivity, benzoin oxime (cupron) XXX was also

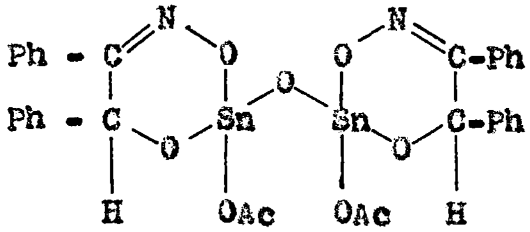


XXX

reacted with triphenyl tin chloride and triphenyl tin acetate by refluxing in benzene. In both cases, distannoxanes of similar structures XXXI and XXXII are formed. It may be noted that all tin-phenyl groups are cleaved and the ligand acts as a bifunctional group. However, unlike in the reactions involving ligands of the type XXIX, no polymeric products are formed. It appears that presence



(XXXI)



(XXXII)

of the delocalized system in XXIX makes it more effective compared to XXX as far as cleavage and polymerisations are concerned.

5. Experimental details and identification of products.

All solvents were purified and dried as described in Vogel's practical organic chemistry (46). The petroleum ether used throughout the investigation had boiling points 60°- 80°.

1-nitroso-2-napthol (Fluka A.G.Switzerland) was recrystallised from petroleum ether, m.p. 106° [lit.(46) 106°] which was used in a number of reactions. Triphenyl tin chloride (Fluka A.G. Switzerland) was recrystallised from petroleum ether, m.p. 106° [lit.(47)m.p. 106°], which was used for the preparation of triphenyl tin acetate, m.p. 121° [lit (49) m.p. 121°- 122°], bis triphenyl tin oxide, m.p 122° [lit (49) m.p 123°- 124°]and in many reactions. Tri cyclohexyl tin bromide (carrol products, New York), m.p. 77° [(lit (47) m.p 77°]and tributyl tin chloride. were used without further purification. Ethyl methyl ketone and n butyl nitrite were purified by redistillation. The former was dried over $MgSO_4$. These two chemicals were used for the preparation of diacetyl mono oxime. Benzil (B.D.H) m.p 94° [lit (46) m.p 94 - 95°] without purification was used for the preparation of alphabenzil mono oxime. Benzoin (B.D.H) after recrystallisation from dilute alcohol m.p. 137° [lit (46)m.p. 137°] was used for the preparation of benzoin oxime (cupron).

(1) Preparation of bis (triphenyl tin) oxide :

Bis (triphenyl tin) oxide was prepared by the reaction of triphenyl tin chloride with sodium hydroxide (48). The crude solid separated furnished bis (triphenyl tin) oxide, m.p. 122 [lit(49) m.p. 122°- 123°] on repeated recrystallisation from a mixture of petroleum ether and benzene. It was dried in air and finally in vacuum at room temperature.

(2) Preparation of tribenzyl tin chloride :

Tribenzyl tin chloride was prepared according to the method of Schmitz - Dumont etat (50) and was recrystallised from acetone, m.p. 142 [lit. (50)m.p. 142°- 144°].

(3) Preparation of triphenyl tin acetate :

Triphenyl tin acetate was prepared by refluxing triphenyl tin chloride with dry potassium acetate in methanol. The crude product was purified by recrystallisation from petroleum ether, m.p. 121° [lit (49) m.p. 121°- 122°].

(4) Preparation of potassium 1-nitroso-2-napthoxide :

Potassium 1-nitroso-2-napthoxide was prepared by refluxing 1-nitroso-2-napthol with potassium hydroxide in methanol. The green crude product furnished shining green crystals, m.p $>$ 360°, d.P $<$ 200° on recrystallisation from methanol.

(5) Preparation of diacetyl mono oxime :

Diacetyl mono oxime was prepared by the method described in Vogel's practical organic chemistry (46). For this preparation ethyl methyl Ketone was treated with n-butyl nitrite in the presence of little hydrochloric acid them treated with concentrated NaOH solution when sodium salt of diacetyl mono oxime was produced. The solution furnished crude diacetyl mono oxime on treatment with ice cold hydrochloric acid. The crude product was purified by recrystallisation from petroleum ether and dried in vacuum for twelve hours, m.p. 75°- 76° [lit (46) m.p 76°] .

(6) Preparation of alpha benzil mono oxime :

Alphabenzil mono oxime was prepared by a method given in the practical book of chemistry by Vogel (46). Pure benzil was treated with hydroxylamine hydrochloride at a temperature below - 5° . To this mixture was added a strong solution of sodium hydroxide below 0° and shaked for 90 minutes. Crude oxime was precipitated by acidification with glacial acetic acid. Crude product was purified by recrystallisation from dilute alcohol then from benzene. It was dried in vacuum for 12 hours, m.p. 140° [lit (46) m.p 140°].

(7) Preparation of benzoin oxime (cupron):

Benzoin oxime was prepared by refluxing benzoin with neutralised hydroxylamine hydrochloride in dilute alcohol (46). The crude product was purified by recrystallisation from dilute alcohol and diethyl ether, m.p. 150° [lit (46), m.p. 151°]. It was dried in vacuum for 12 hours.

(8) Reaction of triphenyl tin acetate with 1-nitroso-2-napthol :

2.4 gms of triphenyl tin acetate was refluxed with 1.2 gms of 1-nitroso-2-napthol in 100 ml benzene for seven hours and then allowed to stand overnight. A red solid (1.69 gms) crystallised out which was filtered, washed repeatedly with hot benzene. The solid was then boiled with chloroform and filtered while hot. A white solid crystallised out on cooling. It was washed with cold pyridine and recrystallised from chloroform (8A). The residue (1.1 gms) after separation of the white compound was washed thoroughly with hot chloroform, then recrystallised from benzene - pyridine mixture which furnished a crystalline red compound (8B).

The original filtrate was treated with excess of petroleum ether when 0·5 gms of a violet coloured compound (8C) crystallised out, it was filtered, washed thoroughly with hot petroleum ether and recrystallised from benzene - petroleum ether mixture.

The final filtrate furnished a green (8B) and a yellow (8E) product upon concentration followed by controlled addition of petroleum ether when the green compound separated out leaving behind the yellow compound in solution. The green fraction was purified by repeatedly dissolving in benzene and reprecipitating with petroleum ether. The yellow fraction was purified in the similar manner.

It may be noted that the yield of the white compound (8A) increased considerably on decreasing the proportion of 1-nitroso-2-napthol.

Evidence for the cleavage of Sn - Ph bonds : Formation of benzene in the reaction

The reaction of triphenyl tin acetate with 1-nitroso-2-napthol was carried out as before in specpure diethylether, the solvent was then distilled out. Spectroscopic examination of the distillate showed the presence of benzene. Blank experiments under similar conditions did not show any benzene.

Identification of 8A

The IR and UV spctra of this compound have been discussed earlier (under the section 'Structural aspects of the products') where the presence of phenyl group, two types of acetate group and Sn-O-Sn ~~S~~keliton in the compound have been suggested.

Reaction with oxine :

On boiling with oxine in ethanol the compound afforded a yellow compound (m.p. 242°). The compound has been unambiguously indeitified as

$$PhSn(Ox)_2OAc \qquad \left[\begin{array}{l} Ox = C_9H_6(N)O - \\ OAc = CH_3COO - \end{array}\right]$$

from its elemental analysis and by its preparation through other reactions, e.g.

$$PhSn(Ox)_2Cl + AgOAc = PhSn(Ox)_2OAc + Agcl \qquad (21)$$

The formation of $PhSn(Ox)_2OAc$ establishes the presence of PhSn(O)OAc group in the molecule.

The polymeric nature of the material is shown by its infusibility as well as insolubility in the common organic solvents.

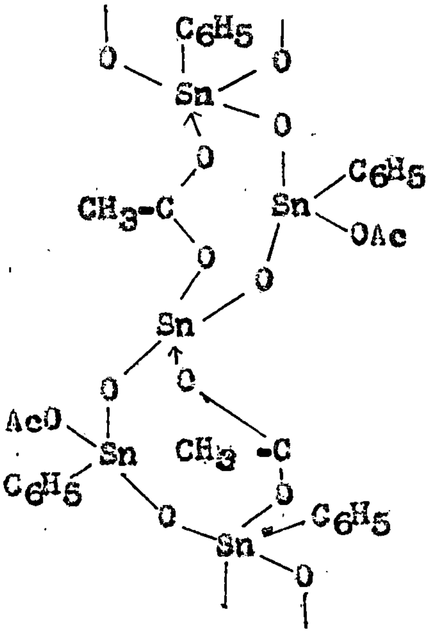
The only structure consistent with all these observations and elemental analysis suggest the following polymeric structure:

$$- O - (C_6H_5)\,Sn(OAc) - O - Sn(C_6H_5)\ \phi\ OAc\ ) -$$

Analytical data :

Found :	C = 35.09% ; H = 2.95% ; Sn = 42.83%
Calculated for	$C_8H_8SnO_3$; C = 35.47% ; H = 2.96% ; Sn = 43.85%

Although a definite structure can be proposed only by a detailed X ray analysis, structure XXXIII in which every third tin atom is bridged by the acetate group is tentatively suggested. The other tin atoms may be tetra or penta co-ordinated depending on whether the other acetate group is ionic or chelating. Such a structure is very favourable in view of the identity period of triorgano tin carboxylates which is 10 Å and which have analogous structure (53)



XXXIII

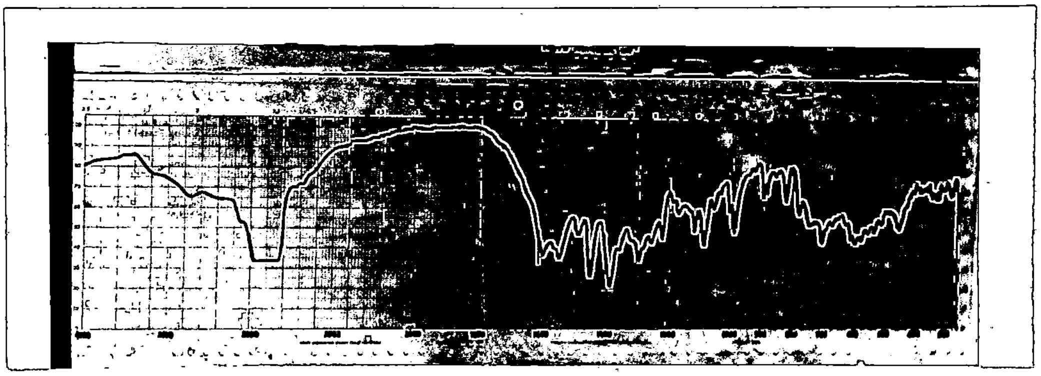


Figure - 13 : Infra red spectrum of $Ph(Ch)_2(OAc)(OH)_4Sn_2$ (XXXIV)

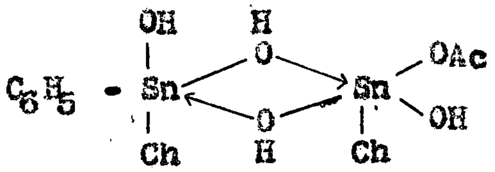
Although NMR spectra would have been of great help in distinguishing the two structurally non equivalent acetate groups, this could not be done due to the low solubility of the compound.

Identification of 8B

This product is also infusible upto 360° and insoluble in the common organic solvents. It is soluble only in pyridine.

IR spectrum of the compound is shown in the figure - 13. The presence of broad, medium intensity bands around 3600 cm^{-1} and 3350 cm^{-1} shows the presence of two nonequivalent hydroxyl groups. The broad and strong absorption at 586 cm^{-1} is due to $\nu(Sn - O)$ (54). The presence of tin - phenyl group is supported by the usual benzene ring vibrations and in particular by the band at 1077 cm^{-1} (52).

On the basis of the above observations and elemental analysis the following structure seems most probable :



Ch = $C_{10}H_6NO_2$ -
OAc = CH_3COO -

XXXIV

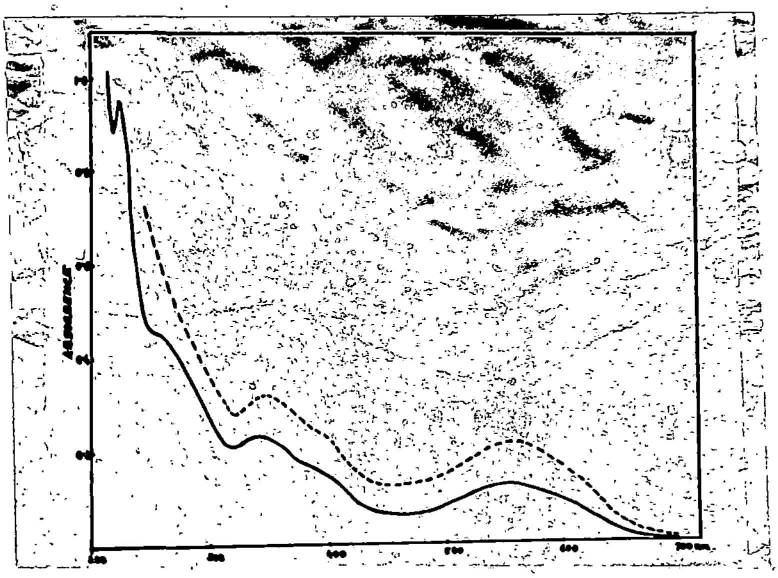


Figure - 14 : Electronic absorption spectra of $[Ph(Ch)(OAc)Sn]_2O$ (XXXV) in

Methanol : ————————

Chloroform : - - - - - - - -

Analysis found : C = 43·71 % ; H = 3·32 % ; N = 3·57 % ; Sn = 30·5 %

Calculated for

$C_{28} H_{24} O_{10} N_2 Sn_2$: C = 42·8% ; H = 3·06% ; N = 3·56% ; Sn = 30·2%

The stability of the structure may be attributed to strong intramolecular Sn ← OH Co-ordination.

Identification of 8C

The violet coloured solid is infusible upto 360°. It has moderate solubility in benzene.

(i) UV - visible spectra :

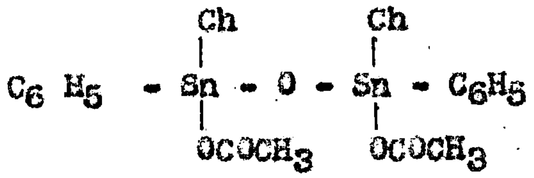
The electronic spectra of the compound in Methanol and choloroform are shown in the figure - 14. The stability and large bathochromic shift of the largest wave length band compared to that in the free ligand indicates the presence of chelated 1-nitroso-2-napthol group.

(ii) IR spectrum :

The following assignment is possible for the major IR absorptions :

The presence of tin-phenyl group is indicated by the absorption at 1077 cm^{-1} (52). The strong absorption at 580 cm^{-1} may be assigned νas (Sn-O-Sn) as Sn-OH band is absent (no hydroxyl absorption)

The above observations and elemental analysis are consistent with the following structure :



$$C_6H_5 - \underset{OCOCH_3}{\overset{Ch}{Sn}} - O - \underset{OCOCH_3}{\overset{Ch}{Sn}} - C_6H_5$$

$[Ch = C_{10}H_6NO_2 -]$

XXXV

Analysis found : C = 50·47% ; H = 3·42% ; N = 3·36% ; Sn = 26·92%

Calculated for

$C_{36}H_{28}N_2O_9Sn_2$: C = 49·7% ; H = 3·23% ; N = 3·23% ; Sn = 27·35%

Identification of 8D and 8E

The solids 8D and 8E are coloured green and yellow respectively. Both of these compounds are fairly soluble in the common solvents but are infusible upto 360°. These compounds are probably polymeric, however they could not be identified because: (i) These were obtained only in extremely low yields and (ii) composition of the products were variable.

(9) Reaction of triphenyl tin chloride with 1-nitroso-2-napthol :

4 gms of triphenyl tin chloride with 2 gms of 1-nitroso-2-napthol was refluxed in about 100 ml benzene for seven hours. On standing overnight a greenish black compound (2.55 gms) crystallised out. It was filtered and the filtrate on concentration furnished an additional quantity (0 91 gms) of the same compound. The solid (9A) was washed thoroughly with hot benzene and recrystallised from a mixture of benzene and dimethyl formamide.

The filtrate after separation of 9A was treated with petroleum ether when 0·78 gms of a green coloured solid (9B) was separated. It was filtered and washed thoroughly with hot petroleum ether and recrystallised from benzene - petroleum ether mixture. The filtrate furnished 1·2 gms of a yellow product(9C) on concentration, followed by controlled addition of petroleum ether. The yellow compound was dissolved in minimum volume of benzene and then reprecipitated with petroleum ether. Purification was achieved by repeating this process.

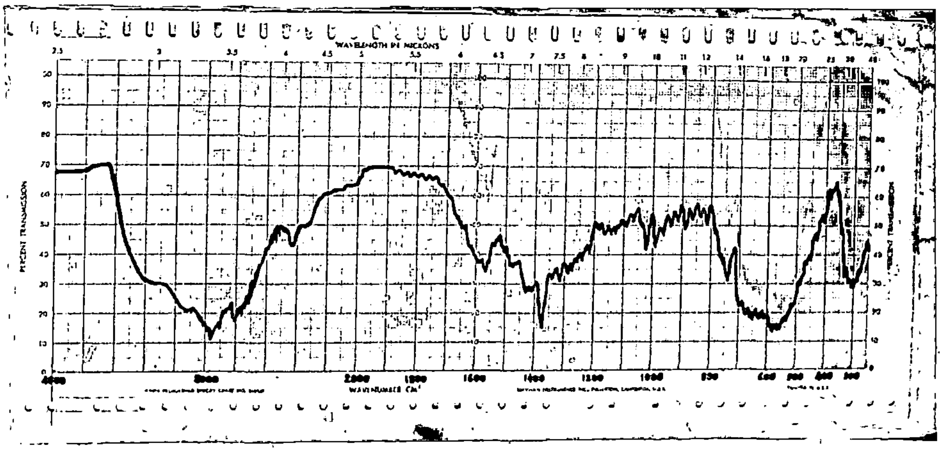


Figure - 15 : Infra red spectrum of XXXVI

The final filtrate was evaporated to dryness when unreacted 1-nitroso-2-napthol was recovered.

Identification of 9A

The compound (9A) has been identified as a polystannoxane derivative on the basis of following observations :

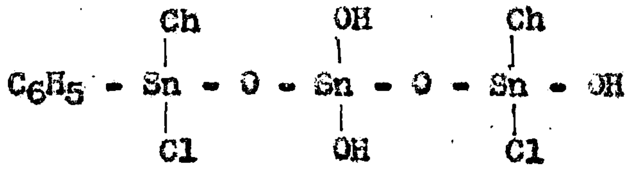
(i) It is infusible upto 360° and insoluble in the common solvents, but sparingly soluble in pyridine and DMF.

(ii)Reaction with mercuric chloride :
The compound was refluxed with mercuric chloride in ethanol for half an hour and filtered. The filtrate on cooling furnished a flaky white solid. The solid has been unambiguously identified as phenyl mercuric chloride from its melting point (m.p. 247°) and mixed melting point with authentic compound. The formation of phenylmercuric chloride establishes the presence of phenyl group in the molecule.

(iii) IR Spectrum :
The IR spectrum of the compound is shown in the figure - 15. The strong and very broad ir absorption around 3400 cm^{-1} indicates the

presence of a large number of hydroxyl groups, which are probably co-ordinated or hydrogen bonded. The presence of a very strong and broad absorption around 580 cm^{-1} [νas (Sn-O-Sn)] is suggestive of polystannoxane structure.

Structure XXXVI is tentatively proposed on the basis of these observations and elemental analysis.



$$C_6H_5-\underset{Cl}{\overset{Ch}{Sn}}-O-\underset{OH}{\overset{OH}{Sn}}-O-\underset{Cl}{\overset{Ch}{Sn}}-OH$$

$[Ch = C_{10}H_6NO_2-]$

$n = 6$

XXXVI

Analysis found : C = 16·82% ; H = 1·82% ; N = 1·83% ; Cl = 4·17% ;
Sn = 52·86%

Calculated for

$C_{26}H_{30}O_{24}N_2Cl_2Sn_8$: C = 17·59%; H = 1·69% ; N = 1·58%
Cl = 4·00% ; Sn = 53·53%

On boiling the compound (XXXVI) with oxine in ethanol the compound afforded a yellow crystalline solid which has been identified as (XXXVII) on

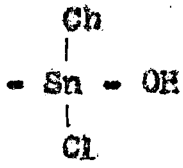
$$\left[Sn\,(Ox)_2\,Cl\right]_2O \qquad \left[Ox = C_9H_6(N)O-\right]$$

(XXXVII)

the basis of elemental analysis and IR spectrum.

Analysis found : C = 46·81% ; H = 2·98%

Calculated for $C_{36}H_{24}O_5Cl_2Sn_2$: C = 48·07% ; H = 2·66%

This is consistent with the presence of  $-\overset{Ch}{\underset{Cl}{Sn}}-OH$ terminal group in the molecule.

In the absence of molecular weight the value of 'n' could not be obtained precisely. We have however, taken this value of 'n' in obtaining the molecular formula which matched most closely with the elemental analysis.

Identification of 9B

The compound has the following characteristics :

(i) The compound is sparingly soluble in common solvents and infusible upto 360°.

(ii) IR Spectrum :

The presence of Sn-O-Sn skeleton is indicated by absorption at 607 cm^{-1} (53). Presence of phenyl group is also indicated by the presence of usual ring vibrations.

Analytical data suggests the molecular formula $Ph_3Ch_2Sn_2O$ which may be written either as XXXVIII or XXXIX.

Ch_3 $Sn-O-SnPh_3$ $\qquad$ $Ch_2(Ph)Sn-O-Sn(Ch)Ph_2$

XXXVIII $\qquad$ XXXIX

$$\left[\begin{array}{l} Ph = C_6H_5 - \\ Ch = C_{10}H_6NO_2 - \end{array}\right]$$

Analysis found : C = 58·72% ; H = 3·03% ; N = 4·48% ; Sn = 24.00%

Calculated for

$C_{48}H_{33}O_7N_3Sn_2$: C = 57·6% H = 3·3% ; N = 4·2% ; Sn= 23·7%

Of the two the later is to be preferred since no triphenyl tin oxinate could be isolated by refluxing with oxine in ethanol which is expected to be formed if the structure XXXVIII is correct.

(10) Reaction of tribenzyl tin chloride with 1-nitroso-2-napthol.

4·2 gms of tribenzyl tin chloride was refluxed with 1·7 gms of 1-nitroso-2-napthol in 75 ml benzene for seven hours. Gradual addition of petroleum ether to the green coloured solution precipitated 2·1 gms of a greenish yellow compound (10A). It was filtered and the filtrate was concentrated and followed by the addition of petroleum ether. The process was repeated when a further crop of 1·57 gms of the same compound (10A) (m.p. 230°C) was obtained. The solid was dissolved in minimum volume of benzene and reprecipitated with petroleum ether. Purification was achieved by repeating this process.

The final filtrate on evaporation to dryness afforded a very small amount of unreacted 1-nitroso-2-napthol.

Identification of 10A

The greenish yellow compound exhibits the following characteristics

(1) It is sparingly soluble in common solvents, but almost insoluble in carbon tetra chloride

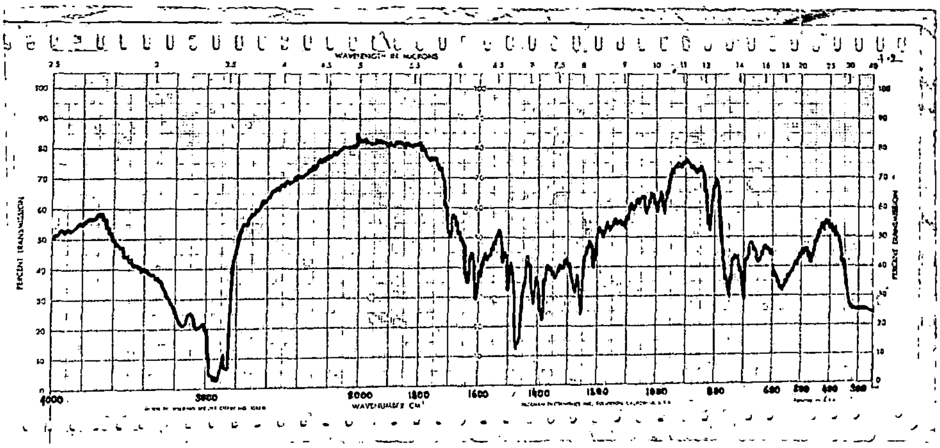


Figure - 16 : Infra red spectrum of $Bz_2(Cb)(Cl)(OH)_2O\ Sn_2$ (XL)

(ii) It melts at 230°C.

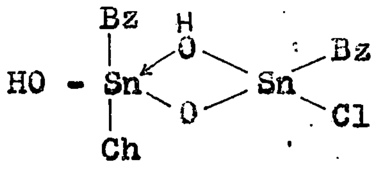
(iii) UV and visible spectra :

The compound shows a sharp absorption band at 232 nm, a shoulder at 275 nm and a broad absorption of moderate intensity at 330 nm in methanol (Table-IV). The absorption spectra is very similar to that of 1-nitroso-2-napthol and other yellow coloured derivatives obtained in the present study. The close similarity of the absorption spectra of this compound with that of 1-nitroso-2-napthol is suggestive of the presence of oximate structure since the later is known to exist almost exclusively in the oxime form (see discussion).

(iv) IR spectrum :

The IR absorption spectrum of this compound is shown in the figure - 16. Presence of hydroxyl group is shown by the broad and medium intensity band at 3250 cm^{-1}. The broad absorption around 565 cm^{-1} may be assigned to ν (Sn-O).

The following structure may be suggested on the basis of elemental analysis and other data :



[Bz = C_7H_7 -

Ch = $C_{10}H_6NO_2$ -]

(XL)

Analysis found : C = 42·52% ; H = 3·42% ; N = 1·94% ; Sn = 34·8%

Calculated for

$C_{24}H_{22}O_5NCl\,Sn_2$: C = 43·1% ; H = 3·29% ; N = 2·09% ; Sn = 35·4%

An intramolecular Sn←OH - Sn co-ordination is postulated to account for the lowering of ν(OH) and the stability of the compounds towards further polymerisation.

(II) Reaction of tricyclohexyl tin bromide with 1-nitroso-2-napthol.

4·5 gms of tricyclohexyl tin bromide with 1·8 gms of 1-nitroso-2-napthol was refluxed in 100 ml benzene for seven hours. On standing 2·1 gms of a green compound (11A) crystallised out. It was filtered and recrystallised from benzene. The filtrate on concentration and gradual addition of petroleum ether furnished 1.2 gms of a green compound (11B). The green compound was purified by repeatedly dissolving in benzene and reprecipitating with petroleum ether. The filtrate afforded 0·8 gms of a yellow compound (11C) on concentration followed by the addition of excess of petroleum ether. The yellow product was purified by washing with hot petroleum ether and recrystallising from benzene-pet mixture. The final

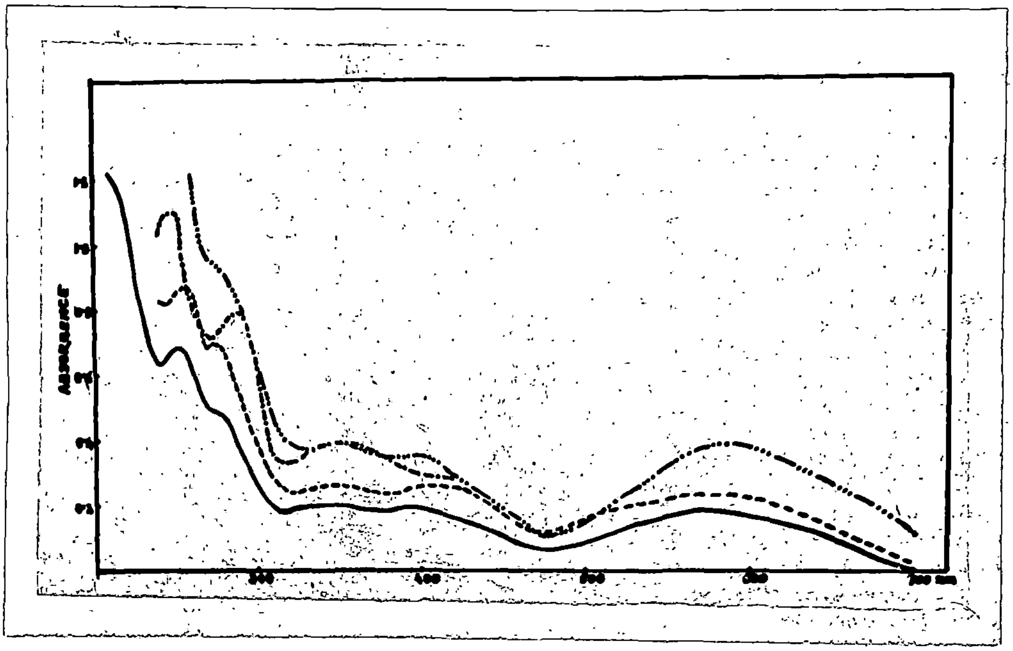


Figure - 17 : Electronic absorption spectra of $Cy_2(Ch)Sn-O-Sn(Cy)Ch_2$ (XLII) in

methanol : ————————

Carbon tetrachloride : - - - - - - - - - -

methanol/NaOH : ————·————·————

DMSO : ————··————··————··————

filtrate was evaporated to dryness. The residue (1·1 gms) was unreacted 1-nitroso-2-napthol admixed with the products which could not further separated.

Identification of 11A

The intense green compound has the following characteristics :

(i) The compound is infusible upto 360°. It is moderately soluble in the common solvents.

(ii) UV - visible spectrum :

The electronic spectra of the compound in methanol, chloroform, carbon tetrachloride and DMSO are shown in the figure - 17 (table-IV). The compound shows a moderately intense absorption band in 580 - 600 nm region. Several other absorption bands at 255 nm, 345 nm, 400 nm and a shoulder at 270 nm are also present. As can be seen the absorption spectra is rather insensitive to solvent polarity and even methanolic NaOH does not produce any marked change. The great stability of the system is indicative of a strong chelated structure involving the 1-nitroso-2-napthol group.

(iii) IR spectrum :

For this compound the presence of Sn-O-Sn linkage is indicated by IR absorption at 768 cm^{-1} (54,55,56) and 570 cm^{-1} (54) [νas(Sn-O-Sn)]

Elemental analysis suggests the following structures :

$Cy_3Sn-O-SnCh_3$

(XLI)

$Cy_2(Ch)Sn-O-Sn(Cy)Ch_2$

(XLII)

[Cy = CyClo C_6H_{11}

Ch = $C_{10}H_6NO_2$ -]

Analysis found : C = 57·31% ; H = 4·3% ; N = 4·8% ; Sn = 22·93%

Calculated for

$C_{43}H_{51}O_7N_3Sn_2$: C = 56·43% ; H = 5·00% ; N = 4·1% ; Sn = 23·32

The stability as well as the large bathochromic shift of the longest wave length suggest the presence of chelated 1-nitroso-2-napthol.

Of the two structures XLI and XLII, the later is to be preferred since the UV-visible spectrum shows the presence of two absorption bands at 395 nm (similar to free ligand) and 580-600 nm respectively indicating the presence of two non equivalent type of ligands.

The products 11B and 11C could not be separated and purified from the admixed unreacted ligand and therefore could not be identified.

(12) Reaction of bis (triphenyl tin) oxide with 1-nitroso-2-napthol

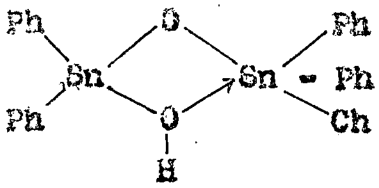
To a solution of 3·6 gms of bis (triphenyl tin) oxide in 50 ml benzene was added a solution of 1 gm of 1-nitroso-2-napthol in 50 ml benzene. The solution was then refluxed for half an hour. To the solution excess of petroleum ether was added when a yellow compound (12A) crystallised out. It was filtered, washed with petroleum ether and finally recrystallised from benzene - petroleum ether mixture. On further concentration and addition of petroleum ether the filtrate furnished an additional quantity of the same compound (decomposition point 160^{o}). The process of concentration and addition of petroleum ether was repeated several times when further crop of (12A) was obtained (total yield 3 gms).

The final filtrate gave a small amount of tarry solid on complete evaporation which could not be purified.

Identification of 12A

The compound is identical with 13A whoes structure has been discussed earlier (under the section 'structural aspects of the products').

The suggested structure (XLIII) and the elemental analysis are given below :



(XLIII)

Ph = C_6H_5 -

Ch = $C_{10}H_6NO_2$ -

Analysis found : C = 55·34% ; H = 4·04% ; N = 1·96% ; Sn = 30·29%

Calculated for

$C_{34}H_{27}O_3NSn_2$: C = 54·37% ; H = 3·60% ; N = 1·87% ; Sn = 31·64%

(13 Reaction of triphenyl tin chloride with potassium 1-nitroso-2-napthoxide.

To a solution of 2·6 gms triphenyl tin chloride in 200 ml methanol was added 1·4 gms of potassium 1-nitroso-2-napthoxide (sparingly soluble potassium 1-nitroso-2-napthoxide quickly dissolves with a colour change from green to yellow). The solution was then refluxed for two hours on a water bath and allowed to stand for two hours when 1·23 gms of a yellow crystalline compound (13A) separated out. It was filtered, washed with cold methanol, and finally recrystallised from benzene - petroleum ether mixture. On further concentration the filtrate furnished another crop of 13A under hot condition (impure, 1·70 gms). This was recrystallised from pet-benzene mixture. The filtrate gave 0.49 gms of a white solid on further concentration, it was filtered. This solid was identified as potassium chloride. The final filtrate afforded 0·21 gms of a tarry residue on complete evaporation.

Identification of 13A

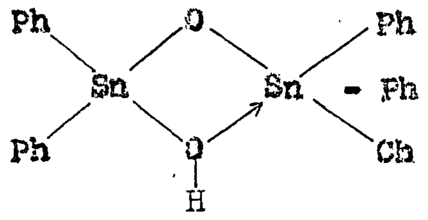
The compound has the following characteristics :

(i) It is sparingly soluble in common solvents, but somewhat more soluble in benzene.

(ii) It decomposes at 160°, though infusible up to 360°.

Electronic spectrum, IR spectrum and other characteristics has been discussed under the section, 'structural aspects of the products'.

On the basis of elemental analysis and spectral data the following structure is suggested :



(XLIV)

Analysis found ; C = 53·87% ; H = 3·68% ; Sn = 30·7%

Calculated for

$C_{34}H_{27}O_{4}NSn_{2}$: C = 54·37% ; H = 3·60% ; Sn = 31·64%

(14) Reaction of tribenzyl tin chloride with potassium 1-nitroso-2-napthoxide

3·6 gms of tribenzyl tin chloride was refluxed with 1·8 gms of potassium 1-nitroso-2-napthoxide in 200 ml methanol for 2 hours.

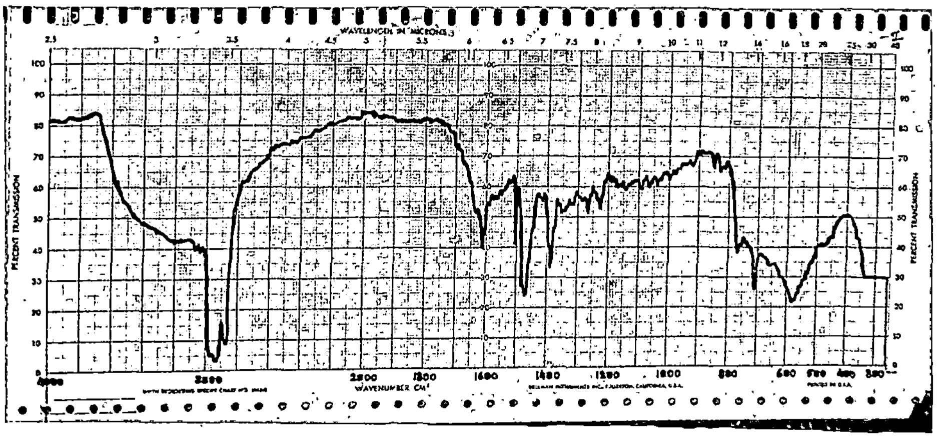


Figure - 18 : Infra red spectrum of (XLV)

0·2 gms of a solid separated out and filtered off. The filtrate furnished 1·25 gms of a green crystalline compound (14A) on standing for three hours. It was filtered, washed with hot methanol and purified by dissolving in benzene and reprecipitating with petroleum ether. On further concentration the filtrate afforded a mixture of KCl and the green compound (14A). The process was repeated several times when finally 0·6 gms of KCl and 0·72 gms of the green compound were obtained. The final filtrate on evapora tion to dryness gave unreacted 1-nitroso-2-napthol.

Identification of 14A

The compound has the following characteristics :

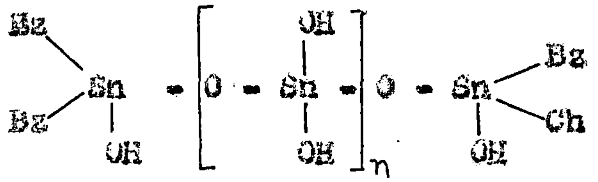
(i) The compound is infusible up to 360°

(ii) It is sparingly soluble in common solvents, but moderately soluble in pyridine.

(iii) IR spectrum :

The IR spectrum of the compound is shown in the figure - 18. A very strong and broad absorption around 3500 cm^{-1} is indicative of hydroxyl groups. The compound shows ir absorptions corresponding to benzyl groups. The absorptions at 1080 cm^{-1} (52) and 727 cm^{-1} are assigned to C - H in plane deformation mode and out of plane vibration of phenyl group respectively. A very broad and strong absorption at 574 cm^{-1} indicates the presence of a polymeric Sn-O-Sn skeleton in the molecule (54). This is also supported by the infusibility and extremely low solubility of the compound. However, the better solubility of this compound in pyridine, a good hydrogen bonding solvent, is suggestive of the presence of large number of - OH groups in the molecule.

On the basis of these considerations and the elemental analysis following structure may be suggested ;



Bz = $C_6H_5CH_2$ -

Ch = $C_{10}H_6NO_2$ -

with n = 4

(XLV)

Analysis found : C = 26·71% ; H = 2·67% ; N = 1·03% ; Sn = 49·24%

Calculated for

$C_{31}H_{37}O_{12}NSn_6$: C = 26·44% ; H = 2·63% ; N = 0·99% ; Sn = 50·6%

'n' could not be determined by molecular weight and as such its value is obtained from the elemental analysis.

(15) Reaction of tributyl tin chloride with potassium 1-nitroso-2-napthoxide

To a solution of 3·2 gms of tributyl tin chloride in 200 ml methanol, 2·1 gms of potassium 1-nitroso-2-napthoxide was added. It was then refluxed for 2 hours. The solution was then concentrated to a small volume when 0·65 gms of potassium chloride separated out which was filtered off. The filtrate was treated with an excess of petroleum ether when 1·2 gms of a green compound (15A) containing some KCl (0·1 gms) separated out. It was filtered, treated with benzene, insoluble KCl was filtered off and the green compound (15A) was reprecipitated with petroleum ether. The compound was purified by repeatedly dissolving in benzene and reprecipitating with petroleum ether.

The filtrate after separation of 15A furnished 1·5 gms of a brown coloured compound (15B) upon concentration. This compound was filtered, washed repeatedly with petroleum ether and then recrystallised from benzene-pet mixture.

Identification of 15A

The compound has the following characteristics :

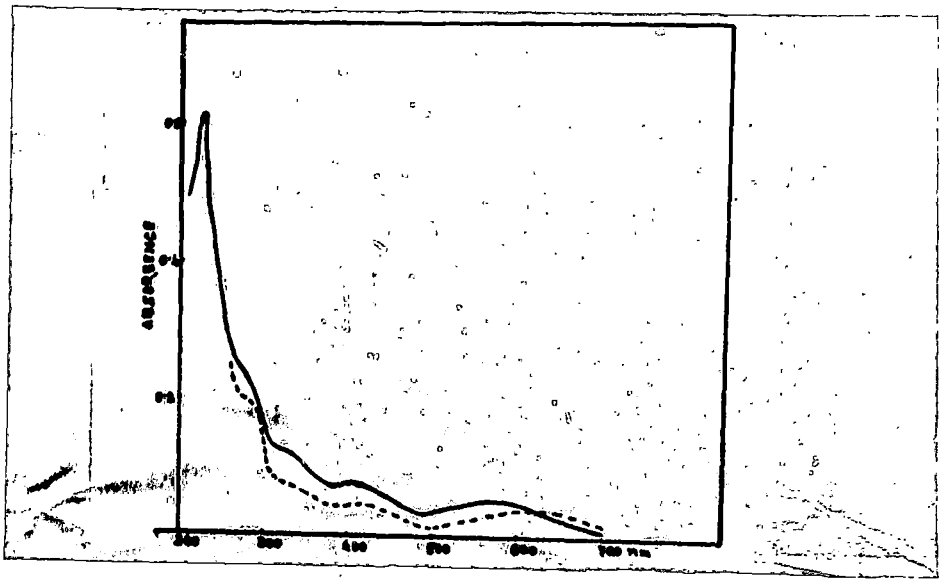


Figure - 19 : Electronic absorption spectra of

$Bu_{10}(Ch)_2(OH)_2O_5Sn_6$ (XLVI) in

Methanol : ————————

CCl_4 : - - - - - - - - - - - -

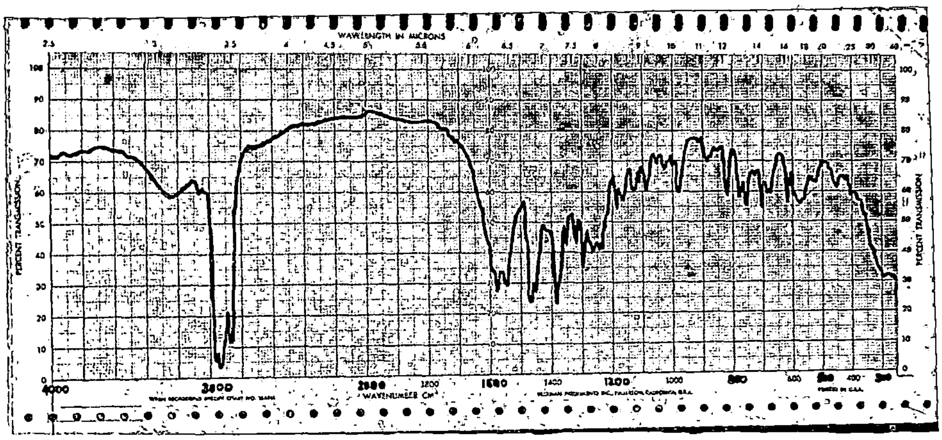


Figure - 20 : Infra red spectrum of $Bu_{10}(Ch)_2(OH)_2O_5Sn_6$ (XLVI)

(i) The compound is infusible upto 360°.

(ii) It is moderately soluble in benzene, sparingly soluble in common solvents.

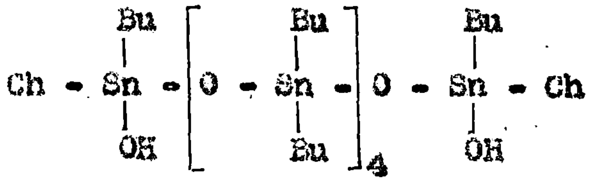
(iii) UV visible spectrum :

The electronic spectrum of the compound is shown in the figure - 19. The compound shows a moderately intense absorption at 570 nm in methanol and at 615 nm in carbontetrachloride, with shoulders at 310 nm and 320 nm respectively in methanol and carbontetrachloride. The spectral pattern is similar to that of the green compound (11A) obtained from tricyclohexyl tin bromide and 1-nitroso-2-napthol. The large bathochromic shift of the longest wave length suggests this compound to contain chelated 1-nitroso-2-napthol group.

(iv) IR spectrum :

The compound shows IR absorptions (figure - 20) corresponding to hydroxyl group and Sn-O-Sn skeleton. A broad and medium intensity band around 3250 cm^{-1} is indicative of hydroxyl group. The presence of a broad, medium intensity band around 570 cm^{-1} indicates Sn - O - Sn linkages (54) which is supported by the presence of sharp ir absorption bands at 750 cm^{-1} and 773 cm^{-1}.

The following structure is consistent with the elemental analysis and spectral data.



$$\mathrm{Ch}-\underset{\mathrm{OH}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\left[\mathrm{O}-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\right]_4\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{Ch}$$

Bu = C_4H_9 -

Ch = $C_{10}H_6NO_2$ -

(XLVI)

Analysis found : C = 41·85% ; H = 6·32% ; Sn = 39·61%

Calculated for

$C_{60}H_{104}O_{11}N_2Sn_6$: C = 41·37% ; H = 5·98% ; Sn = 40·92%

Identification of 15B

The compound exhibits following characteristics :

(i) It is fairly soluble in common solvents.

(ii) It melts at 238 - 40° with decomposition

(iii) UV - visible spectrum :

The compound shows a sharp absorption band at 228 nm and two

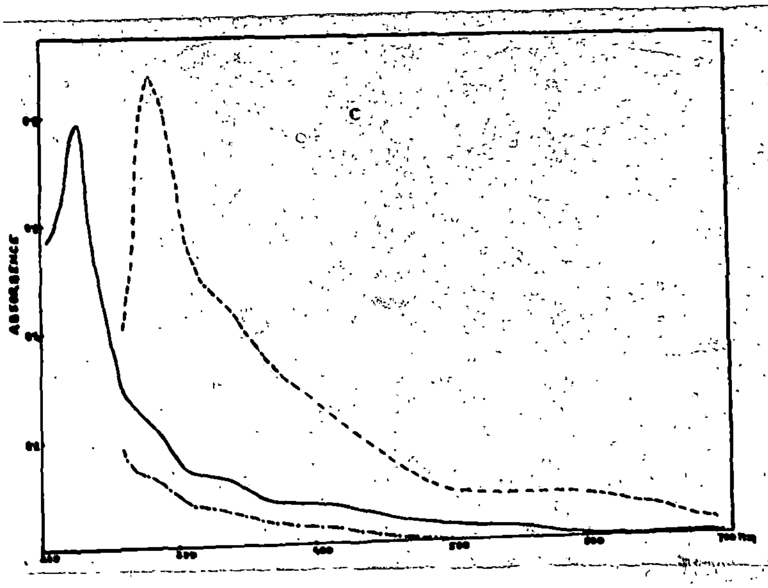


Figure - 21 : Electronic absorption spectrum of $[(C_4H_9)_2ChSn]_2O$ (XLVII) in

Methanol : ————————

DMSO : - - - - - - - - - -

CCl_4 : —•—•—•—

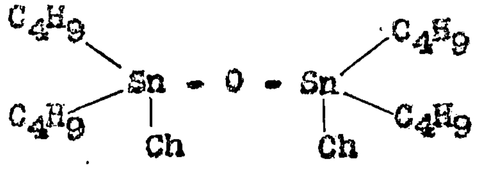
shoulders at 280 nm and 330 nm. The pattern of absorption is similar to 1-nitroso-2-napthol and those of yellow compounds obtained in the present study. Moreover the position of absorption bands remains unchanged in DMSO indicating strong co-ordination with the tin atom. The electronic spectra is shown in the figure - 21.

(iv) IR spectrum :

The IR spectrum of the compound shows the presence of Sn-O-Sn linkage (610 cm^{-1}, 573 cm^{-1}).

The compound is identical with the compound prepared by Mehrotra etal (44) by the reaction of dibutyl tin dichloride with 1-nitroso-2-napthol.

Elemental analysis corresponds to the formula XLVII



$[Ch - C_{10}H_6NO_2 -]$

(XLVII)

Analysis found : C = 53·84% ; H = 5·98% ; N = 3·13% ; Sn = 28·20%

Calculated for

$C_{36}H_{48}O_5N_2Sn_2$: C = 52·2% ; H = 5·8% ; N = 3·38%; Sn = 28·30%

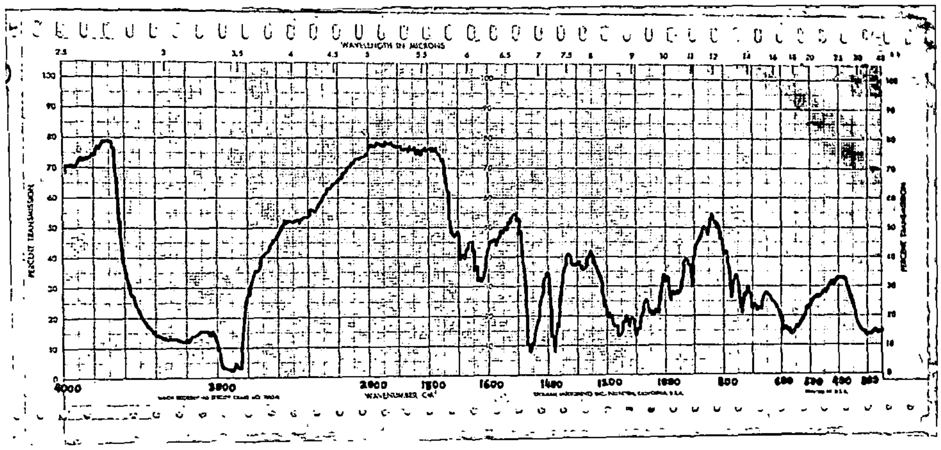


Figure - 22 : Infra red spectrum of (XLVIII)

(16) Reaction of triphenyl tin chloride with diacetyl monooxime.

3·8 gms of triphenyl tin chloride was refluxed with 1·1 gms of diacetyl monooxime in 100 ml benzene for seven hours. The white solid (0·75 gm, 16A) which separated was filtered off. It was purified by washing repeatedly with hot benzene. The filtrate on further heating furnished the same white solid slowly over a long period.

Identification of 16A

The compound has the following characteristics :

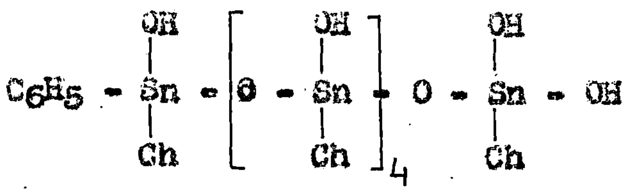
(i) It is infusible upto 360°.

(ii) It is insoluble in all common solvents.

(iii) IR spectrum (figure - 22)

A very broad and strong absorption around 3400 cm^{-1} indicates the presence of hydroxyl groups. The strong absorption at 1095 cm^{-1} is indicative of tin - phenyl group, which is assigned to a C - H in plane deformation mode (52). The presence of phenyl group is [redacted] further supported by the presence of characteristic phenyl ring vibrations. Presence of $-Sn-O-$ moiety is shown by the absorption at 570 cm^{-1} (54).

On the basis of present data no definite structure can be suggested. However, the analytical data corresponds to formula XLVIII which is also consistent with the spectral data and physical characteristics.



$$C_6H_5-\underset{Ch}{\overset{OH}{\underset{|}{\overset{|}{Sn}}}}-\left[O-\underset{Ch}{\overset{OH}{\underset{|}{\overset{|}{Sn}}}}\right]_4-O-\underset{Ch}{\overset{OH}{\underset{|}{\overset{|}{Sn}}}}-OH$$

$[Ch = C_{10}H_6NO_2-]$

(XLVIII)

Analysis found : C = 23·78% ; H = 3·76% ; N = 6·09% ; Sn = 43·20%

Calculated for : C = 22·67% ; H = 3·02% ; N = 5·29% ; Sn = 44·84%

$C_5H_8O_4NSn$

(17) Reaction of triphenyl tin acetate with diacetyl mono oxime

To a solution of 4·1 gms of triphenyl tin acetate in 100 ml benzene was added 1 gm of diacetyl mono oxime. Then it was refluxed for seven hours. The residue (a mixture of a white and a yellow solid) was filtered off. The mixture was boiled with chloroform and filtered while hot. The filtrate furnished 1 gm of a white crystalline compound on cooling (17A). The yellow product (17B) remained insoluble. The latter was purified by washing repeatedly with hot chloroform. The filtrate afforded 0·93 gms of the white compound and 0·52 gms of the yellow product after repeatation of this process.

Identification of 17A

The compound has been identified as phenyl stannoic acetate $[C_6H_5Sn(OCOCH_3)O]_n$, because of complete identity of its IR spectrum with that of 8A.

Identification of 17B

The product is infusible upto 360° and insoluble in common solvents. The composition is variable and as such no definite formula can be suggested.

(18) Reaction of triphenyl tin chloride with alphabenzil mono oxime

3·8 gms of triphenyl tin chloride with 2·2 gms of alpha-benzil mono oxime was refluxed in 100ml benzene for several hours. The reaction was extremely slow and furnished only a small amount of insoluble and infusible white solid along with unreacted alpha - benzil mono oxime (m.p. 139°). The white solid is probably a mixture of a number of polymers as elemental analysis does not correspond to any simple formula as such the solid could not be characterised.

(19) Reaction of triphenyl tin acetate with alpha - benzil mono oxime

4·1 gms of triphenyl tin acetate was refluxed with 2·2 gms of alpha-benzil mono oxime for seven hours in benzene. On standing for one hour 2·1 gms of a white crystalline compound (19A) was crystallised out. It was filtered, washed several times with hot benzene, then recrystallised from chloroform. The filtrate furnished 1·5 gms of unreacted α-benzil mono oxime and 0·7 gm of triphenyl tin acetate.

Identification of 19A

This compound is infusible upto 360° and sparingly soluble only in chloroform. The IR spectrum is identical with that of phenyl stannoic acetate, $[C_6H_5Sn(OCOCH_3)O]_n$, thus showing the white solid to be phenyl stannoic acetate.

(20) Reaction of triphenyl tin chloride with benzoin oxime(cupron).

To a solution of 3·8 gms of triphenyl tin chloride in 100 ml benzene was added 2·2 gms of benzoin oxime. It was refluxed for seven hours. On standing for one hour 0·6 gm of a white compound crystallised out. It was filtered, washed several times with petroleum ether and cold methanol and finally recrystallised from benzene - pet mixture. The filtrate was concentrated and the small amount of the precipitate was filtered off. To the filtrate petroleum ether was added when 3·5 gms of a white crystalline compound (20A) separated out. This compound was wahsed with hot petroleum ether and cold methanol and finally purified by recrystallisation from benzene - pet mixture (m.p. 250°d)

Identification of 20A

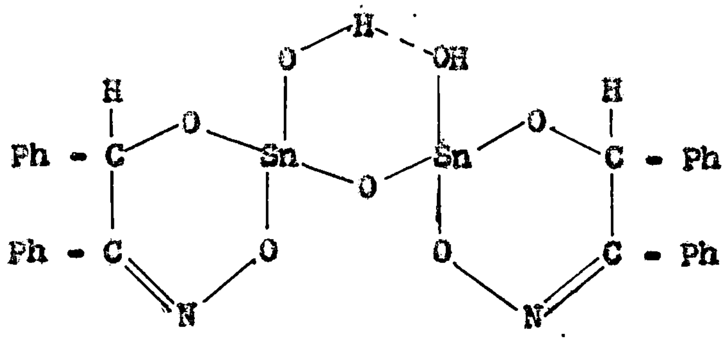
The compound has the following characteristics :

(i) It is moderately soluble in the common solvents.

(ii) It melts at 250° with decomposition.

(iii) IR spectrum :

The IR spectrum of this compound has been discussed in detail under the section 'structural aspects of the products', where the following structure has been suggested.



(XLIX)

Analysis found : C = 44°89% ; H = 3°52% ; Sn = 31·85

Calculated for

$C_{28}H_{24}O_7N_2Sn_2$: C = 45°56% ; H = 3°25% ; Sn = 32·2

(21) Reaction of triphenyl tin acetate with benzoin oxime (cupron).

1·1 gms of triphenyl tin acetate was refluxed with 1·1 gms of benzoin oxime in 100 ml benzene for seven hours. It was then treated with excess of petroleum ether when 1·9 gms of a white compound (21A) crystallised out. It was filtered, washed with petroleum ether and finally recrystallised from benzene - petroleum ether mixture (m.p. 232°). The filtrate on concentration furnished a small quantity of unreacted triphenyl tin acetate.

Identification of 21A

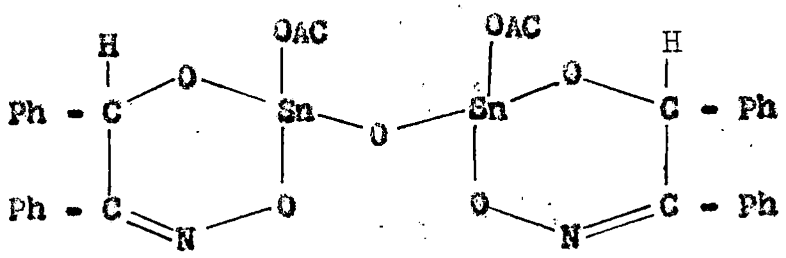
The compound exhibits following characteristics :

(i) It is moderately soluble in common solvents.

(ii) It melts at 232°.

(iii) The IR spectrum and other characteristics are discussed in detail under the section, 'structural aspects of the products'.

On the basis of these data and elemental analysis the following structure has been suggested.



(L)

Analysis found : C = 45·06% ; H = 3·70 ; Sn = 27·98

Calculated for

$C_{32}H_{28}O_9N_2Sn_2$: C = 45·76% ; H = 3·57% ; Sn = 28·28%

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