REACTIONS OF NITROSO NAPTHOLS AND RELATED MOLECULES ON SOME ORGANOTIN COMPOUNDS

Thesis Submitted for the Doctor of Philosophy (Science)
of the
UNIVERSITY OF NORTH BENGAL
1977

By
GOURANGA BISWAS, M. Sc.

ACKNOWLEDGEMENT

The author deems it a pround privilege to convey his profound sense of indebtedness to Mr. B.Majee, Reader, the department of Chemistry, North Bengal University for invaluable guidance, whole hearted co-operation and active supervision of his research work. The author takes the oppertunity of extending his heartiest thanks to the authorities of North Bengal University and the teachers and staff members of the department of chemistry in general and to Prof. H.N.Khastgir, the then Head of the department of chemistry in particular for their ungrudging help.

The author gratefully acknowledges the help of Mr.S.L.Dutta, the Scientific Officer, chemistry department, N.B.U. in recording IR spectra embodied in the present thesis. Thanks are due to the Librarian and his staff, North Bengal University for their co-operations.

Avove all, encouragement which was received from his colleagues and fellow workers in hours of remorse and disappointment would be gratefully remembered by the author.

G. Biswas,
Department of Chemistry,
North Bengal University.

FOREWARD

The work embodied in the present thesis was undertaken initially to synthesise and study the organotin derivatives of nitroso-napthols and related ligands which, a survey of the literature showed, received very little attention compared to other ligands, e.g., 8-hydroxy quinoline and its derivatives, hydroxamic acids, acetylacetone etc. It was, however, soon realised that reaction of 1-nitroso 2-napthol or 2-nitroso-1-napthol with organotin compounds never yielded the desired R_3SnCh type compounds (Ch = 1-nitroso-2-napthol or 2-nitroso-1- napthol), instead functionally substituted stannoxanes of varying complexities were invariably produced irrespective of whether the reaction was carried according to eqn(1) or (2), the two most frequently adopted procedures for synthesising such derivatives.

$$R_3Sn\,X + K(Na)\,Ch \longrightarrow \text{Products.} \qquad (1)$$

$$R_3SnOSnR_3 + 2HCh \longrightarrow \text{Products.} \qquad (2)$$

It was therefore decided to investigate the reactions between organotin compounds and nitroso napthols and related compounds in order to understand the anomalous behaviour of the nitroso - napthols. However, the complexcities of the products, their polymeric nature and extremely low solubility, in most cases, in common solvents made the separation, purification and thorough identification of all the products extremely difficult. As such, structures of the products have to be inferred primarily from the analysis of IR and electronic absorption data together with elemental analysis.

The thesis is divided into four chapters. A brief survey of the organotin chemistry is presented in chapter I.

Since extensive tin-carbon bond cleavage is one of the notable features of the reactions of nitroso-napthols with organotin compounds, a short review of the tin-carbon bond cleavage reactions has been presented in chapter II.

The reactions of 1-nitroso-2-napthol and its k-salt with organotin halides and stannoxanes have been discussed in chapter III. In order to high-light the effect of structural features on these reactions, the reactions of a number of structurally related molecules, e.g., diacetyl monooxime, α-benzil mono-oxime and benzoin mono-oxime have also been studied and included in this chapter. IR and electronic spectral data of the products have been discussed and tentative structures have been proposed in a number of cases. Probable mechanism for the formation of the different products have been suggested.

In the last chapter preparation of some organotin carboxylates by the reaction of esters with organotin hydroxides has been presented. This work was undertaken with a view to synthesising mono (triorgano tin) esters of dicarboxylic acids, e.g., oxalic acid, malonic acid etc., which could not be satisfactorily prepared by the usual methods.

CONTENTS

Chapter I

A short review of organotin chemistry

Chapter II

Cleavage of tin - carbon bonds

Chapter III

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

Chapter IV

On preparation of organotin carboxylates by the reaction of organotin hydroxides with esters

CHAPTER I

A Short Review of Organotin Chemistry

IA Introduction

Organotin compounds are substances containing at least one carbon tin bond. The first chemist to report an organotin compound seems to have been E.Frankland (1,2). But his work appears to have remained unknown to most of his contemporaries as well as to later authors. The work of C.Lowig (3) in 1852 has usually been considered to represent the beginning of organotin chemistry. Apart from the compounds described by lowig, many significant contributions were made in this field during the next few decades.

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

$$R_4Sn,\ R_3Sn\ X\ ,\ R_2Sn\ X_2\ ,\ R\ Sn\ X_3$$

R can be identical or different, substituted or unsubstituted, aliphatic or aromatic groups. X can be negative groups such as OR, -SR, -OCOR, $-OSnR_3$, $-NR_2$, or halogen or some other acid radicals or neutral ligands such as -H, or electropositive ones such as Li or Na. The three series of organotin hydrides R_3SnH, R_2SnH_2 and RSnH (4,5,6,7) have recently assumed considerable importance.

Stannyl metal compounds of the type R_3SnM and R_2SnM_2(8-9), $Ph_3SnSiph_3$, $Ph_3SnSi(Geph_3)_3$, $R_3Sn - SnR_3$(8), $Ph_3SnZnSnPh_3$and $Ph_3SnCdSnPh_3$ are also known where R may be aliphatic or aromatic, M may be Li,Na or K.

The discovery of industrial applications of organotin compounds as stabilisers of polyvinyl chloride plastics, rubber antioxidants, catalyst in the polymerisation of olefins, agricultural fungicides and as active ingredients in certain veterinary medicine (10) and also an increased general scientific interest produced a striking renaissance of organotin chemistry starting from about 1949 and continuing to the present day.

IB Bonding in Organotin compounds

The electronic configuration of tin is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$; the ground state being 3p state derived from $s^2p^2$of configuration (11) the common tetracovalent state is derived from the sp^3 hybridisation by promoting one of the paired S electrons to the next higher P level. The tetra covalent state occurs much more frequently than divalent state and a great number of organotin compounds contain tetravalent tin atom. Organo derivatives of group IVA metals are generally more stable and less reactive than the corresponding compounds of group III or V metals. The increased stability may be attributed to the Sp^3 hybridisation Thus, tetravalent tin is unreactive towards air and water but trimethyl Indium and trimethyl antimony have a strong affinity towards these reagents. The marked increase in stabilities of R_4Sn compounds over R_2Sn types also demostrate the effect of increased hybridisation on the stability. Metal - Carbon bond strengths have been reviewed by Skinner (12) who noted that mean bond dissociation energies ($\bar{D}$) fall as the subgroup is descended so that $\bar{D}$ (C-R) $\bar{D}$ (Si-R) $\bar{D}$ (Ge-R) $\bar{D}$ (Sn-R) $\bar{D}$ (Pb-R). The mean values of the bond dissociation energies are C-C : 87, C-Si : 70, C-Ge:60, C-Sn : 50, C-Pb : 31-37 K cal/mole. These values are, ofcourse, further dependent on the nature of the alkyl group i.e. on the stabilisation of the corresponding alkyl radicals by hyperconjugation etc.

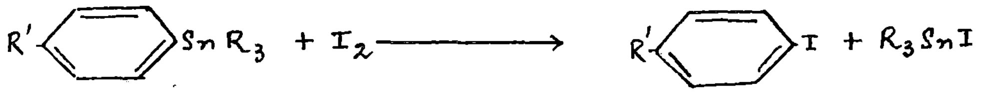
The covalent radius of Sn atom is 1.40 Å and is surprisingly independent of the nature of the ligands. Only when there is an accumulation of strongly negative ligands round the tin there is some decrease in bond lengths. The bonding of the tin would thus appear to be almost entirely covalent at least in crystalline solids, in non polar media and in the vapour. However, the electronegativity of tin being less than most of the common ligands, e.g., carbon, nitrogen, oxygen, halogen and even hydrogen, the bonds are expected to be sufficiently polar. The dipole moment of various Sn - X bonds have also been estimated. The dipole moment of alkyl tin bond, mostly estimated as 0.45 - 0.6D (13 - 15) depends both in magnetude and direction on the nature of alkyl group (16 - 17).

The electronegativities of the elements of group IV have been investigated extensively by different workers (20 - 23). The results, a selection of which is given in Table 1, always differ according to the method of measurement and the compounds selected. This is not surprising since the electronegativity, not being a uniquely defined parameter, depends on the method of measurement and the surrounding of the atom in question. In practice, therefore, one generally works not with an 'electronegativity of tin' but with a value for tin in a particular combination i.e. allowance will have to made for the influence of all ligands.

Table - 1

	Pauling	Sanderson	Fineman Daignault	Allred Rochow
C	2.5	2.47	2.57	2.60
Si	1.8	1.74	1.90	1.90
Ge	1.8	2.31	2.02	2.00
Sn	1.8	2.02	2.47	1.93
Pb	1.8			2.45

Closely connected with this is the inductive effect which tin atoms or stannyl groups exert on their surroundings. The bond polarisation $C^{\delta-}$ - $Sn^{\delta+}$, which is there in principle, may be changed by substitution at C as well as at Sn.NMR data on organotin compounds (18 - 19) and semiempirical calculations of Majee and Gupta (43) emphasises this. According to Eaborn etal (24) polarisation is increased by electron donor substituents R' in the p - position in a phenyl group, as shown by the increase in the rate of scission of the C - Sn bond by iodine according to reaction (I). The reaction thus belongs to the class of electrophilic aromatic substitution (24 - 25).



(1)

As expected, electron attracting groups R' decrease the rate of lowering the nucleophilicity of the ring carbon attached to tin. The sequence of relative reaction rates is for R' = OMe > - Bu > i - Pr > Et > Me > H > Br > F > Cl > CooH.

Electron donor properties increase in the series (R = Me) : $SiR_3 < GeR_3 < SnR_3$, as may be seen from the relative rates of acidolysis of P - R_3MCH_2CH - SnR_3 . These are for M = Si 1.00, Ge 1.36, Sn 3.21 (26). A similar sequence emerges from I.R and NMR measurements (27) and also from IR studies on esters of the type $MeCOOMMe_3$ which give M = C,Si,Ge (28).

One difficulty which often arises in experiments designed to measure relative inductive effects is that there may be some π- character in a bond between tin and an element possessing p electrons (29 - 30). Thus in a Sn - X bond where X is $C(Sp^2)$, N,O,S or halogen it is possible that, opposing the inductive electron drift in Sn - X, there may be some overlap between a filled p - orbital on X and an empty 5d orbitals on Sn causing a transfer of electron density in the opposite direction. Despite many controversies (31 - 34), it is widely accepted that there are significant ($p\pi$ - $d\pi$) contributions to the Sn - N bonds in compounds such as the plannar trisilyl amine (35). There is some evidence that in phenyl tin compounds, interaction occurs between the electrons of the phenyl groups and the 5d orbitals of tin. This conclusion is based on the interpretation of NMR (36 - 37), infrared (38), ultraviolet (38) and dipole moments (39) of phenyl tin compounds and the acid strength of the substituted benzoic acids $p\text{-}Me_3MC_6H_4COOH$ (M = C,Si,Ge,Sn). It can not be assumed that other aromatic groups behave similarly since pKa values for a series of pyridine having Me_3M(M=C,Si,Ge,Sn), substituents in the 2-position indicated the absence of $p\pi - d\pi$ bonding in the tin-pyridine link (40). Calculation based upon nuclear quadrupole resonance measurements indicated π - character in the Sn-I bonds of diethyl tin diiodide whereas it was concluded from the dipole moments of organotin chlorides that the Sn-cl bond order is close to unity (39). There is evidence for $d\pi - P\pi$ interaction in the bonds formed between tin and certain transition metals (41 - 42). On the other hand Gupta and Majee have shown in a series of papers (43) that most of the properties of organotin compounds may be interpreted without assuming any $d\pi - p\pi$ interaction. However in a more recent article (44) Majee has demonstrated that the success of earlier Del Re calculations does not necessarily rule out such interactions.

IC Catenation Properties of Sn in Organotin Compounds

Tin like other members of group IVA shows the tendency to catenation. A number of excellent reviews are now available on tin - tin compounds (45 - 49). The ditin compounds may be prepared by a number of methods (47), the alkyl derivatives are generally liquid and the aryl derivatives tend to be solid at ordinary temperature. A good number of compounds of the type

$[R_2Sn]_n$ with the number of tin ranging from 2-6 have been described (47). The reaction of metallic sodium in liquid ammonia with Me_2SnCl_2 leads mainly to the compounds $[Me_2Sn]_n$, which are linear molecules with chain length n = 12-20 and perhaps more, and at least to one cyclic compound $[Me_2Sn]_6$.

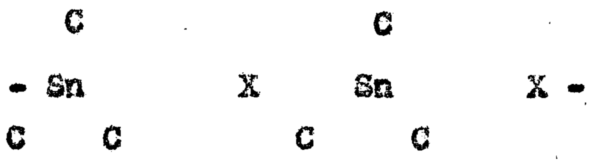
There is no evidence for branching of the chains (50-51). Similar results have been obtained with other alkyl and aryl compounds (51), e;g. cyclic hexamer of Et_2Sn, the cyclic pentamer and hexamer of Ph_2Sn, the cyclic tetramer of $(t\text{-}Bu)_2Sn$ etc. Williamson and Vander Kerk (52-53) have however reported a branched chain compound $(Ph_3Sn)_4Sn$ by the reaction of Ph_3SnLi with $SnCl_4$. Some coloured products reported in the synthesis of dialkyl tin compounds are due to the formation of partially branched tin chains (54). NMR studies indicate the formation of poly tin hydrides during thermal decomposition of butyl tin trihydride (47). Carboxylates and halide derivatives of di and poly tin compounds. have also been reported (55-56).

ID Organotin Complexes

Organotin compounds can form various types of complexes with ligands. The structural aspect of those compounds has been exhaustively reviewed by Ingham etal (8), Poller (57), Gielen and Sprecher (58) and more recently by Ho and Zukermann (58a).

The most interesting example is afforded by $R_3\overset{X}{Sn}$ type compounds which form various types of adducts with Lewis bases (8). These adducts are generally penta co-ordinated (59-60). For X = cl, Br or I, Me_3SnX type compounds are usually tetrahedral but for X = ClO_4^-, F^-, CO_3^-, BF_4^-, NO_3^-, AsF_6^-, $OCOR^-$, the compounds are five coordinate about tin where anions are probably either bridging or chelate types (61-62). The aquoion $Me_2Sn(H_2O)_4^{+2}$ has a linear C-Sn-C group, there being presumably four water molecules weakly co-ordinated in the equitorial plane (63). Similarly R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents such as 8 hydroxy quinoline (64-66), acetyl acetone (67-68), 1,10 Phenanthroline (65,68) etc. which may be five, six or sometimes even eight co-ordinated compounds.

The most general feature of the penta co-ordinated tin is a polymeric structure formed by the bridging of an anionic group to the tin atom from either side of the plane of the trialkyl tin group. This kind of structure is designated as type I. Type I compounds can be devided into three sub groups as shown in the table-2.



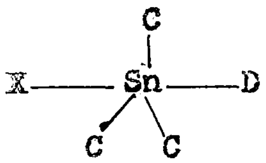
Type - I

Table-2

Sub group	Compound
(a)	$(CH_3)_3SnF$, $(CH_3)_3SnOH$
(b)	$R_3SnOOCR'$, $(C_4H_9)_3$ Sn(imidazole), $(CH_3)_3SnNO_3$, $(CH_3)_3SnClO_4$, $(CH_3)_3SnSiF_6$, R_3Sn $AlCl_4$
(c)	$(CH_3)_3SnCl$, $(CH_3)_3SnBr$, $(CH_3)_3SnCN$, R_3SnN_3 , $(CH_3)_3SnNCS$, $(CH_3)_3SnNCO$.

The compounds in the (a) subgroup of this classification contain tin atoms bridged by the anionic groups in the manner, -Sn - X - Y - X -, where X represents a halogen, an oxygen or a nitrogen atom and Z represents the reminder of the resulting group. The compounds in both (a) and (b) subgroup compounds are assumed to contain planner SnC_3 moities, but in so far as they have been studied, those in the (c) subgroup have no such planar arrangement.

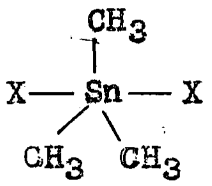
In compounds of structure type II, a donor molecule is co-ordinated to a triorganotin halide to give a trigonal bipyramidal arrangement. The best studied example is the 1 : 1 addition compounds of $(Ch_3)_3$ SnCl and pyridine.



(D = donor molecule)

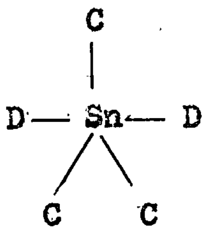
Type II

A halide ion can also act as a Lewis base to trimethyl tin halide, giving a symmetrical bipyramidal configuration of type III



Type III

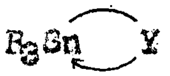
In cases where the anionic groups have no co-ordinating sites, for example $B(C_6H_5)_4^-$, two molecules of a mono-anionic Lewis base such as water can occupy the co-ordination sphere, giving a planar SnC_3 arrangement with a penta co-ordinated tin atom (type IV)



(Type IV)

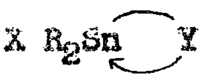
This finding may well be applied to interpret the structure of 1 : 2 addition compounds of formula $R_3SnX.2D(8)$ as that containing a bipyramidal $[R_3SnD_2]^+$ and X anion, and may preclude the existence of hexa-co-ordinated tin atoms in such triorganotin complexes.

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



Type V

In the case of di-organotin derivatives, both penta co-ordinated and hexa co-ordinated tin compounds have been reported. Penta co-ordinated tin is observed in dialkyl tin halide, carboxylates, dialkyl tin halide oxinates and dimethyl (1,3-dimethyl triazono) tin halides (69) (type VI)



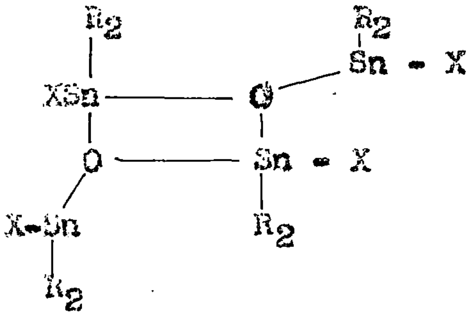
Type VI

The 2 : 1 addition compound of $(C_6H_9)_2Sn(NCO)_2$ and bipyridine is another type of penta co-ordinated di-organotin structure (VII)

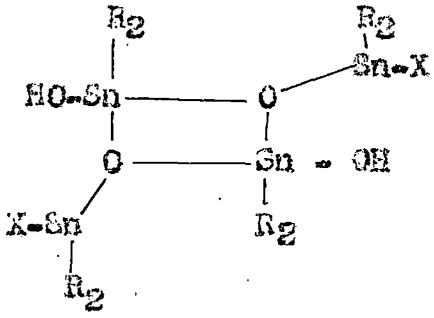
$$X_2R_2Sn \longleftarrow D - D \longrightarrow SnR_2X_2$$

Type VII

The dimeric tetraalkyl distannoxenes $(XR_2SnOSnR_2X)_2$ and $(XR_2SnOSnR_2OH)_2$ are unique because they are believed to contain both tetra-co-ordinated and penta co-ordinated tin atoms (Type VIII and VIII$'$)

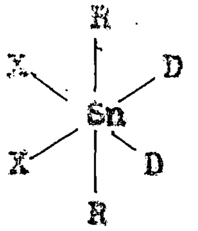


Type VIII



TypeVIII

Infrared spectroscopic investigations have shown that the addition compounds of R_2SnX_2 (X = halogen) and monodentate amines in 1 : 2 mole ratio, or bidentate amines in 1:1 mole ratio, are of the type IX

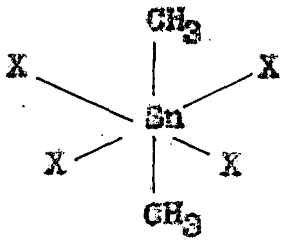


Type IX

Many di-organotin bis (Chelates) have been isolated (64,65,69-75) and found to contain hexa co-ordinated tin atom. Some representative compounds are acetyl acetonates, oxinates, and carboxylates. The alkyl group in these compounds exists predominantly in the trans position (type X), though X-ray crystallography on dimethyl tin dioxinate shows this to have a very much distorted structure (85)

Type X

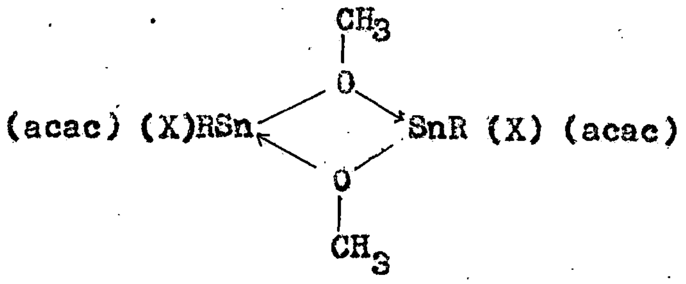
The most symmetric specis is the $(CH_3)_2 SnX_4^{-2}$ anion (X = F,Cl,NCS) where structure is represented by (XI). Tobias etal have shown that there are analogous specis, $[(CH_3)_2 Sn(OH)_4]^{2-}$ as well as cationic hydrated specis in aqueous solution of dimethyl tin compounds (73,76,77)



Type XI

Reports on mono-organotin compounds indicate that some of these might have hexa co-ordinated and even hepta co-ordinated tin atoms. However, little work has been done on their detailed configurations. Mono-organotin halide bis acetyl acetonates (78) and bis oxinates (79) as well as the addition compounds of formula $RSn X_2 .2D$(80) are examples of hexa co-ordinated tin compounds.

The complex compound $[(acac)XRSn(OCH_3)]_2$, obtained by partial alcoholysis from $RXSn(acac)_2$ is unique in that it contains two bridging methony groups forming a four membered Sn-O ring as shown in structure XII



Type XII

A hepta co-ordinated tin is observed in phenyl tin tris (tropolonate) and probably in mono organo tin tris (carboxylates).

Several organo tin (IV) complexes with quadri and tetradantate anionic schiff base ligands have been prepared and investigated in the solid state (81 - 83). Mossbauer parameters derived from both zero field and magnetically perturbed spectra suggest that the R_2Sn(salen)*, R = Me, Et, Ph and Me_2Sn(Saldap-2-OH)** complexes have distorted trans octahedral structures. However in Ph_2Sn(H-Saldap-2-O) the ligand appears to be only terdentate leading to a penta-co-ordinate structure similar to those of the $R_2Sn(Sal-N-2-OC_6H_4)$ derivatives (R = Ph,Me).

---

* H_2Salen - N,N′ ethylene bis (salicylaldimine)

** H_2saldap-2-OH - N,N′ (2-hydrony trimethylene) bis (Salicylaldimine)

Recently organotin complexes of strong π acids of the type Me_3Sn TCNQ, $MeCP_2Sn$.TCNQ, $MeCP_2Sn$.nTCNE(n =1,2) and SnX_4. TCNE.THF(X=cl,Br) (84) have been prepared (TCNQ = Tetra cyano p - quinodimethane, TCNE = tetracyano ethylene). The infrared spectra of the complex Me_3Sn.TCNQ exhibits a single band at 555 cm^{-1} in the tin-carbon streching region which is assigned to the anti-symmetric mode of a planar Me_3Sn moiety, with bridging TCNQ residues resulting in a trigonal bipyramidal configuration at the tin. The intense colouration of the compound is indicative of the formation of $(TCNQ)^-$ radical anion on complexation. The complex is therefore best represented by the canonical from $(Me_3Sn)^+$. $(TCNQ)^-$ and thus provides the first example of an isolable paramagnetic organotin complex.

BIBLIOGRAPHY

1. E. Frankland, Liebigs.Ann.Chem 171 esp -71 (1849) 212
2. E Frankland, J.Chem.Soc 2 (1850) 267
3. C. Lowig, Liebigs.Ann.Chem.84 (1952) 308
4. A.E.Finhalt, A.C.Bond, Jr,K.E.Wilzback and H.I. Schlesinger, J.Amer.Chem.Soc. 69 (1947)2692
5. G.J.M.VanderKerk,J.G. Noltes and J.G.A.Luijten, J.Appl.Chem. 7(1957) 366
6. M.Lesbre and I.Scree de Roch, Bull.Soc.Chim,France(1956)754
7. W.P.Neumann,H.Niermann and R.Sommer, Liebigs.Ann.Chem 659(1962)27
8. R.K.Ingham,S.D.Rosenberg, H.Gilman, Chem.Rev.60(1960) 459
9. G.W.Watt, Chem.Rev.46(1950)317
10. R.K.Ingham,S.D.Rosenberg and H.Gilman, Chem.Rev.60 (1960)520-525
11. C.E.Moore , Atomic energy levels,Circular 467, National Bureau of Standards Vol-1, Government Printing office, Washington D.C. (1949)

12. H.A.Skinner, Adv.Organometal.Chem.2(1964)49

13. I.P.Gol'dstein,E.N. Gur'yanova,E.D.Delinskaya K.A.Kocheskov, Doklady.Akad.Nauk SSSR 136(1961) 1079

14. J.Lorberth and H.Noth, Chem.Ber.100(1967)3511

15. M.Meixner, Exam.Thesis.Quoted in the 'Organic Chemistry of tin' by Wilhelm.P.Neumann (1970) 8

16. H.A.Staab, Einfuhrung in die theoret. Organ.Chemie.Verleg Chemie, Weinheium/Bergstr, (1962) 212

17. P.Taimsalu and J.L.Wood, Spectrochim acta. 20(1964)1043

18. N.Flitcroft and H.D.Kaesz, J.Amer.Chem.Soc 85(1963)1377

19. J.R.Holmes and H.D.Kaesz, J.Amer.Chem.Soc. 83(1961)3903

20. A.L.Allred and E.G.Rochow, J.Inorg.Nucl.Chem 5(1958)269,17(1961)215

21. M.A.Fineman and R. Daignault, J.Inorg.Nucl.Chem. 10(1959)205

22. H.O.Pritchard,H.A.Skinner, Chem.Rev. 55(1955)745

23. H.Spiesecke and W.C. Schneider, J.Chem.Phys 35(1961)722

24. R.M.Bott,C.Eaborn and J.A.Waters, J.Chem.Soc. (1963)681

25. S.Boue, M.Gielen and J.Nasielski, Bull.Soc.Chim.Belges. 73(1964)864

26. R.W.Bott, C.Eaborn and D.R.M.Walton, J.Organometal.Chem. 2(1964)154

27. O.J.Scherer and M.Schmidt, J.Organometal.Chem. 1(1964)490

28. T.N.Srivastava and M.Anyszchuk, Cannd.J.Chem. 41(1963)1244

29. N.A.Matwioff and R.S.Drago, J.Organometal.Chem. 3(1965)393

30. R.West, J.Organometal.Chem. 3(1965)314

31. E.A.V.Ebsworth, Chem.Comm.(1966)530

32. M.G.Hogben, A.G.Oliver and W.A.G.Graham, Chem.Comm.(1967)1183

33. E.W.Randall and J.J.Zuckermann, Chem.Comm (1966)732

34. E.W.Randall and J.J.Zuckermann, J.Amer.Chem.Soc.(1968)90

35. P.G.Perkins, Chem.Comm. (1967)288

36. J.C.Maire, J.Organometal.Chem. 9(1967)271

37. L.Verdork and G.P. Vander Kelen, Bull.Soc.Chim.Belges 74(1965)361

38. I.I.Lapkin and V.A. Dumler, Chem.Abstr. 64(1966)12045e

39. H.H.Huang,K.M.Hui and K.K.Chiu, J.Organometal Chem. 11(1967)515

40. D.G.Anderson,J.R. Chipperfield and D.E. Webster, J.Organometal.Chem. 12(1968)323

41. R.C.Edmondson and M.J. Newlands, Chem.Ind.(1966)1888

42. W.Jelz,P.B.Simons, J.A.J.Thompson and W.A.G.Graham, Inorg.Chem.5(1966)2217

43. R.Gupta and B.Majee, J.Organometal.Chem. 29(1971)419,33(1971)169, 36(1972)71,40(1972)97, 49(1973)191,197,203

44. B.Majee, Rev.Si,Ge,Sn and Pb

45. K.M.MacKay and R.Watt, Organometal.Chem.Rev A4,137(1969)

46. A.G.MacDarmid, Organometallic Compounds of the group IV elements, Marcel Dekker, New York (1968)

47. A.K.Sawyer, edited by Organotin compounds, Marcel Dekker, New York (1972)

48. R.C.Poller, The Chemistry of Organotin compounds, Logos Press (1970)

49. W.P.Newman , The Organic Chemistry of tin, (English),John Willey and Sons, London, New York (1970)

50. T.L.Brown and G.L.Morgan, Inorg.Chem.,2,736(1963)

51. W.V.Farrer and H.A.Skinner, J.Organometal.Chem.,1,434(1964)

52. L.C.Willamsons and G.J.M.Vander Kerk, Investigation in the field of Organolead Chemistry, Inst.Organic Chem. T.N.O.Utrecht,Holland (1965)

53. L.C.Willdmasons and G.J.M.Vander Kerk, J.Organometal.Chem., 2,260(1964)

54. W.P.Neumann, Angew.Chem.,75,225(1963)

55. A.K.Sawyer and H.G.Kuivila, J.Am.Chem.Soc.,82,5958(1960)

56. A.K.Sawyer and H.G. Kuivila, J.Org.Chem.,27,610(1962)

57. R.C.Poller, J.Organometal.Chem. 3(1965)321

58. M.Gielen and N.Sprecher, Organometal.Chem.Rev 1(1966)455

58a. B.Y.K.Ho and J.J. Zukermann, J.Organometal.Chem.Review 49(1973)1

59. N.A.Matwiyoff and R.S.Drago, Inorg.Chem.3(1964)357

60. R.Hulme, J.Chem.Soc.(1963)1524

61. H.C.Clark,R.J.O'Brien, Inorg.Chem.2(1963)740,1020

62. H.C.Clark,R.J.O'Brien, and J.Troller, J.Chem.Soc.(1964)2339

63. R.S.Tobias and C.E. Freidline, Inorg.Chem.4(1965)215

64. D.Blake,G.E.Coates and J.M.Tate, J.Chem.Soc.(1961)756

65. T.Tanaka,M.Komura,Y. Kawasaki and R.Okawara, J.Orgamometal.Chem. 1(1964)484

66. K.Ramiah and D.F.Martin, Chem.Comm.130(1965)

67. A.W.Watlake and D.F. Martin, J.Inorg.Nucl.Chem.27(1965)1579

68. D.L.Alleston and A.G. Davies, Chem.Ind.(1961)551

69. F.E.Brinckmann,H.S. Haiss and R.A.Robb, Inorg.Chem.4(1966)936

70. W.Gerrard,E.F.Mooney and R.G.Rees, J.Chem.Soc(1964)740

71. M.M.McGrady and R.S. Tobias, J.Am.Chem.Soc.87(1964)1909

72. Y.Kawaski,T.Tanaka and R.Okawara, Bull.Chem.Soc.Japan 37(1964)903

73. M.M.McGrady and R.S. Tobias, Inorg.Chem.3(1964)1157

74. W.H.Nelson and D.F.Martin, J.Inorg.Nucl.Chem27(1965)1579

75. W.H.Nelson and D.F. Martin, J.Organometal.Chem. 4(1965)67

76. M.Yasuda and R.S. Tobias, Inorg.Chem.2(1963)207

77. H.N.Farrey,M.M.Mc.Grady and R.S.Tobias, J.Am.Chem.Soc 87(1965)5019

78. R.Ueeda,Y.KawasKi,Y. Tanaka and R.OKawara, J.Organometal.Chem. 5(1966)194

79. G.Faraglia,L.Roncucci and R.Barbieri, Ric.Sci 35(11-A) (1965)205

80. I.R.Beattie and G.P. McQuillan, J.Chem.Soc.(1963) 1519

81. K.Kawakami and T.Tanaka, J.Organometal.Chem 60(1973)409

82. J.N.R.Ruddick and J.R.Sams, J.Organometal.Chem. 60(1973)233

83. J.N.R.Ruddick and J.R.Sams, Abstracts 6th Int.Conf. Organometal.Chem.

84. J.A.Richards and P.G.Harrison, J.Organometal Chem. 64(1974)63

85. E.O.Schlemper, Inorg.Chem.6(1967)2012

CHAPTER II

Cleavage of tin-carbon bonds

IIA Introduction

Much of the experimental work in the field of organotin chemistry has been inspired by a desire to understand as fully as possible the reactivity of these compounds. Hundreeds of alkyl tins, especially those with different ligands, were prepared with a view to studying the fission of tin-carbon bond which may be represented as

$$>\mathrm{Sn} - \mathrm{C}< + \mathrm{A{-}B} - >\mathrm{Sn} - \mathrm{A} + >\mathrm{C} - \mathrm{B} \qquad (I)$$

Although the reactivity of the tin-carbon bond depends on a number of factors, they are susceptible to attack by a wide variety of reagents so that A - B in the above equation may be halogen, mineral acid, carboxylic acid, thiol, phenol, alcohol, metallic or nonmetallic halide, alkali, alkali metal etc.

These reactions are not only of utmost theoretical and practical importence in organotin chemistry, but also has some bearing on the present work. As such a brief discussion on the subject is presented here.

The most frequenly studied reaction of tin-carbon bond is the cleavage by halogen; one or more organic moieties are split off depending upon the condition of the reaction according to the following scheme :

$$R_4Sn + X_2 \rightarrow R_3SnX + RX \qquad (2)$$

$$R_3SnX + X_2 \rightarrow R_2SnX + RX \qquad (3)$$

$$[X - Cl, Br, I]$$

when unsymmetrical organotin compounds of the type R_3SnR' are treated with one molecular proportion of the reagent, organic groups are usually cleaved from tin in the order (1) :

O - tolyl > p - tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > iso-butyl > iso-amyl > amyl > hexyl > heptyl > octyl.

This series is of practical value in synthetic organotin chemistry since (2) usually predicts correctly the products of cleavage. However predictions are less reliable with $R_2SnR'_2$ type of compounds. Though the sequence have been compiled from reactions using dirrerent cleavage reagents under a variety of conditions, careful examination of the literature reveals a number of contradictions (3), the actual situation being much more complicated.

The mechanism of tin-carbon bond cleavage has been clarified in a series of papers (3-5) by Gielen and co-workers. On the basis of their mechanistic studies these reactions are to be classified essentially as electrophilic substitution at the carbon atom. The geometry of the transition state is however greatly influenced by the solvent and the electrophile which may co-ordinate with the tin atom under proper conditions thereby causing profound variation in the rates. The different types of organotin derivatives are treated separately in the following discussion :-

Tin-carbon bond cleavage in symmetrical tetra alkyl tins

These compounds can be cleaved by a number of electrophiles (1) or radicals (7-8). Among the electrophiles, one may use halogens, halogen acids, tin (IV) halides and also other inorganic halides [eg BX_3(9), $HgCl_2$, $HGeCl_3$, [redacted] (10), PF_5(11)] , Organometallic halides [$RBCl_2$, R_3SnCl (12)] , or oxidants [CrO_3(13)] . Alkyl halides react in presence of tetra alkyl tins to give tri- alkyltin halides (14-15). Halogens can also be used as radical sources (16).

IIB . Electrophilic substitution at a saturated carbon atom

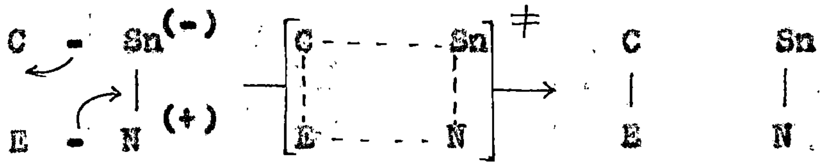
Kienetic studies have shown that tetraalkyltins react with electrophiles [I_2 (17), Br_2 (5), HgX_2 (19-20), CrO_3 (21)] by a complex mechanism (22) which involves a predetermining equilibrium between the organotin substrate and a nucleophile. The step is then followed by the reaction of an electrophile with the activated carbon-tin bond. Depending on the solvent polarity two different situations may be distinguished :

(1) Reaction in "nonpolar" solvents :

In nonpolar media, the most nucleophic species available in the solution is the electrophile E-N itself [X-X(22),H-cl(23), O_2Cr-O(21)] , which may complex with the organotin molecules through the tin atom as follows :

$$C - Sn + N - E \rightleftharpoons C - \overset{(-)}{Sn} - \overset{(+)}{N} - E \qquad (4)$$

The representation is only formal indicating the transfer of electron from N to tin. The complex formed in this equilibrium contains activated C atoms and an enhanced electrophilic species. An intramolecular reaction, which seems thus a reasonable way in which this complex might give reaction products, is observed when the structure of the complex allows such a cyclic transition state. Gielen and Nasielski (44) use the symbol SF 2 (substitution four centred bimolecular) to indicate this mechanism, Abraham and Hill (19) however prefer to call it SEi.


(5)

This complex which contains rather nucleophilic carbon atoms, may also react with another electrophile E - N to give the cleavage of a carbon-tin bond :

$$N - E + C - \overset{(-)}{Sn} - \overset{(+)}{N} - E \longrightarrow C - E + N - \overset{(-)}{Sn} - \overset{(+)}{N} - E \quad (6)$$

A third possibility cannot be excluded : it is the reaction of the electrophilic part of this complex with another organotin molecule :

$$C - \overset{(-)}{Sn} - \overset{(+)}{N} - E + C' - Sn' \longrightarrow C' - E + Sn' - N + C - Sn \quad (7)$$

This mechanistic picture explains a large number of findings such as :

a) The presence of a third over term : The rate of reaction between tetra iso-propyl tin and bromine in chlorobenzene may roughly be described by :

$$- d[X_2]/dt = K_2[R_4 Sn][X_2] + K_3[R_4Sn][X_2]^2 \quad (8)$$

where the third order term may be considered as due to the existance of reaction (6).

b) The mixing effect : Tetraethyltin reacts 11.7 times faster than tetramethyltin with Br_2 in chlorobenzene. A mixture of tetramethyl and tetraethyltin, reacting with Br_2 in chlorobenzene yields a ratio $[Et\text{-}Br]/[MeBr] = 4.3$. It has been shown (22) that the presence of tetraethyltin influences the reaction of Br_2 with tetramethyltin. This mixing effect is readily explained by reaction (7).

The observed reactivity sequence (24) for halodemetallation of R_4 Sn type compounds in nonpolar solvents is :

$$i - Pr > Et > Bu \sim Pr > Me.$$

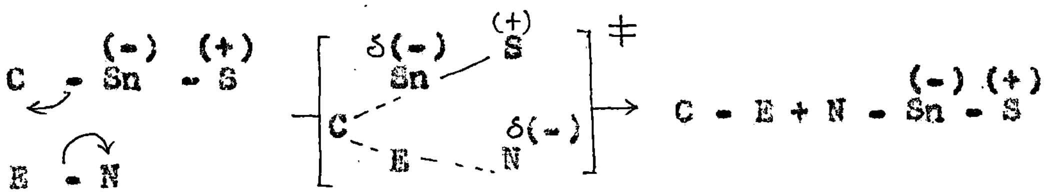
However the rate constants lie close together and deviations from the sequence often occure depending on the experimental conditions.

(ii) Reaction in polar solvent

In this case, the solvent co-ordinates with the metal atom which may be formally represented as :

$$C - Sn + S \rightleftharpoons C - \overset{(-)}{Sn} - \overset{(+)}{S} \qquad (9)$$

Formation of such complex (which may be a true or a collision complex) would increase the electron density at the carbon atom which may be easily attached by an electrophile, yielding an open transition state whose existance has been fairly well established by Abraham and Spalding (20) :



(10)

Co-ordination withthe metal generally does not make the solvent electrophilic enough to compete with the electrophile E - N and to reat either intermolecularly or intramolecularly with a carbon-tin bond and these two steps thus seem to be the only possible reaction. Indeed neither a third order term nor any mixing effect could be detected in nucleophilic solvents such as methanol.

The nucleophilicity of the solvent toward tin, which seems to be the most important factor affecting the polarity of the solvents for electrophilic aliphatic substitution (17) may be estimated by the ability of the medium to complex the tin atom of trimethyl tin chloride (25,44). Using NMR spectroscopy the following sequence has been found :

HMPT $>$ DMSO $\simeq$ DMF $>$ Py $>$ MeOH $\simeq$ i-PrOH $>$

t - BuOH $\simeq$ MeCOMe $\simeq$ MeCOOMe $>$ Dioxane $>$ MeCN $>$

MeCOOH $>$ PhCl $\simeq$ CCl_4 $\simeq$ Cyclohexene.

The reactivity sequence observed in polar solvents is :
R = Me $>$ Et $>$ Bu $>$ Pr $>$ i-Pr $>$ t - Bu.

(iii) Radical substitution at a saturated carbon atom :

Symmetrical tetraalkyltins may also be attacked by radicals. Following mechanistic picture has been proposed for the reaction of these organo-matellic molecules with halogens in chlorobenzene in an inert atmosphere under illumination

$$Br_2 \xrightarrow{h\nu\,(410mm)} 2\,Br. \qquad (11)$$

$$Br\cdot + R_4Sn \longrightarrow R_4\overset{(-)}{Sn} - \overset{(+)}{Br}\cdot \qquad (12$$

$$R\,\overset{(-)}{Sn_4} - \overset{(+)}{Br}\cdot \longrightarrow R_3SnBr + R\cdot \qquad (13)$$

and

$$R_4\overset{(-)}{Sn} - \overset{(+)}{Br}. + R'_4Sn \longrightarrow R_4Sn + R'_3SnBr + R'\cdot \qquad (14)$$

forming a chain with

$$R\cdot + Br_2 \rightarrow R - Br + Br\cdot \qquad (15)$$

Oxygen seems to modify the stoichiometry, the reaction products and thus the mechanism of the analogous reaction of tetraethyltin with iodine (27) is :

$$I_2 \xrightarrow{h\nu\,(430mm)} 2I\cdot \qquad (28)$$

$$I\cdot + Et_4\,Sn \longrightarrow EtI + Et_3\,Sn\cdot \qquad (29)$$

which then reacts :

in the absence of oxygen $Et_3Sn\cdot + I_2 \rightarrow Et_3SnI + I\cdot$ (30)

chain reaction $\phi >> 1$

in presence of oxygen $Et_3Sn\cdot + O_2 \rightarrow Et_3Sn-O-O\cdot$ (31)

$Et_3Sn-O-O\cdot \rightarrow$ Stable products (32)

Razuvaev and co-workers (15,28-29) have obtained a considerable body of evidence for the participations of trialkyltin radicals in the photolysis of tetraalkyltins and in the reactions of these derivatives with carbon tetra-chloride initiated by oxygen or by peroxide :

$$R_4\,Sn \longrightarrow R_3\,Sn\cdot + R\cdot \qquad (33)$$

$$R_3\,Sn\cdot + X - C{<} - \quad R_3SnX + \cdot C{<} -$$

IIC . Symmetrical vinylic, acetylenic and aryl derivatives.

Tetravinyl tin reacts more than 20 times faster with iodine than tetraethyl tin but is less reactive than vinyl trialkyltins (30). Little is known about the more reactive symmetrical acetylenic organotin compounds (31). The reactivity of vinylic and acetylenic derivaties is in accordence with the order of bond polarity :

$$Sn - C\ (\varnothing p^3) < Sn - C\ (\varnothing p^3\ ) < Sn - C\ (\varnothing p).$$

Tetraaryltins are also more prove to cleavage than tetraalkyl tins; one or two aryl groups are cleaved off the tin atoms in the cleagave reactions depending on experimental condition.

In carbon tetrachloride bromine gives Ar_2SnBr_2 whereas iodine in chloroform at - 40° produces mono-substituted product (1,33 - 34). The most widely used reaction is the disproportionation with $SnCl_4$ which furnish good yields of triaryltin chloride, diaryltin dichloride and aryltin trichloride (1,34,35-39) under proper experimental condition. Sulpher reacts with tetraphenyl tin to yield phenyltin — sulpher polymer chains and diphenyl sulphide; selenium yields only a monoinsertion product (40-42). No mechanistic study has been made on symmetrical tetraaryl tin compounds, the mechanism of aryl-tin bond cleavage has been derived from unsymmetrical compounds.

IID. Unsymmetrical Organotin Compounds

1. Unsymmetrical tetraalkyltins

The kienetic scheme which describes the reaction of symmetrical tetraalkyltins with electrophiles E - N is also valid for the same reaction on mixed tetraalkyltins and can be used to explain most of the experimental data. Only the important difference between this case and the former one are the nonequivalence of the alkyl groups bound to the metal atom in mixed derivatives; this introduces a new parameter : the selectivity, which depends dramatically on experimental conditions.

(i) Reactions in nonpolar solvents :

The reaction of bromine with propyl trimethyltin in chlorobenzene is described by a ratio $K_2(Me)/K_2(Pr) = 60$, showing a rather low selectivity. However the ratio decreases to 4.3 in the presence of tetraethyl tin (22), although it does not vary with concentration of Me_3SnPr. The mixing effect may be ascribed to the following reactions :

$$R\,Sn\,Me_3 + X_2 \rightleftharpoons R\,Me_3\,\overset{-}{Sn} - \overset{+}{X_2} \begin{array}{l} \nearrow RX + X\,Sn\,Me_3 \\ \searrow MeX + X\,Sn\,Me_2\,R \end{array} \qquad (34)$$

$$R'_4\,Sn + X_2 \rightleftharpoons R'_4\,\overset{-}{Sn} - \overset{+}{X_2} \longrightarrow R' - X + R'_3\,SnX \qquad (35)$$

$$R\,Sn\,Me_3 + R'_4\,\overset{-}{Sn} - \overset{+}{X_2} \begin{array}{l} \nearrow RX + X\,Sn\,Me_3 + R'_4\,Sn \\ \searrow MeX + SnMe_2\,R + R'_4\,Sn \end{array} \qquad (36)$$

Since $R'_4\,\overset{-}{Sn} - \overset{+}{X_2}$ would be more electrophilic than X_2, the selectivity of the cleavage would decrease.

On the contrary the presence of trialkyltin halides have two important effects on the reaction of tetraalkyltins with halogens :

a) A decrease of the relative importance of the third order term;

b) An increase of selectivity. $K_2\,(Me)/K_2\,(Pr)$ increases from 6.0 to 7.1 when triethyltin bromide is added to the chlorobenzene solution.

This may be ascribed to the formation of penta co-ordinate species due to association of the trialkyltin halide with the tetraalkyl tin compounds.

The observed reactivity sequence for halodemetallation of Me_3SnR in chlorobenzene is $R = t - Bu > Me \simeq i\text{-}Pr > Pr \simeq Bu$ with the rate constants lying quite close together so that halogen in solvents of low polarity does not discriminate well between different alkyl groups. Abraham and Hill (19) has classified the reactions in nonpolar solvent as SEi (substitution, electrophilic, internal) which includes cases lying in between pure SE2 and SE^c (substitution, electrophilic, via co-ordination) mechanism.

The low selectivity observed for the reaction of halogens with mixed tetraalkyltins in nonpolar solvents has been used for qualitative identification of organic groups through the alkyl halides formed as products of the cleavage (43).

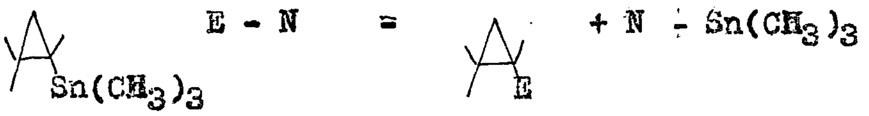
(ii) Reactions in polar solvents

As discussed earlier polar solvents render nucleophilic assistance to the tin atom thereby increasing the polarity of Sn - C bonds. The reactivity sequence observed for cleavage of R group from Me_3SnR or Et_3SnR is $R = Me > Et > Bu \sim Pr > t-Bu$. The spread of the rate constants in a such series is considerable so that there is a high degree of selectivity in halodemetallation reaction in polar solvents. The reactivity of R group in R_3SnR' is also profoundly affected by the nature of the leaving group R_3Sn.

The high degree of selectivity of halodemetallations in methanol has been exploited in the first practicable synthesis of fully unsymmetrically substituted tetra alkyl tin (6,43). The same principle has been utilised for the synthesis of chiral tin compounds (50)

2. Stereochemistry of bimolecular electrophilic substitution at a saturated carbon :

Not many studies have so far been made on the stereochemistry of SE^2 reactions in organotin compounds. However, the results so far obtained indicate that reactions involving open transition state(SE 20) proceed with complete inversion of configuration (44) as shown by Jensen (45) on the bromodemetallation of sec-butyl trineopentyltin in Methanol. On the contrary SE^{2c} reactions, which go through a cyclic transition state, should occur with retention of configuration (46). Of course, substrates for which the inversion of configuration is unfavourable such as Cis or trans - 2 - methyl-cyclopropyl trimethyltins or (+) - (1-methyl-2,2 diphenyl cyclopropyl) - trimethyltin (47) for instance react with retention of configuration even in polar solvents.



(37)

This general hypothesis seems also to be valid for SE^2 reactions on other organometallic substrates, as shown by Brown (48) who studied the bromodemetallation of tri-exo-norbornyl-boron, which occurs with full retention of configuration in THF whereas the same reaction takes place with full inversion of configuration in the same solvent in the presence of methoxide ion.

3. The reactivity sequence and SE^1 mechanism

The reactivity sequence for the bimolecular replacement of a constant R_3Sn group by an electrophile (iodine or bromine in methanol or in acetic acid (5), HgX_2 in methanol (20) or bromine in chlorobenzene (5) :

$$R' - Sn\,R_3 + E - N \quad = \quad R' - E + N - SnR_3 \qquad (38)$$

can be described by :

$$R' = C_6H_5 - CH_2 > CH_3 > CH_2 = CH_2 > (CH_3)_2\,CH > (CH_3)_3C.$$

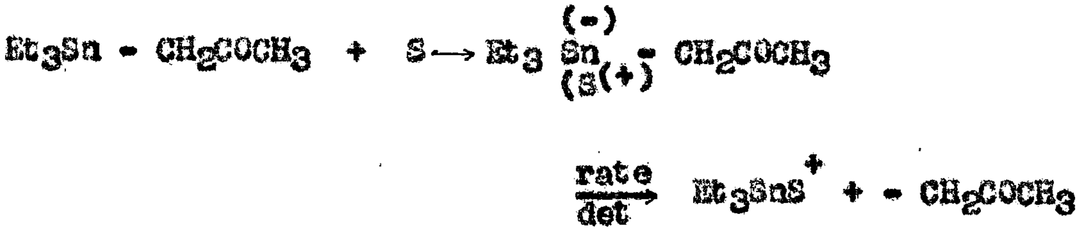
This sequence, generally associated with SE 1 reaction, shows that that the stabilization of the partial negative charge appearing on the different carbon atoms affer this first complexation step

$$N + R_3SnR' \rightleftharpoons R_3R'\overset{-}{Sn} - \overset{+}{N} \qquad (39)$$

plays a very important role. Electron-attracting substituents accelerate the substitution reaction and it is reasonable to expect that strong electron-attracting substituents could sufficiently stabilize the incipient carbanion so that the complexation would be no longer dependent on the attack of the electrophile on the carbon atom, giving then a monomolecular electrophilic substitution. However, it has not yet been possible to find an aliphatic electrophilic substitution with a first-order rate equation.

The reaction of benzyltrimethyltin with iodine in methanol is a second order reaction, but poorly electrophilic reagents do not react with this organotin molecule if a strong nucleophile is present. Eaborn (49) has indeed shown that the reaction of m-chlorobenzyltrimethyltin with water in ethanol yields m-chlorotoluene and is catalysed by hydroxyl ion. The electrophile is unfortunately present in large excess and it is thus impossible to determine whether it has to be included in the transition state or not. Nevertheless the nucleophilic catalysis is once more important and kinetic results suggest that there is a considerable negative charge on the separating benzyl group in the transition state. This reaction might be an example of a monomolecular electrophilic substitution SE ^{1} at a saturated carbon atom.

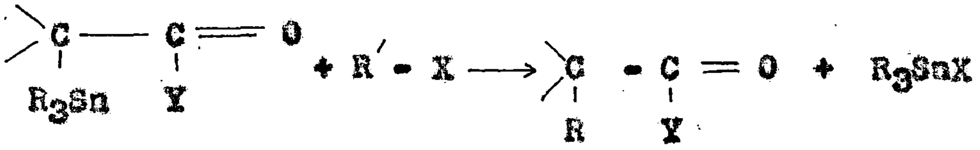
Triethylstammyl acetone (44) reacts very fast with iodine in polar solvents (like methanol, DMSO) is probably SE^1 reaction, but is not confirmed



$$Et_3Sn-CH_2COCH_3 + S \rightarrow Et_3\overset{(-)}{\underset{(S(+)}{Sn}}-CH_2COCH_3 \xrightarrow[det]{rate} Et_3SnS^{+} + -CH_2COCH_3$$

(40)

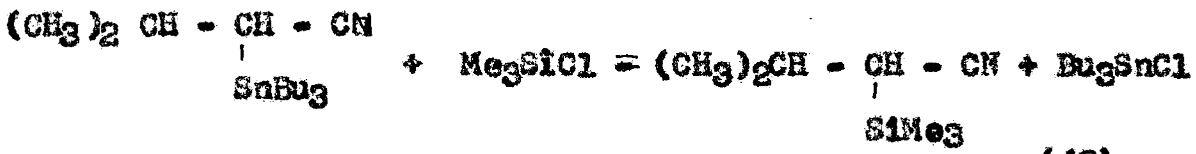
The high reactivity of α - functionally substituted organotin compounds could be ascribed also to a possible monomolecular mechanism. Trialkylstannylacetone or the corresponding ester or nitrile react with poorly electrophilic reagents such as benzyl-halides



(41)

Y = CH_3 or OR''

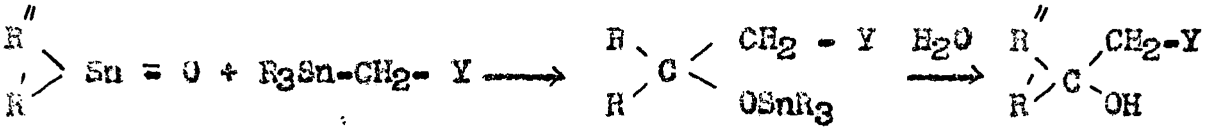
or with trimethyl silicon chloride (61) :



$$(CH_3)_2CH-\underset{SnBu_3}{CH}-CN + Me_3SiCl = (CH_3)_2CH-\underset{SiMe_3}{CH}-CN + Bu_3SnCl$$

(42)

Reformatsky - type reactions can also be made with those derivatives showing that aldehydes and ketones are electrophilic enough to cleave the C - Sn bonds of these functionally substituted organotin derivatives. The formation of corresponding β- triorganostannoxy derivatives :



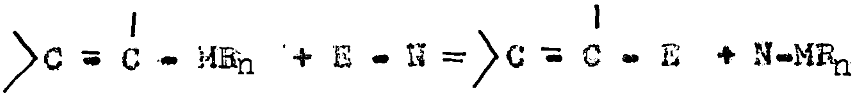
(43)

is almost quantitative and the products formed are very pure. This is therefore, an especially facile organometallic method of functional chain extension (52).

IIB. Unsymmetrical vinylic and acetylenic derivatives :

a) Electrophilic substitution at an olefinic carbon atom

1) Stereochemistry of bimolecular electrophilic substitution reactions at an olefinic carbon atom : retention of configuration : The reaction of the type :



$$>C=\overset{|}{C}-MR_n + E-N = >C=\overset{|}{C}-E + N-MR_n \qquad (44)$$

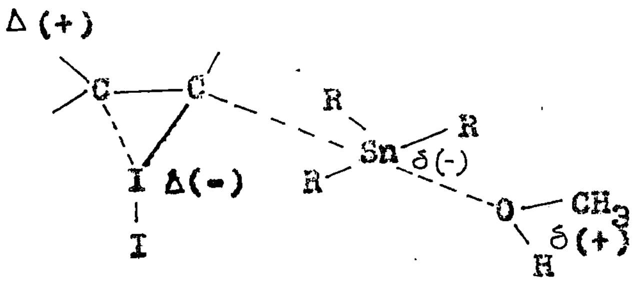
Occurs generally with retention of configuration, in agreement with the rule stated in 1948 by Nesmeyanov and Borisov (53).

Cis-or trans-dipropenyltin dichloride react with HgX_2 to give pure cis-or trans-propenyl-mercury chloride respectively (53).

Tetrapropnyltin also reats with retention of configuration with butyllithium (54) and phenyllithium (55).

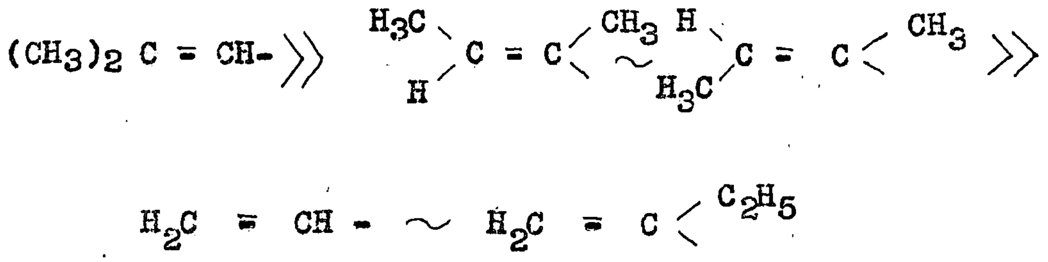
Cis-or trans - 2 - butenyltrimethyltin react with iodine in methanol also with retention of configuration (30).

(ii) Mechanism of bimolecular electrophilic substitution at an olefinic carbon atom : The rates of reaction of a series of vinylic organotin compounds with iodine suggests that the transition state must bear a rather localised positive charge centered around the -carbon atom. A fully dipolar structure involving a complete breakdown of the bond should be disregarded since this would lead to free rotation around the central C - C bond. A highly polar transition state :



is suggested (30) in order to interpret the reactivity sequences (a) and (b) :

(a)



$$(CH_3)_2C=CH- \gg \begin{matrix}H_3C\\ H\end{matrix}\!>\!C=C\!<\!CH_3 \sim \begin{matrix}H\\ H_3C\end{matrix}\!>\!C=C\!<\!CH_3 \gg H_2C=CH- \sim H_2C=C\!<\!C_2H_5$$

(b) $R = CH_3 \sim C_2H_5 > nC_4H_9 > iso\ C_3H_7$

and the observed salt effect and the retention of configuration of vinyl group.

(b) Electrophilic substitution at an acetylenic C atom : The high polarity of alkynyl - tin bonds facilitates both electrophilic attack at the carbon atom and nucleophilic attack on the tin atom (56 - 58) making $Sn - C \equiv C -$ bonds extremely labile. Thus Cu^{++} and Ag^{+} break $Sn - C \equiv C$ bonds (56) while $R_3Sn - C \equiv C - CH_2 - CH_2 - O - CH = CH_2$ reacts easily with butanol with the cleavage of $Sn - C \equiv C$ bond (58).

$Cl - C \equiv C - SnMe$ reacts instantaneously with water (59). Tricyclohexyltin halides are electrophilic enough to cleave the acetylenic carbon - tin bonds of bis- (trimethyl stannyl) butadiyne (60 - 62). Bromine cleaves diethyl (triethyl - stannyl ethynyl) phosphonate $Et_3Sn - C\equiv C - P(O)(OEt)_2$ (58). Aldehydes and ketones are able to cleave the Sn - C bond of $C_6H_5 - C\equiv C - SnEt_3$. Chloral (63) and cyclohexanone (64) also react with these compounds.

In the presence of bases, $R_3Sn - C\equiv C - CH_3$ is isomerized into the allenic and propergylic compounds (65).

$$R_3Sn - C\equiv C - CH_3 \xrightleftharpoons{B} R_3Sn - CH=C=CH_2 \xrightleftharpoons{B} R_3Sn - CH_2 - C\equiv CH \qquad (45)$$

IIF. Unsymmetrical aromatic derivatives

As would be expected from bond polarity aryl - tin bond is more reactive than alkyl - tin bond consequently aryl - tin bond is first to be broken whenever both types of groups are bonded to tin (1).

It has been found that dry HCl in methanol or even in benzene, cleaves only one aryl group (44), whereas halogenation has to be carefully controlled to achieve the same result (33). The most general sequence for electrophilic Sn - C bond c~~e~~leavage is thus :

allyl ≫ aryl, vinyl > alkyl.

However, free radical and alkyl or aryllithum induced cleavage (44) may follow other sequences.

It should be stressed that no reaction involving C - Sn bond cleavage could reasonably be regarded either as a purely electrophilic substitution at the carbon atom or as a nucleophilic displacement at the tin atom. Kinetic studies can, however, be used to determine whether a given reaction is closer to an electrophilic substitution or a nucleophilic displacement.

Where kinetic or mechanistic studies are not available, the situation is obscure and no decision can be reached, as in the insertion reactions of S or Se in a carbon - tin bond of tetraphenyltin (40 - 42) or in the pyrolytic bimolecular elimination of trimethyl iodide from iodobenzene and hindered phenyltrimethyltins (68).

a) Electrophilic substitution at an aromatic C atom. Aryl' trialkyltins have been cleaved under a variety of conditions, and kienetic results are available for iodine in carbon tetrachloride (69), in methanol (70 - 74), in chlorobenzene and cyclohexane (44), for HCl (76) and bromine (77) in methanol, for $HClO_4$ in methanol - water (78 - 79), for mercurie acetate in tetrahydrofuran (80) and for the solvolysis in acetic acid (81). Iododestannylation in nonpolar solvents like carbon tetrachloride, cyclohexane etc. is second order with respect to the electrophile, the cleavage is therefore believed to occur by participation, in the rate determining step, of iodine - aryl stannane complex with a second iodine molecule (69). The second iodine molecule probably acts as a nucleophile on the tin atom since very small amount of methanol added to cyclohexane strongly increases the rate and progressively restore a first order reaction with respect to halogen (44). Despite this a reasonably good correlation between the rates and substitution constants (69) has been observed. With mercuric acetate in THF (80) there is linear correlation of log ($^{K}/Ko$ Vs σ rather than σ^{+} as in classical aromatic substitution, suggesting that a localised σ complex is a poor approximation to the true transition state. On the other hand, halodemetallation in more polar solvents like methanol and acetic acid is strictly first order with respect to the electrophile; the cleavage can be regarded as a simple aromatic substitution. The rate constants also reasonably correlate with σ^{+} substituent constants.

The rate of cleavage is also affected by the size of the leaving group, the rate being decreased as the size of the alkyl group increases (71). This has been attributed to a steric inhibition opposing the attack by the entering electrophile (73). Ortho effects show up as a delicate balance between retardation of electrophilic attack and acceleration by steric decompression :

when the leaving group is - $Sn(CH_3)_3$, two orthomethyl groups have no special influence at all, but with bulkier - $Sn(n\ C_3H_7)_3$ group, the two ortho methyls induce a slight rate enhancement because of the relief of the overcrowding in the starting material (74). This steric acceleration is, however, much less pronounced here than in the case of analogous silicon compounds (83,84), the difference between Si and Sn derivatives is due to longer C - Sn bond which holds the interacting groups further apart. Because of its negligible effect on the electronic properties of the aromatic systems (72,86 - 87) trialkyltin group may be used to study electrophilic substitution on the aromatic carbon atom.

Though mechanistic or kinetic studies are not available many other electrophilic substitutions, such as the redistribution with tin tetrahalides (88 - 89), reaction with $C_6H_5PCl_2$ (90), BCl_3(88) or BBr_3 (91) have found interesting synthetic uses.

b) Nucleophilic displacement at the tin atom.

Substituted phenyltrimethyltins react with sodium methoxide in methanol to yield trimethyltin methoxide and the corresponding substituted benzene. The kinetics of this reaction have been studied by Eaborn (92), the substituent effects roughly parallel the results for the base catalysed hydrogen exchange reaction in aromatic hydrocarbons, suggesting that the transition states bear some resemblance to analogous phenyl carbanions.

Perhalo aryltins undergo facile base catalysed cleavages. Thus $(C_6F_5)_4Sn$ is cleaved by KOH as easily as by HCl (93); $C_6F_5Sn(CH_3)_3$ solvolyzes in aqueous methanol, but a trace of acid completely inhibits the reaction (94); crystallization of $C_6H_5Sn(CH_3)_3$ in ethanol containg some KF gives pentafluorobenzene and trimethyl tin fluoride (95).

Reactions of phenyl tin chlorides with chelating agents such as 8-hydroxyquinoline etc. in DMSO (18,96-97,26) at elevated temperatures in which Benzene is formed through tin-phenyl bond cleavage probably proceed through nucleophillic attach at the tin. Other examples include the cleavage of carboranyl - tin bond by KOH (32), or the very fast solvolysis of 2-pyridyltrimethyl tin in hydroxylic solvents (85).

Bis (triphenyl tin) oxide, when stirred with CdI_2 in diethyl ether, slowly breaks into polymeric diphenyl stannoxane, $(Ph_2SnO)_x$, and benzene (75), apparently by the action of water present in the solvent. Interestingly, CdI_2 does not take part in the overall reaction. This reaction probably goes through a nucleophilic attack by water at the tin atom which may be rendered sufficiently electronegative through withdrawal of electron density by the formation of complex of the type $(Ph_3Sn)_2O - CdI_2$. This is supported by the fact that similar cleavage cannot be induced by CdI_2 in triphenyl tin oxinate or triphenyl tin carboxylates (82) which contain already pentaco-ordinated tin atom.

As would be expected nucleophilic displacement at the tin atom is facilitated by electron withdrawing group. The reactivity sequence for the nucleophilic attack is :

Ethynyl, fluorenyl $>$ aryl $>$ saturated alkyl.

On the basis of preceding discussion the following generalisation may be made concerning the reactivity of tin-carbon bond :

(1) The reactivity of the tin-carbon bond increases with its polarity. Since the polarity is dependent on the hybridisation of the bonded carbon atom, the reactivity sequence is :

$$C(SP) - Sn > C(SP^2) - Sn > C(SP^3) - Sn.$$

(2) The mechanism of electrophilic destannylation is strongly influenced by the solvent - polarity. Highly polar solvents like methanol and acetic acid favour the formation of open transition state (S_E2) and the reaction generally proceeds through inversion

of configuration at the carbon atom, while nonpolar or weakly polar media generally favour the formation of cyclic transition state (SF^{2} or SE^{i}), retention of configuration being the normal feature.

(3) The reactivity sequence for destannylation in methanol or acetic acid for the group R in $R'_{3}SnR$ is $R = Me > Et > Bu \sim Pr > i - Pr > t - Bu$. High degree of selectivity is possible in these solvents and may be therefore used for the synthesis of unsymmetrical tin derivatives.

(4) No definite reactivity sequence exists for nonpolar solvents; usually the rate constants lie close together resulting in a very poor selectivity for the alkyl groups.

(5) Under favourable conditions tin-carbon bond cleavage through nucleophilic displacement at the tin atom may also occure, but it is less common than electrophilic substitution at the carbon atom. The nucleophilic attack at the tin atom is facilitated by electron withdrawing groups.

On the basis of "isolated molecule approximation", Majee and Gupta has proposed two theoretical reactivity parameters, viz; the

Z - index and bond polarisability index (66,9899) for the interpretation and correlation of the reactivity of organometallic compounds. The experimental rate constants in a large number of cases have been shown to corretale fairly well with their calculated reactivity indices. The effect of C - M (M = Si, Ge, Sn, Pb) bond energy on its reactivity and the large spread in rate constants have also been interpreted by Majee. In a more recent study Majee has proposed a new approach to the interpretation of the metal-carbon bond cleavage reactions using the concept of isovalent hybridisation which is capable of explaining almost all the experimental features including stereochemistry at the reaction centre (67).

BIBLIOGRAPHY

1. Ingham, R.K.Rosenberg,S.D. and Gilman, H. Chem.Rev. 1960,60,479

2. Zimmer,H and Miller, J.J. Natur Wissens Chaften, 1966,53,38.

3. Gielen,M. and Nasielski,J. J.Organometal,Chem. 1963,1,173.

4. Gilen, M and Nasielski, J. J.Organometall.Chem. 1967,7,273.

5. Boue',S.,M.Gielen and Nasielski, J. J.Organometal.Chem. 9,443 (1967).

6. M.Gielen,J.Nasielski and J.Topart, Rec.Trav.Chim.87,1051(1968).

7. K.C.Bass, Lab.Practice,14,47(1965).

8. K.C.Bass,, Lab.Practice,14,145(1965).

9. H.Noth and H.Vahrenkamp, J.Organometal.Chem., 11,399 (1968).

10. V.F.Mironov and A.L. Kravchenko, Zhur.Obshchei Khim., 34,1356 (1964); J.Gen.Chem. USSR, 34,1359 (1964).

11. P.M.Treichel and R.A. Goodrich Inorg.Chem,4,1424(1965)

12. G.Tagliavini,G.Pilloni, and G.Plazzogna, Ric.Sci.,36, 114(1966).

13. C.Deblandre,M.Gielen and J.Nasielski, Bull.Soc.Chim.Belges, 73,214(1964)

14. M.Dao-Huy-GiaO, Compt.Rend,260C,6937(1965)

15. G.A.Razuvaev,N.S.Vyazankin, Y.I.Dergunov and E.N.Gladyshev, Izv.,848(1964); Bull.Acad.Sci.USSR, Div.Chem.Sci.,794(1964)

16. S.Boue', M.Gielen and J. Nasielski J.Organometal.Chem, 9,461(1967)

17. M.Gielen and J.Nasielski J.Organometal.Chem. 1,173(1963).

18. W.H.Nelson, and D.F.Martin, J.Inorg.Nucl.Chem., 27,89(1965).

19. M.H.Abraham and J.A.Hill, J.Organometal.Chem., 7,11(1967).

20. M.H.Abraham and T.R.Spalding, Chem.Commun., 46(1968).

21. C.Deblandre,M.Gielen and J.Nasielski, Bull.Soc,Chim. Belges., 73,214(1964).

22. S.Boue', M.Gielen and J.Nasielski J.Organometal.Chem., 9,481(1967)

23. M.Gielen and J.Nasielski Rec.Trav,Chim, pays-Bas,82,228(1963)

24. J.C.Jungers,L.Sajus,I. de Aguirre and D.Decroocq, Rev.Inst.France Petrole, 21,342(1966)

25. M.Gielen and J.Nasielski, J.Organometal.Chem., 7,273(1967)

26. W.H.Nelson, and D.F.Martin, J.Organometal.Chem. 4,67(1965)

27. A.V.Savitskii and Y.K. Syrkin, Dokl,Phys.Chem., 146,700(1962).

28. G.A.Razuvaev,N.S.Vyazankin and O.A.Shchepetkova, Tetrahedron.,18,667(1962).

29. G.A.Razuvaev,N.S.Vyazankin, E.N.Gladyshev and I.A.Borodavko, Zhur.Obshchei Khim., 32,2154(1962).

30. P.Baekelmaus,M.Gielen, P.Malfroid and J.Nasielski Bull.Soc.Chim.Belges, 77,85(1968)

31. L.K.Luneva, Usp.Khim., 36,1140(1967); Russ.Chem.Rev.,36,467(1967); through CA,68.21975R(1968).

32. V.I.Bregadze and O.Y.Okhlobystin, Izu.Akad,Nauk.SSSR. Ser Khim., 2084(1967)

33. M.LeQuan, Compt.Rend., 226C,832(1968)

34. R.W.Weiss, Organometallic Compounds — Method of synthesis,Physical Constants and Chemical Reaction (M.Dub,ed.) Vol II: Compounds of Ge,Sn and Pb including biological activity and commercial application, Springer Verlag, New York. 1967, 2nd ed.

35. J.M.Holmes, R.D.Peacock J.C.Tatlow, Proc.Chem.Soc., 108(1963).

36. E.J.Kupchik, J.A.Ursino and P.R.Bond Jouk, J.Organometal.Chem., 10,269(1967).

37. J.C.Maire, J.Organometal.Chem., 9,271(1967).

38. J.L.Wardell, J.Organometal.Chem., 9,89(1967)

39. J.L.Wardell J.Organometal.Chem., 10,53(1967)

40. M.Schmidt, H.J.Dersin and H.Schumaun, Chem.Ber., 95,1428 (1962).

41. M.Schmidt and H.Schumann, Chem.Ber., 96,462(1963).

42. M.Schmidt and H.Schumann, Chem.Ber., 96,780(1963).

43. S.Boue', M.Gielen and J. Nasielski Tetrahedron Letters., 1047(1968).

44. M.Gielen and J.Nasielski Organo tin compounds with Sn - C bonds, Organo tin compounds, Vol III, edited by A.K.Sawyer, Mercel Dekker, Inc., New York, 1972.

45. F.R.Jensen and D.D.Davis J.Am.Chem.Soc., 93(1971)4047,4048.

46. P.Backelmans, M.Gielen and J.Nasielski, Tetrahedron Letters., 1149(1967)

47. K.Sisido, S.Kozima and K.Takizawa, Tetrahedon Letters, 33(1967)

48. H.C.Brown and C.F.Lane, Chem.Comm(1971),521

49. R.W.Bott, C.Eaborn and T.W. Swaddle, J.Chem.Soc.,2342(1963)

50. M.Gielen Accounts of Chemical research (1973)

51. M.Pereyre, G.Colin and J.Valade, Compt.Rend.,264C,1204 (1967)

52. J.G.Joltes,H.M.J.C. Creemers and G.J.M. Vander Kerk J.Organometal.Chem., 11,P21(1968)

53. A.N.Nesmeyanov and A.E. Borisov, Tetrahedron., 1,158(1957)

54. D.Seyferth J.Organometal.Chem., 1,201(1964).

55. D.Seyferth and L.G. Vanghan J.Am.Chem.Soc.,86,883(1964).

56. L.K.Luneva, Usp.Khim., 36,1140(1967); Russ.Chem.Rev.,36,467(1967); through CA,68,21975R(1968).

57. V.M.Vlasov,R.G.Mirskov and V.N.Petrova, Zhur.Obshchei Khim., 37,954(1967);J.Gen.Chem. USSR,37,902(1967) through CA,68,13114U(1968).

58. V.S.Zavgorodnii, B.I. Ionin and A.A.Petrov, Zhur.Obshchei Khim., 37,949(1967); J.Gen.Chem. USSR, 37,898(1967).

59. W.Steingross and W.Zeil, J.Organometal.Chem., 6,109(1966).

60. H.Hartmann, B.Karbstein and W.Reiss, Naturwiss., 52,59(1965).

61. H.Hartmann and K.Meyer, Naturwiss.,52,303(1965).

62. H.Hartmann and M.K.el Assam, Naturwiss., 52,304(1965)

63. A.G.Mirskov and V.M.Vlasov, Zhur.Obshchei Khim., 36,562(1966); through CA,65,744B(1966).

64. K.Konig and W.P.Neumann, Tetrahedron Letters, 495(1967).

65. G.Pourcelot, M.Le-Quan,W. Chodkiewiez and P.Cadiot, XIXth IUPAC Congress, London, 1963, Abstr.A.P.177.

66. R.Gupta and B.Majee, J.Organometal chem., 40(1972)107.

67. B.Majee, Rev.Si,Ge,Sn and Pb compounds (Freund)2,1(1975)

68. D.Seyferth and A.B.Evnin, J.Am.Chem.Soc., 89,1468(1967).

69. R.W.Bott,C.Eaborn and J.A.Waters J.Chem.Soc.,681(1963).

70. O.Buchman, M.Grosjean and J.Nasielski, Helv.Chim.Acta., 47,1679(1964).

71. O.Buchman, M.Grosjean, J.Nasielski and B.Wilmet-Devos, Helv.Chim.Acta,47,1688(1964).

72. O.Buchman, M.Grosjean, J.Nasielski, Helv.Chim.Acta, 47,2037(1964)

73. J.Nasielski, M.Grosjean, O.Buchman and E.Hannecart, Bull.Soc.Chim,Belges., 77,15(1968).

74. J.Nasielski, O.Buchman,. M.Grosjean,J.J.Schurter and G.Vadendunghen, Bull.Soc.Chim.Belges, 77,349(1968).

75. D.Dutta Ph.D.Thesis, North Bengal University, India

76. O.Buchman, M.Grosjean and J.Nasielski Helv.Chim.Acta., 47,1695(1964)

77. C.Alcais and J.Nasielski J.Chim.Phys.,66,95(1969).

78. R.W.Bott, C.Eaborn and D.R.M.Walton J.Organometal.Chem., 2,154(1964).

79. C.Eaborn, J.A.Waters J.Chem.Soc., 542(1961).

80. H.Hashimoto, and Y. Marimoto J.Organometal.Chem., 8,271(1967).

81. J.Nasielski, O.Buchman, M. Grosjean, and M.Jauquet, J.Organometal.Chem., 19,353 (1969).

82. A.Roy, Ph.D. Thesis, North Bengal University, India.

83. R.A.Benkeser, R.A.Hickner, D.I.Hoke and D.H.Thomas, J.Am.Chem.Soc.,80,5294(1958).

84. C.Eaborn, and R.C.Moore J.Chem.Soc., C,1364(1967).

85. D.G.Anderson, M.A.M.Bradney, B.A.Loveland, and D.E.Webster, Chem.Ind., 505(1964).

86. D.G.Anderson, J.R.Chipperfield, and D.E.Webster J.Organometal.Chem., 12,323(1968).

87. J.Chatt, and A.A.Williams, J.Chem-Soc., 4403(1954).

88. T.Chivers, and B.David, J.Organometal.Chem., 10,P35(1967).

89. E.J.Kupchik, J.A.Ursino, and P.R.Bondjouk, J.Organometal.Chem., 10,269(1967)

90. E.J.Kupchik, and V.A. Pericante, J.Organometal.Chem., 10,181(1967).

91. J.L.W.Pohlmann, F.E. Bruikmann, G.Tesi, and R.E.Donadio, Z.Naturforsch., 20B, 1(1966)

92. C. Eaborn, H.L.Hornfeld, and D.R.M.Walton, J.Chem.Soc.,B,1036(1967).

93. C.Tamborski, E.J.Soloski, And S.M.Dec, J.Organometal.Chem., 4,446(1965)

94. C.Eaborn, J.A.Treverton, D.R.M.Walton, J.Organometal.Chem., 9,259(1967).

95. T.Chivers, and B.David, J.Organometal.Chem., 13,177(1968).

96. D.F.Martin, P.C.Mabury, and R.D.Walton, J.Organometal.Chem., 7,362(1967)

97. D.F.Martin, and R.D.Walton, J.Organometal.Chem., 5,57(1966).

98. R.Gupta and B.Majee, J.Organometal Chem., 49(1973)191.

99. R.Gupta and B.Majee J.Organometal.Chem., 49(1973)197.

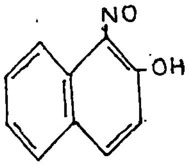
CHAPTER - III

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

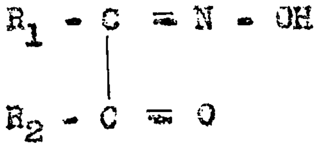
Introduction :

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



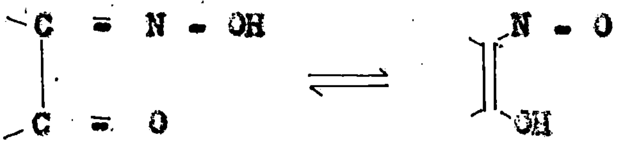
I



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

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 :

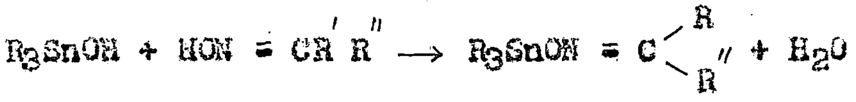
(i) By the reaction of the sodium or lithium salts of oximes with organotin halides (20 - 22) :

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

(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) :



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

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).

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

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

C. Organotin derivatives of N - benzoyl hydroxylamines :

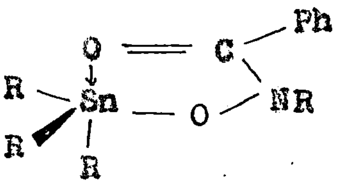
In addition to the organotin hydroxylamines a few O-triorganotin N-benzoyl hydroxylamines have also been reported (30) : These are :

$R_3SnONHCOPh$ (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 :



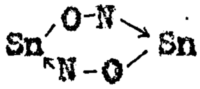
(IV)

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.

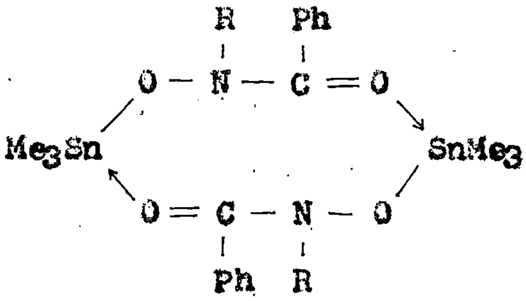
Diorganotin diethyl hydroxylamines of the type $Bu_2Sn(OR)(ONE^{t})_2$ (R = E^{t}, iPr) are reported to give molecular association ~ 3·0 in boiling benzene. The association of these derivatives is thought to be more likely through the SnONSnON ring. The presence of Sn - O - N bond has been established 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

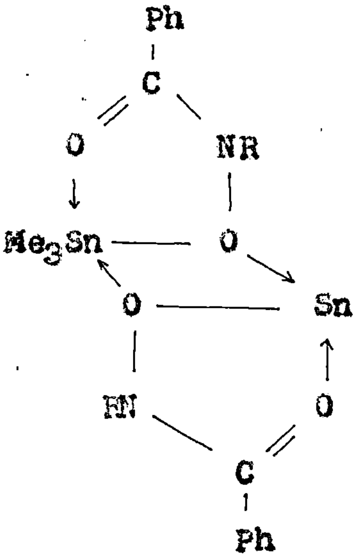
$(CH_3)_3$ SnONHCOPh shows some association via hydrogen bonding.

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 = O stretching frequency from 1620 cm^{-1} in the parent hydroxylamine to 1540 cm^{-1} in the O-triphenyl derivatives.

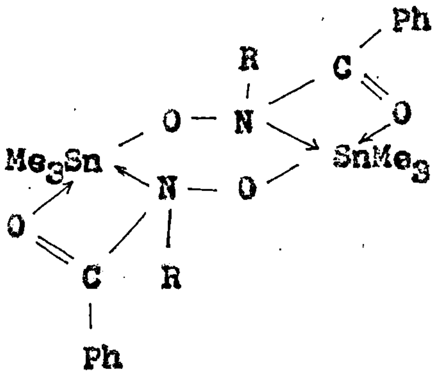
Though $Ph_3SnONPhCOPh$ is monomeric, the corresponding methyl derivative is associated in the solid state into dimeric species which may have the following structures :



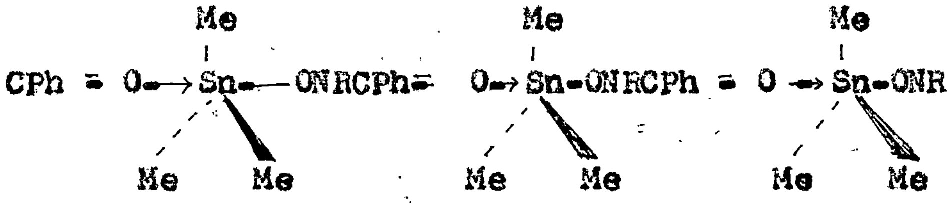
(A)



(B)



(C)

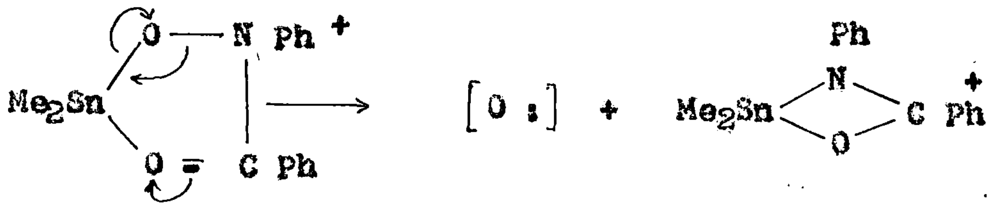


$$\mathrm{CPh = O \rightarrow \underset{Me\ \ Me}{\overset{Me}{Sn}} - ONRCPh = O \rightarrow \underset{Me\ \ Me}{\overset{Me}{Sn}} - ONRCPh = O \rightarrow \underset{Me\ \ Me}{\overset{Me}{Sn}} - ONR}$$

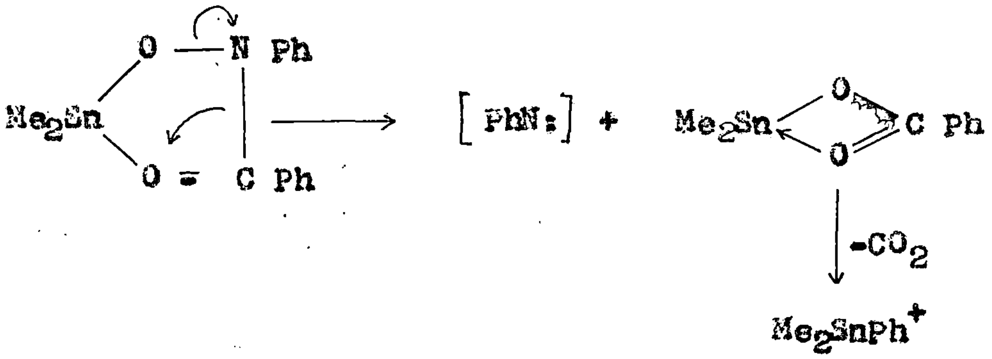
(D)

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).

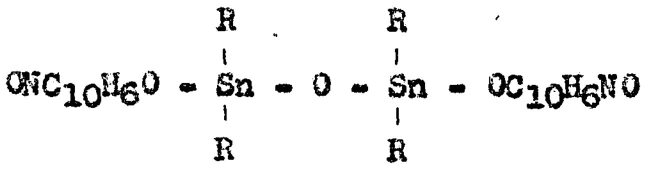
IR spectra (33) of these compounds show a lowering of ν(C = O) stretching frequency from 1620 cm^{-1} in the parent hydroxylamine HONPhCOPh to 1540 - 1557 cm^{-1} in the compounds of the type $R_3SnONPhCOPh$.

The hydroxylamine HONHCOPh gives two bands for ν(C = O), 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.

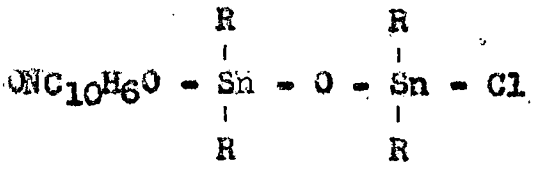
E. Objective and scope of the present work :

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.



$$ONC_{10}H_6O - \overset{R}{\underset{R}{Sn}} - O - \overset{R}{\underset{R}{Sn}} - OC_{10}H_6NO$$

$[R - CH_3-, C_2H_5 -]$



$$ONC_{10}H_6O - \overset{R}{\underset{R}{Sn}} - O - \overset{R}{\underset{R}{Sn}} - Cl$$

$[R - nC_3H_7-, nC_4H_{10}-]$

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.

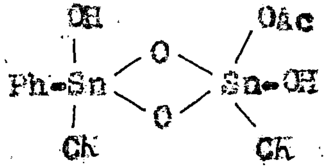
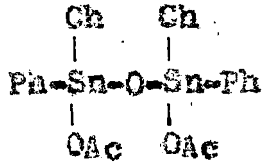
Tri organo tin compounds	Mole ratio Triorgano tin compounds/Ligands	Conciditon used	Nature of the Products			Analysis found (Calculated for)%				The products and their probable structures
			Colour	mp/Decomposition point °C	Solubility	C	H	N	Sn	
Ph_3SnOAC	1 : 1 (a slight excess of the ligand was used)	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 (2.23)	26.92 (27.35)	 $Ph-\underset{OAc}{\overset{Ch}{Sn}}-O-\underset{OAc}{\overset{Ch}{Sn}}-Ph$

Table- 1 Contd.

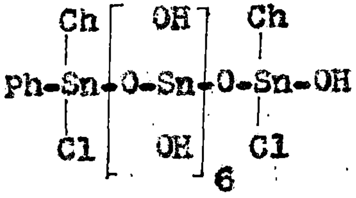
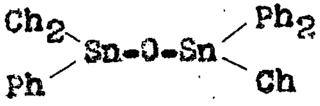
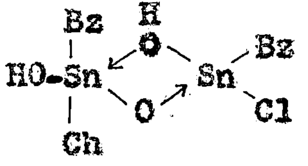
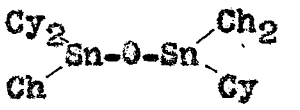
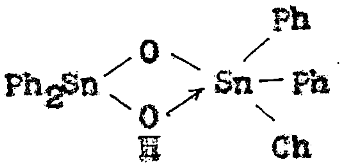
Tri organo tin compounds	Mole ratio Triorgano tin compounds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					The products and their probable structures
			Colour	mp/ Decomposition point °C	Solubility	C	H	N	Cl	Sn	
			D)Green	>360°	Sparingly soluble in common solvents.	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 hours 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)	 $\mathrm{Ph-\overset{Ch}{\underset{Cl}{Sn}}-\left[O-\overset{OH}{\underset{OH}{Sn}}\right]_6-O-\overset{Ch}{\underset{Cl}{Sn}}-OH}$
			B)Green	>360°	Sparingly soluble in common solvents	58.72 (57.6)	3.03 (3.3)	4.48 (4.2)		24.00 (23.7)	 $\mathrm{(Ch_2)(Ph)Sn-O-Sn(Ph_2)(Ch)}$

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°	Fairly soluble in benzene and alcohol	50.01 (50.62)	3.02 (2.75)	5.19 (5.14)		22.3 (21.77)	$\mathrm{PhSnch_2(Cl).}$ $\mathrm{Sn(Ch_2)\ (Cl)\ OH}$ Or
						(49.79)	(2.89)	(5.05)		(21.42)	$\mathrm{PhSnch_2(Cl).}$ $\mathrm{Sn(Ch_2)\ Cl\ OH,\ H_2O}$

[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.

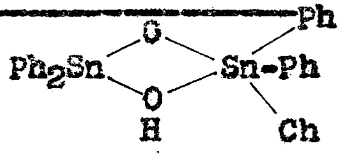
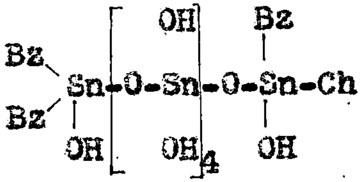
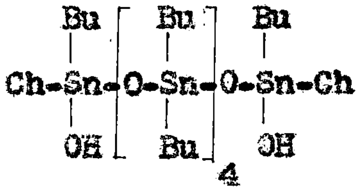
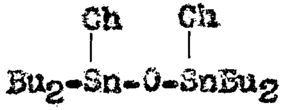
Tri organo tin compounds	Mole ratio Triorgano tin compouds / ligands	Condition used	Nature of the Products			Analysis found (Calculated for) %					The products and their probable structures
			Colour	mp/ Decomposition point °C	Solubility	C	H	N	Cl	Sn	
Ph_3SnCl	1 : 1	Refluxes for 2 hours in Methanol	Yellow	160^{od}	Moderately soluble in common solvents	53.87 (54.37)	3.68 (3.60)			30.92 (31.64)	
Bz_3SnCl	1 : 1 (a slight excess of ligand was used)	Refluxed for 2 hours in methanol	Green	>360°	Insoluble in common solvents sparingly soluble in pyridine	26.71 (26.44)	2,67 (2.63)	1.03 (0.99)		49.24 (50.6)	 $\mathrm{Bz_2Sn(OH)\text{-}[O\text{-}Sn(OH)_2]_4\text{-}O\text{-}Sn(Bz)(OH)\text{-}Ch}$

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_3SnCl	1 : 1	Refluxed for 2 hours in methanol	A)Green	$>360^\circ$	moderately soluble in common solvents	41.85 (41.37)	6.32 (5.98)			39.61 (40.92)	 $Ch-\underset{OH}{\overset{Bu}{Sn}}-\left[O-\underset{Bu}{\overset{Bu}{Sn}}-\right]_4 O-\underset{OH}{\overset{Bu}{Sn}}-Ch$
			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)	 $Bu_2-\overset{Ch}{Sn}-O-\overset{Ch}{Sn}Bu_2$

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

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

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_3SnOAc	Diacetyl mono-oxime	1 : 1 Refluxed for 7 hours in benzene	A)While	>360°	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

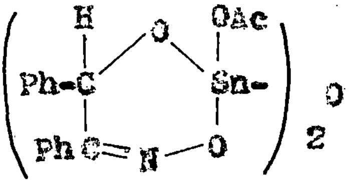
Triorgano tin compounds	Legands	Mole ratio $\frac{\text{triorganotin compounds}}{\text{ligands}}$	Nature of the Products			Analysis found(Calculated for)%				Products and their probable structures.
			Colour	m.p/ Dcomposition point °C	Solubility	C	H	N	Sn	
Ph_3SnOAc	α-benzil oxime	1 : 1 (a slight excess 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.

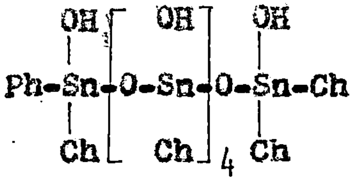
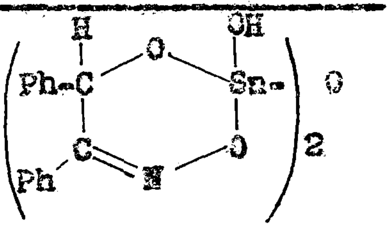
Triorgano tin compounds	Legands	Mole ratio triorganotin compounds / ligands	Nature of the Products			Analysis found(Calculated for)%				Products and their probable structures.
			Colour	M.p/ Decomposition point °C	Solubility	C	H	N	Sn	
Ph_3SnCl	Diacetyl mono oxime	1 : 1 (a slight excess of ligand was 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)	 $\mathrm{Ph{-}\overset{OH}{\underset{Ch}{Sn}}{-}\left[O{-}\overset{OH}{\underset{Ch}{Sn}}\right]_4{-}O{-}\overset{OH}{\underset{Ch}{Sn}}{-}Ch}$ $[Ch = (CH_3)_2COCNO-]$
Ph_3SnCl	α-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: Colour	m.p/ Dcomposition point	Solubility	Analysis found(Calculated for)%: C	H	N	Sn	Products and their probable structures.
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.

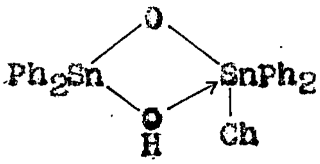
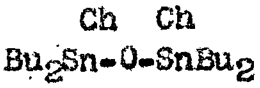
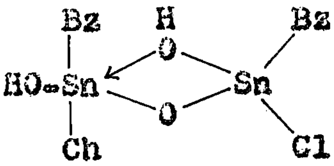
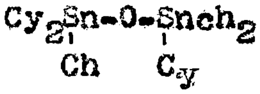
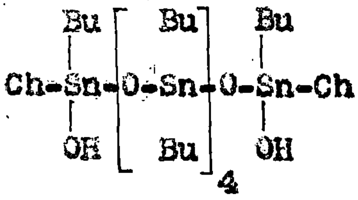
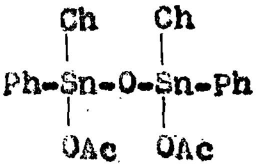
Compound Formula (Colour)	Solvent	λ max in nm
Potassium-1-nitroso-2-napthoxide. (Green)	Methanol	215, 261, 370
	Concentrated solution in Methanol	605
	Methanol	215, 260, 370
	CCl_4	[illegible] 275, 377
(Yellow)	MeOH/NaOH	260(inflex), 292, 374, 420
 $\overset{Ch}{Bu_2Sn}-O-\overset{Ch}{SnBu_2}$	Methanol	223, 280(Sh),330(Sh)
(Brown).	DMSO	280, 330(Sh)
 (Greenish Yellow)	Methanol	233, 280, 330

Table-IV Contd.

Compound Formula (Colour)	Solvent	λmax in nm.
 $\underset{Ch}{Cy_2Sn}-O-\underset{Cy}{SnCh_2}$	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 $C_6H_{11}-$;

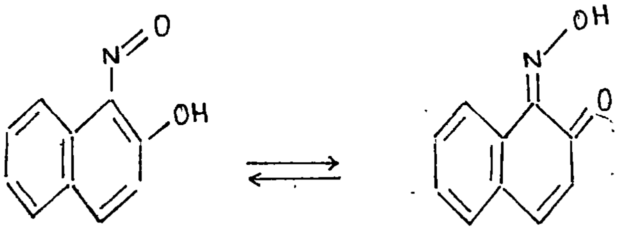
Ch = $-OC_{10}H_6NO$.

(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 :

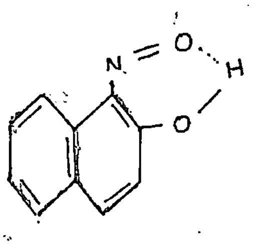
a) General :

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 :

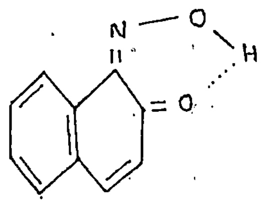


(V) (VI)

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)

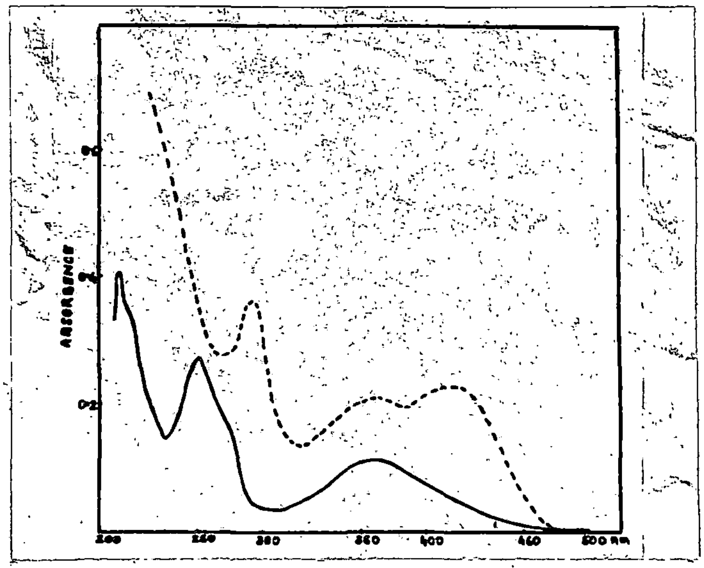


Figure - 1 : Electronic absorption spectra of 1-nitroso-2-napthol in

Methanol: ————————

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

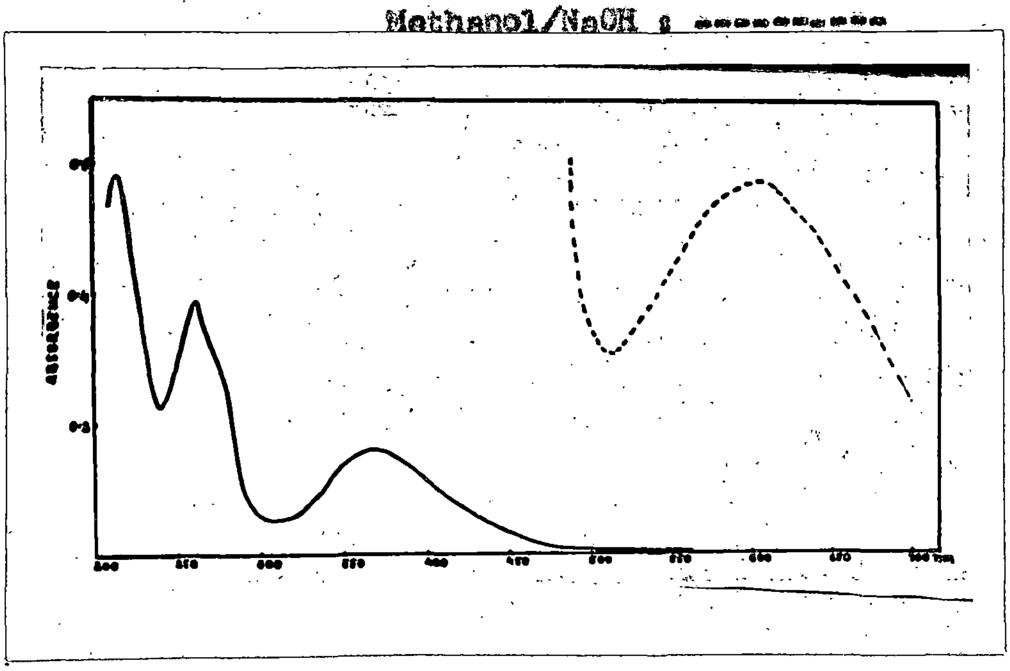


Figure - 2 : Electronic absorption spectra of potassium 1-nitroso-2-napthoxide in

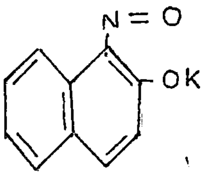
Methanol :————————

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)

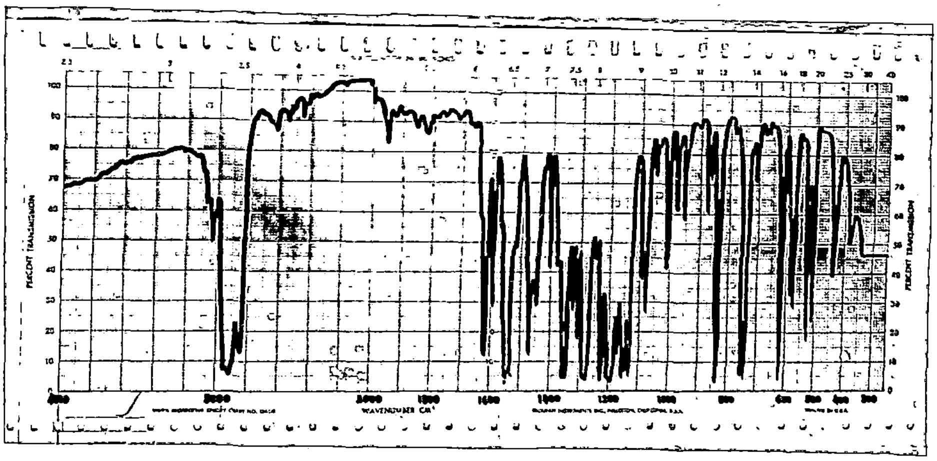


Figure - 3 : Infra red spectrum of potasium 1-nitroso-2-napthoxide

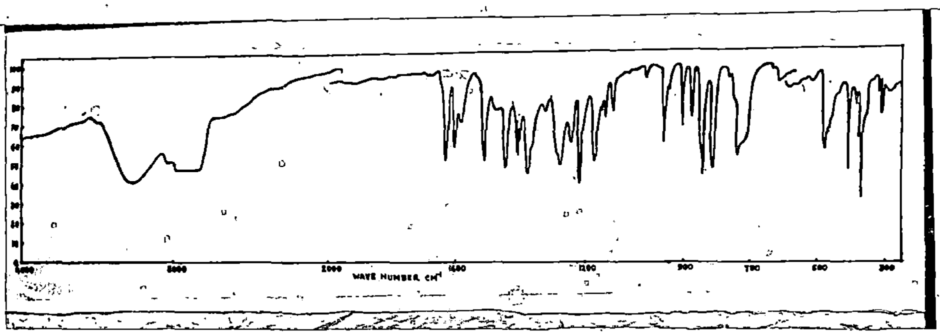


Figure - 4 : Infra red spectrum of 2-napthol

The IR spectra of the potassium derivative (figure-3) shows a 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 = 0). 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 = 0) by Mehrotra 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 = 0) by 30 - 40 cm^{-1} may not be unreasonable if conjugation of the N = 0 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.

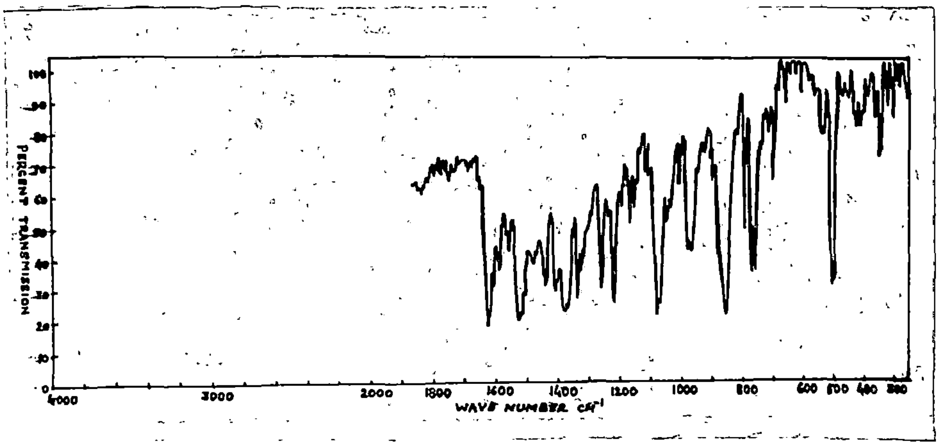


Figure - 5 : Infra red spectrum of 1-nitroso-2-napthol

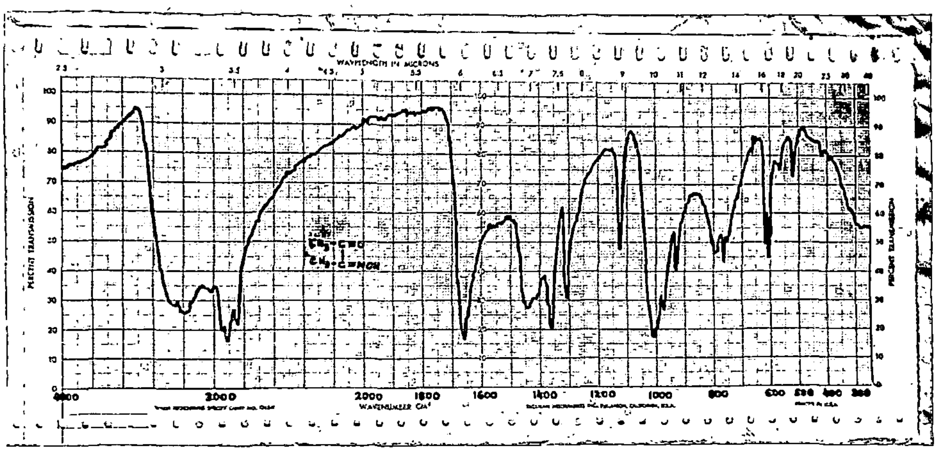
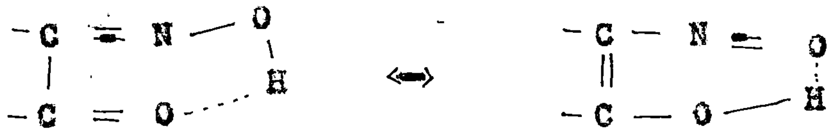


Figure - 6 : Infra red spectrum of diacetyl mono oxime

(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.

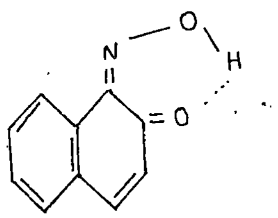
Table - VII

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)	1606 (ms)	1595 (ms)	
1580 (ms)	1586 (ms)		
	1555 (w)		ν(C = 0 + C = N)
		1550	ν(N = 0)
		1540	
	1525 (s)		ν(C = 0 + C = N)
1510 (s)	1508 (ms)	1520 (ms)	Ring
1365 (ms)			δ(OH)
1270 (s,br)		1195 (s,br)	ν(C - 0)
	1070 (s)		ν(N - 0)

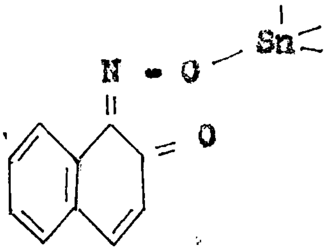
S = Strong ; ms = Medium strong ; w = weak ; br = broad.

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 $\overset{\cdots}{-}$ 0 and C $\overset{\cdots}{-}$ 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 $\overset{\cdots}{-}$ N) and ν(C $\overset{\cdots}{-}$ 0). The structure of 1-nitroso-2-napthol should therefore be represented as in XII.



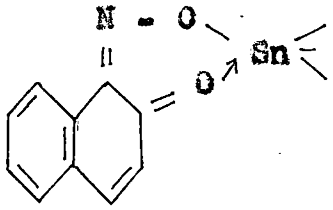
(XII)

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

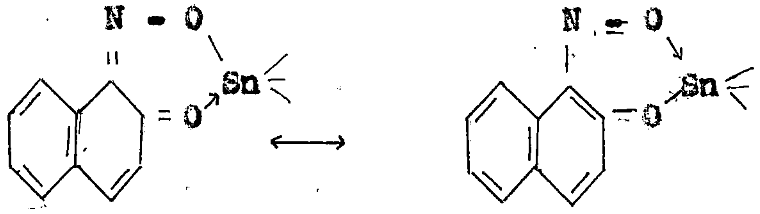
The uncoordinated oximate structure would be expected to show :

(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) (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

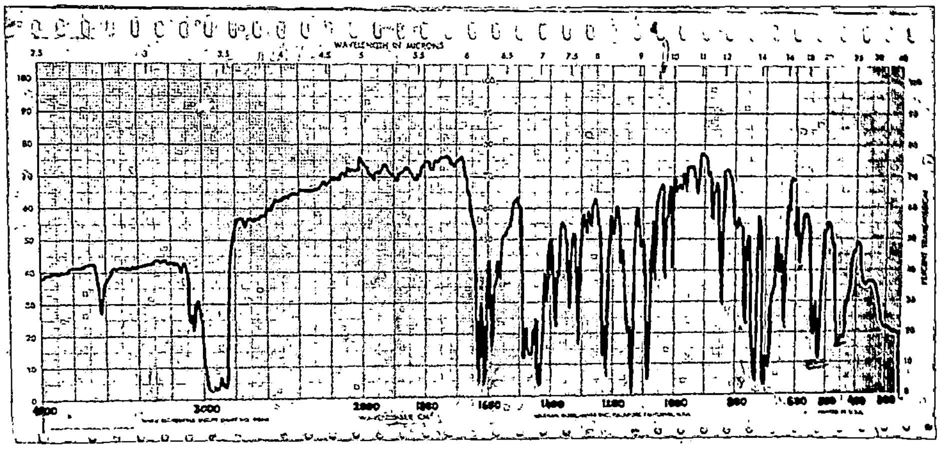


Figure -7: Infra red spectrum of $Ph_4ChSn_2(OH)O$

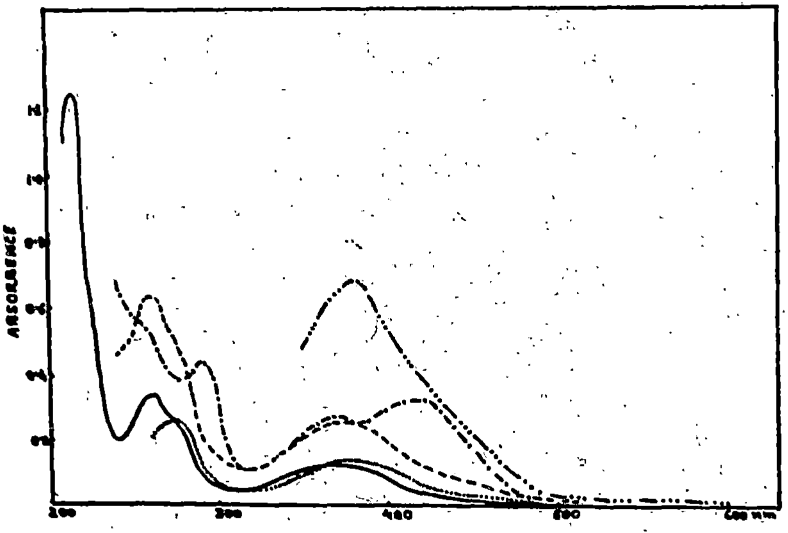


Figure - 8: Electronic absorption spectra of $Ph_4ChSn_2(OH)O$ in

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 $\sim$1590 cm^{-1} [ν(C = O), coordinated to tin].

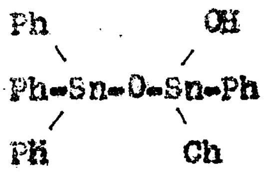
(b) Some selected compounds :

(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 :

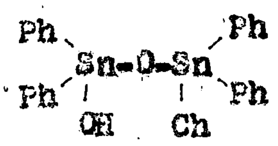
The analytical data on this product suggests a molecular formula of $Ph_4ChSn_2(OH)O$ [Ph = $-C_6H_5$; Ch = $-ON(O)C_{10}H_6$]. The presence of a moderately short medium intensity IR band at 3610 cm^{-1} shows the presence of $-OH$ group attached to tin atom (cf. Ph_3SnOH). This is further supported 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.

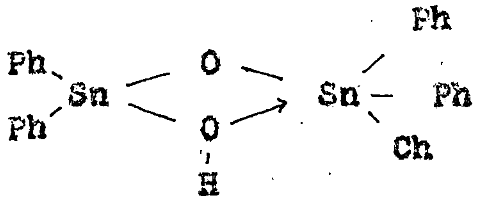


Or



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

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)

$[\mathrm{Ph} = -\mathrm{C_6H_5}$

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

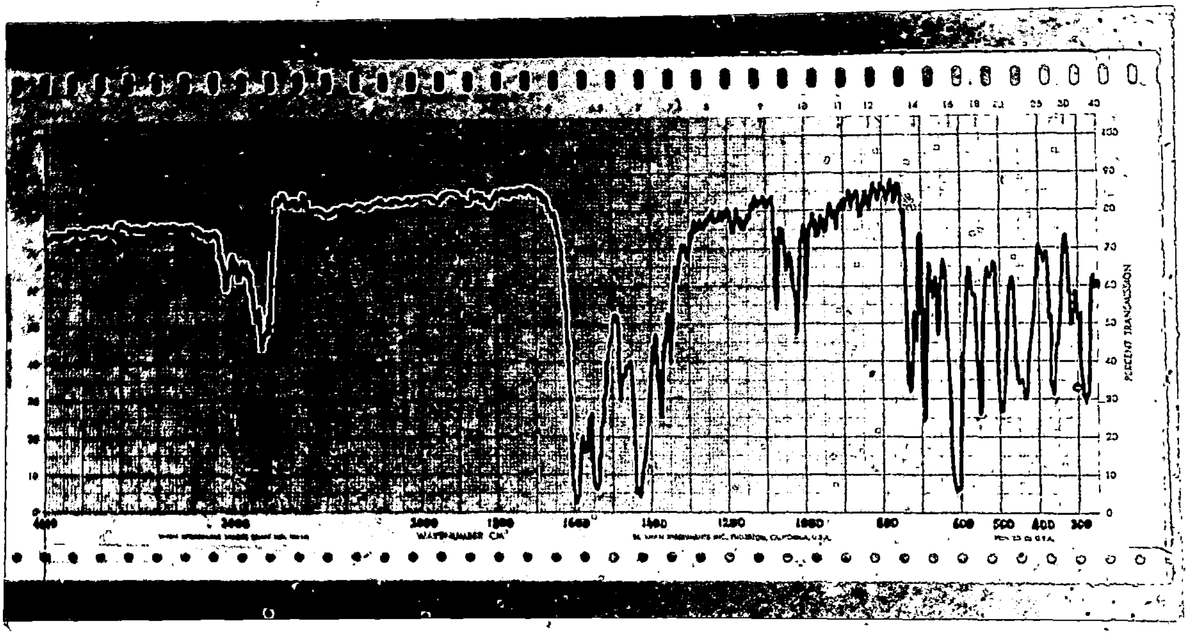


Figure - 9 : Infra red spectrum of $-O-(Ph)Sn(OAc)-O\ Sn(Ph)(OAc)-$

(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)

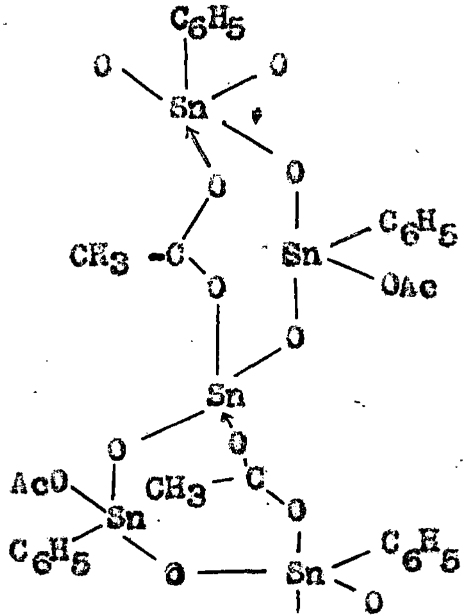
where OAc is $-OCOCH_3$. The structure has been established on the basis of spectral study and elemental analysis and its reaction with oxine.

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.

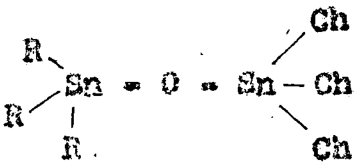


(XIX)

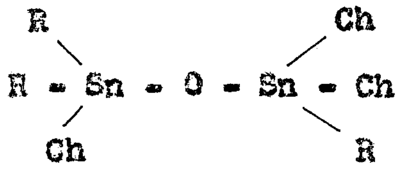
(iii) Distannoxanes of the type $R_3Ch_3Sn_2O$:

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

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



Or



(XX)

(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

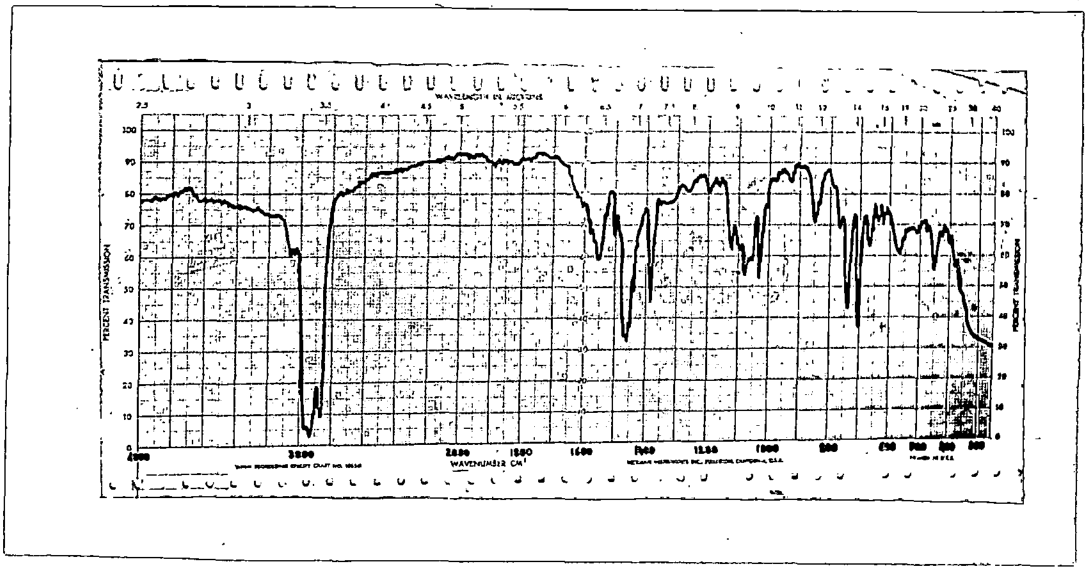


Figure - 10 : Infra red spectrum of XXII

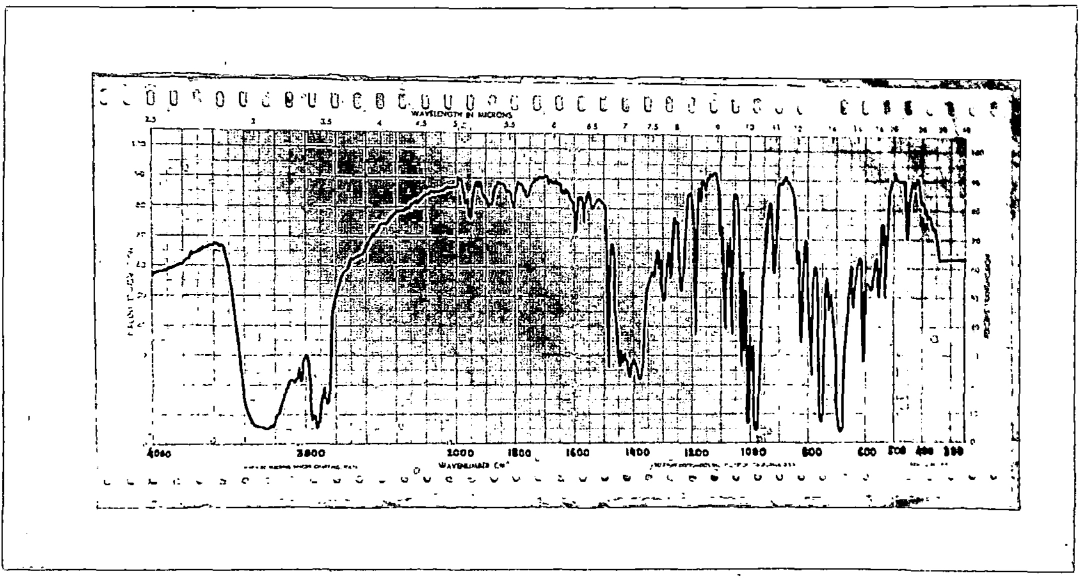
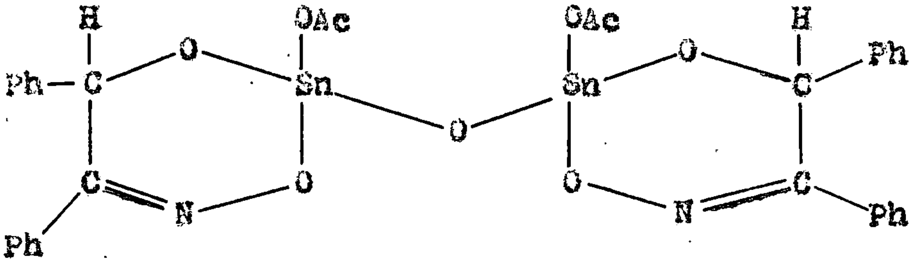


Figure - 11 : Infra red spectrum of benzoin oxime a white compound (m.p 232°). The IR spectrum of the compound shown in figure 10 shows absence of any absorption due to -OH group indicating that the ligand uses both the oxime and hydroxyl H - atoms for salt formation. Presence of COO group is indicated 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.

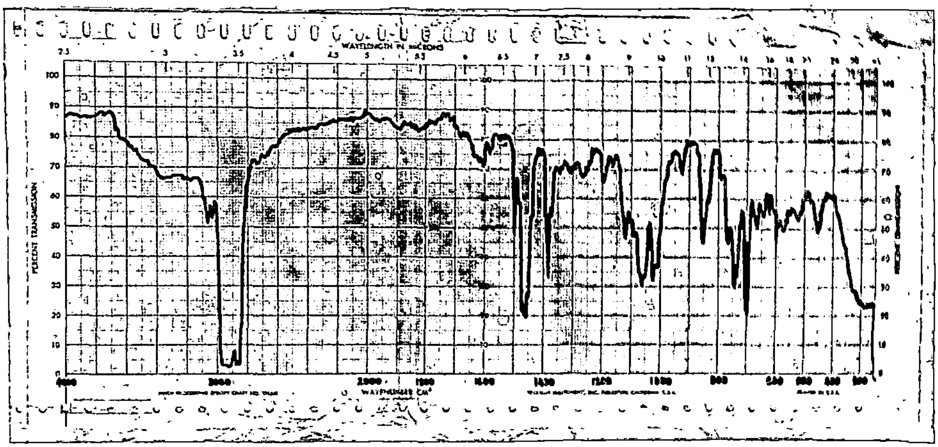
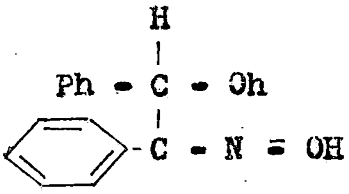
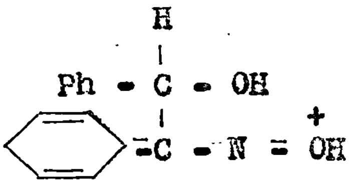


Figure - 12 : Infra red spectrum of XXV

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)

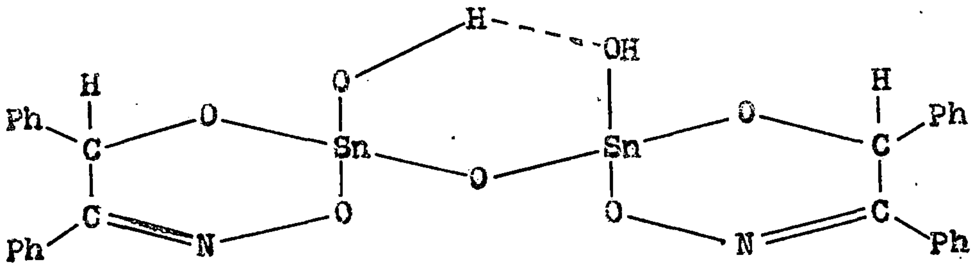


(XXIV)

(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 :

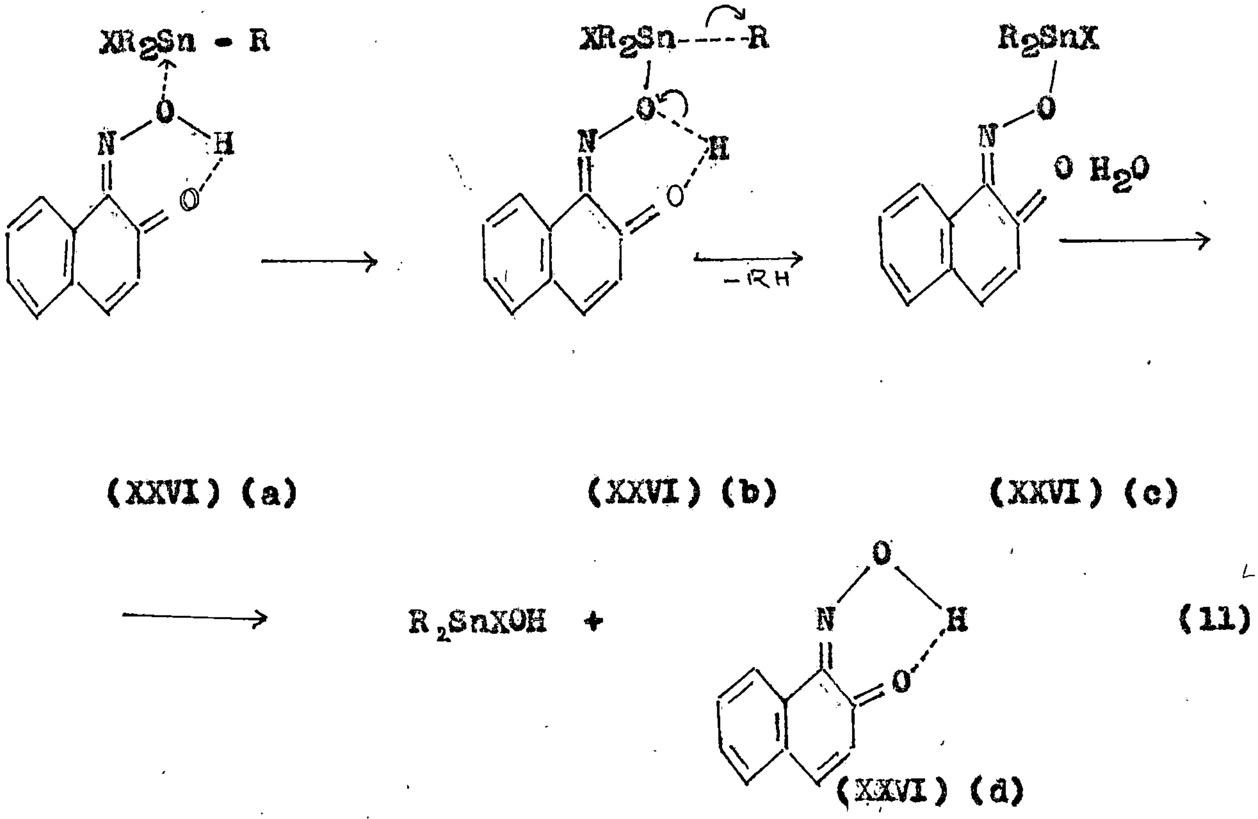
Polystannoxanes formed in the reactions studied do not fall into any general type and as such their probable structures have been discussed under the corresponding reactions separately.

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 bond, a nucleophilic attack at the tin atom which lowers the effective electronegativity of the tin atom and thereby increases the $\geq\overset{\delta+}{\mathrm{Sn}}-\overset{\delta-}{\mathrm{C}}\leq$ 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



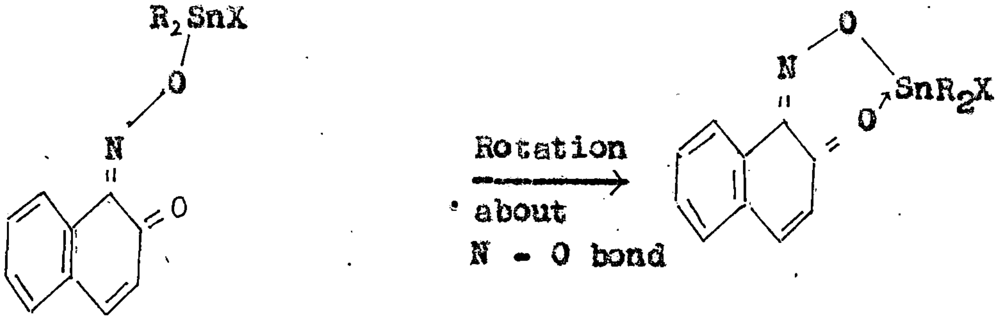
(XXVI) (a) (XXVI) (b) (XXVI) (c)

(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



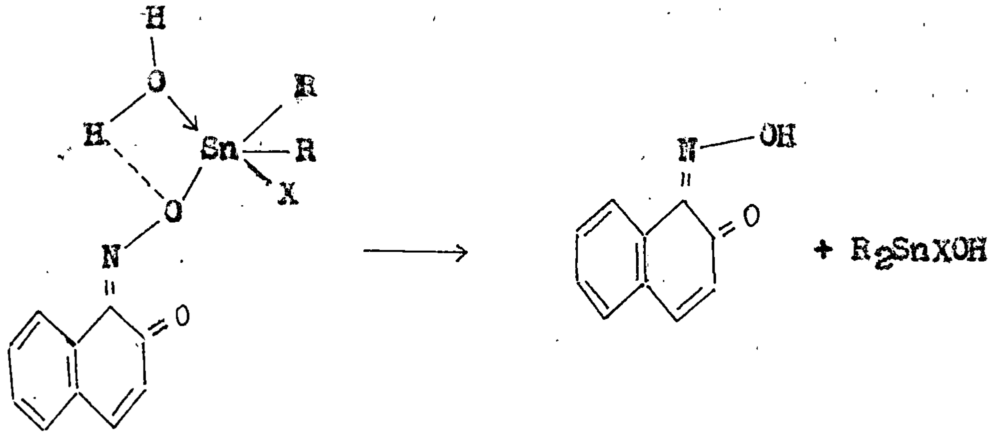
(12)

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)

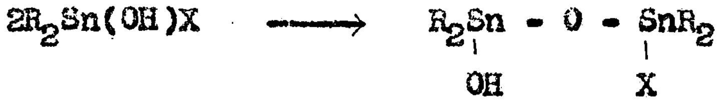
It is evident from XXVIII, because of its very favourable steric disposition the H-atom of the co-ordinated water molecule can interact strongly with the NO group. This would not only hinder the rotation about the N - O bond necessary for chelation, but slight electronic rearrangement as shown may lead 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 :

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

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

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

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



$$2R_2Sn(OH)X \longrightarrow \underset{\displaystyle OH}{\underset{|}{R_2Sn}} - O - \underset{\displaystyle X}{\underset{|}{SnR_2}} \qquad (18)$$

$$>Sn - OH + X - Sn< \longrightarrow >Sn - O - Sn< + HX \qquad (19)$$

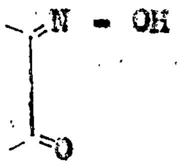
$$>Sn - OH + HO-Sn< \longrightarrow >Sn - O - Sn< + H_2O \qquad (20)$$

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.

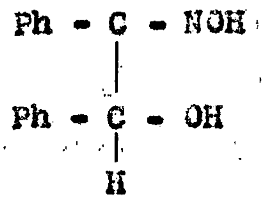
Though the above mechanism has been discussed with 1-nitroso-2-napthol, the arguments apply to all ligands containing the structural unit XXIX, i.e, to all 1,2 diketo mono oximes.



(XXIX)

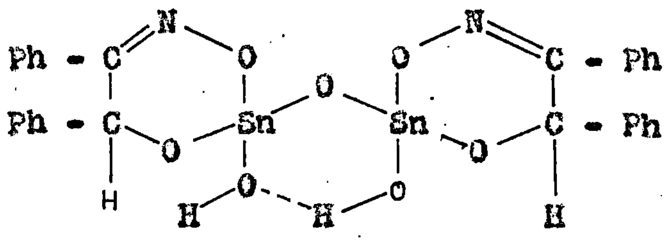
It is therefore not surprising to see that both diacetyl mono oxime $CH_3CO.C(=NOH).CH_3$ and α benzil oxime lead to same type of polymeric products when reacted with triphenyl tin acetate and triphenyl tin chloride.

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

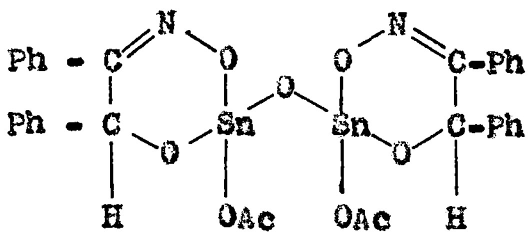


XXX

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 then 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 spetra 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

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

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

$$\mathrm{PhSn(Ox)_2Cl + AgOAc = PhSn(Ox)_2OAc + AgCl} \qquad (21)$$

The formation of $\mathrm{PhSn(Ox)_2OAc}$ establishes the presence of $\mathrm{PhSn(O)OAc}$ 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:

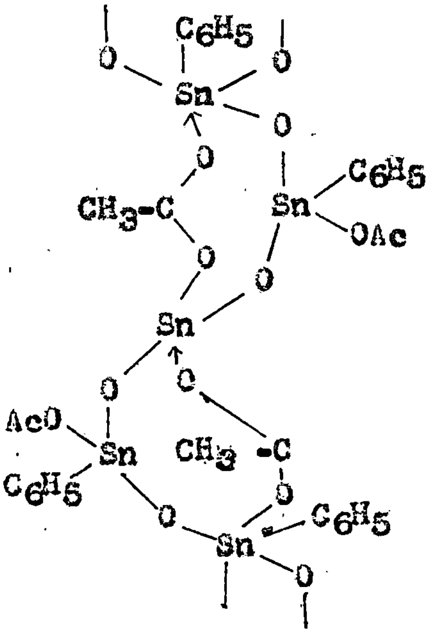
$$\mathrm{- O - (C_6H_5)\,Sn(OAc) - O - Sn(C_6H_5)\,(\,OAc\,) -}$$

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

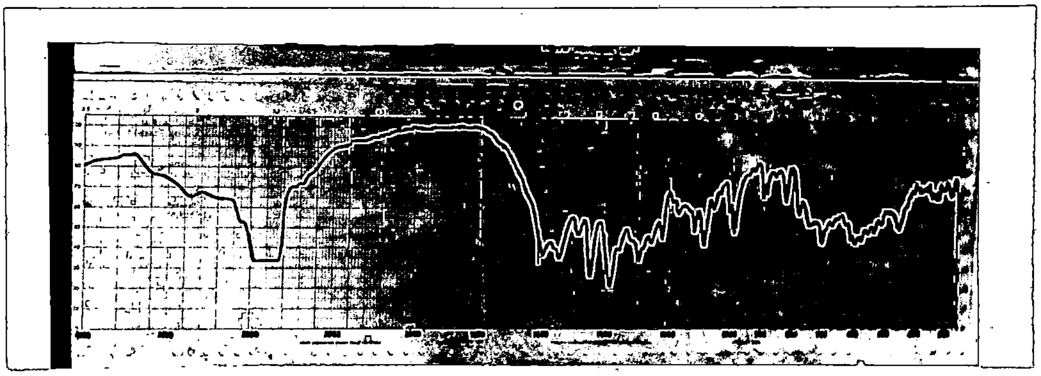


Figure - 19 : Infra red spectrum of Ph(Ch)$_2$(OAc) (OH)$_4$Sn$_2$ (XXXIV)

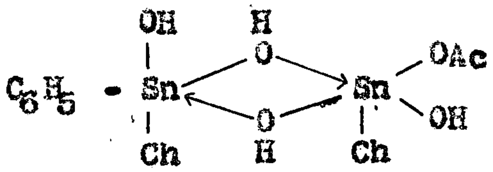
Although NMR spectra would have been of great help in distinguishing the two structurally non equivalent acetate groups, this could not be done due to the low solubility of the compound.

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 ν(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

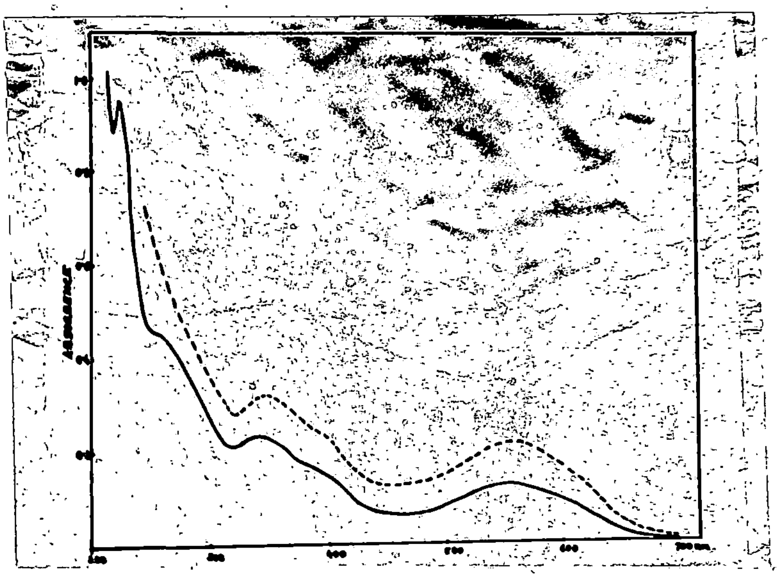


Figure - 14 : Electronic absorption spectra of $[Ph(Ch)(OAc)Sn]_2O$ (XXXV) in

Methanol : ————————

Chloroform : - - - - - - - - -

Analysis found : C = 43·71 % ; H = 3·32 % ; N = 3·57 % ; Sn = 30·5 %
Calculated for
$C_{28}H_{24}O_{10}N_2Sn_2$: 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 :

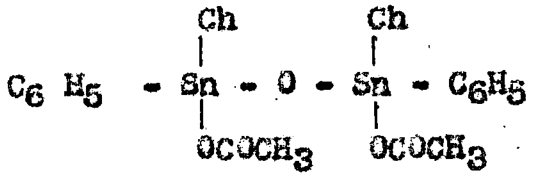
The electronic spectra of the compound in Methanol and choloroform are shown in the figure - 14. The stability and large bathochromic shift of the largest wave length band compared to that in the free ligand indicates the presence of chelated 1-nitroso-2-napthol group.

(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 ν_{as} (Sn-O-Sn) as Sn-OH band is absent (no hydroxyl absorption)

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



$$C_6H_5 - \underset{\displaystyle OCOCH_3}{\overset{\displaystyle Ch}{Sn}} - O - \underset{\displaystyle OCOCH_3}{\overset{\displaystyle Ch}{Sn}} - C_6H_5 \qquad [Ch = C_{10}H_6NO_2 -]$$

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^{o}. 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.

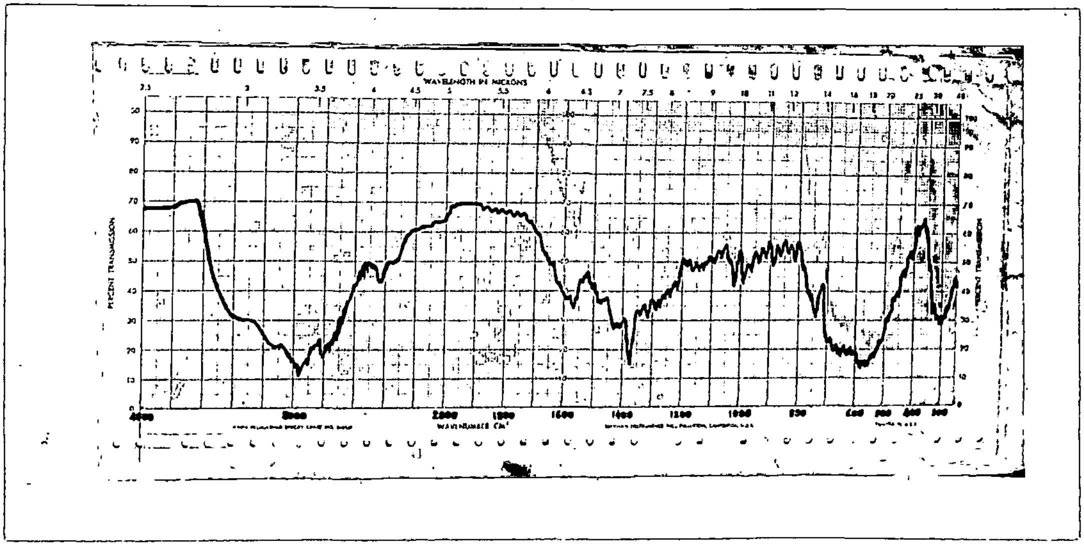


Figure - 15 : Infra red spectrum of XXXVI

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.

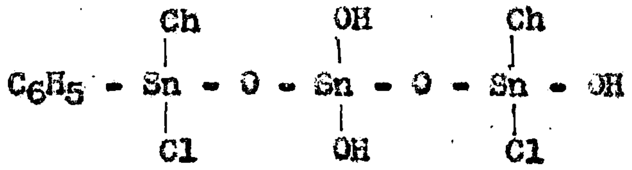
(ii)Reaction with mercuric chloride :

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 = 1·53%
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

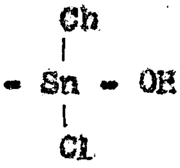
$$\left[Sn\,(Ox)_2\,Cl\right]_2 O \qquad \left[Ox = C_9H_6(N)O-\right]$$

(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  $-\overset{\displaystyle Ch}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{Sn}}}}-OH$ 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.

<u>Identification of 9B</u>

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 $\mathrm{cm^{-1}}$ (53). Presence of phenyl group is also indicated by the presence of usual ring vibrations.

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

$\mathrm{Ch_3\ Sn\text{-}O\text{-}SnPh_3}$ XXXVIII

$\mathrm{Ch_2(Ph)Sn\text{-}O\text{-}Sn(Ch)Ph_2}$ XXXIX

[Ph = $\mathrm{C_6H_5}$ -

Ch = $\mathrm{C_{10}H_6\ NO_2}$ -]

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

Calculated for

$\mathrm{C_{48}\ H_{33}\ O_7\ N_3\ Sn_2}$: 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

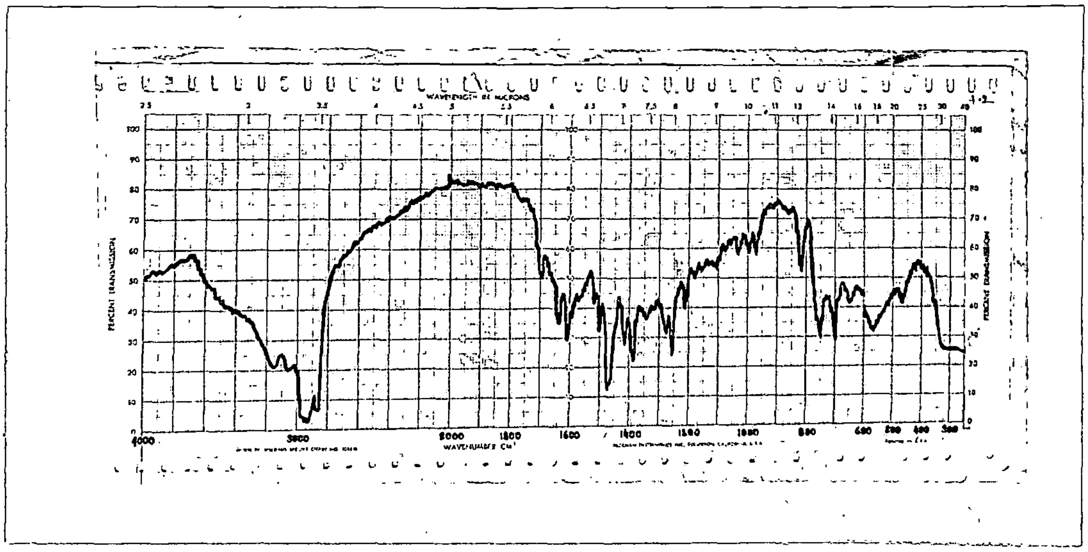


Figure - 16 : Infra red spectrum of $Bz_2(Cb)(Cl)(OH)_2O\ Sn_2$ (XL)

(ii) It melts at 230°C.

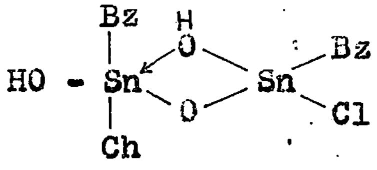
(iii) UV and visible spectra :

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 :



(XL)

[Bz = C_7H_7 -

Ch = $C_{10}H_6NO_2$ -]

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

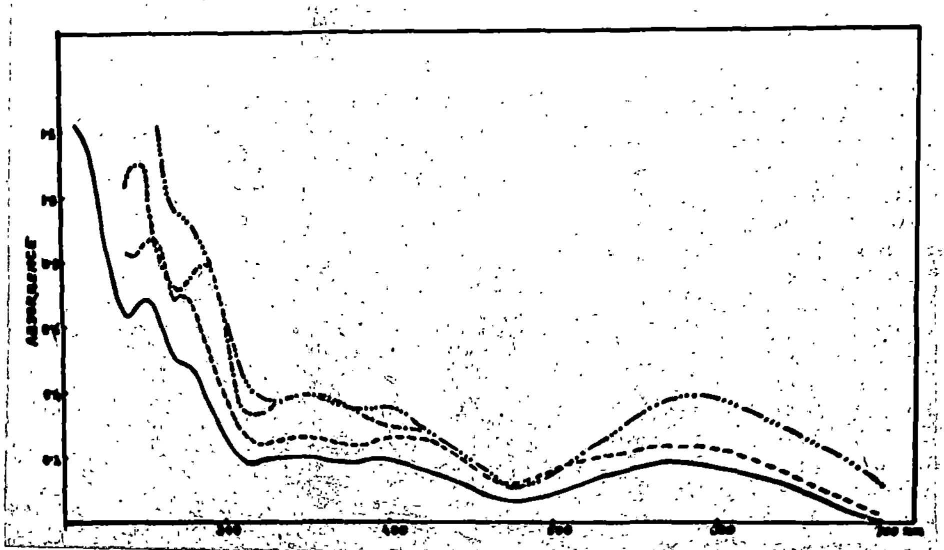


Figure - 17 : Electronic absorption spectra of $Cy_2(Ch)Sn-O-Sn(Cy)Ch_2$

(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 :

$Cy_3Sn\text{-}O\text{-}SnCh_3$

(XLI)

$Cy_2(Ch)Sn\text{-}O\text{-}Sn(Cy)Ch_2$

(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

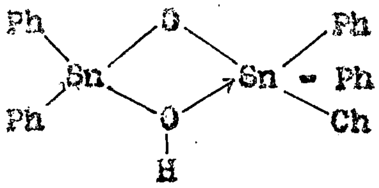
To a solution of 3·6 gms of bis (triphenyl tin) oxide in 50 ml benzene was added a solution of 1 gm of 1-nitroso-2-napthol in 50 ml benzene. The solution was then refluxed for half an hour. To the solution excess of petroleum ether was added when a yellow compound (12A) crystallised out. It was filtered, 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°). 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

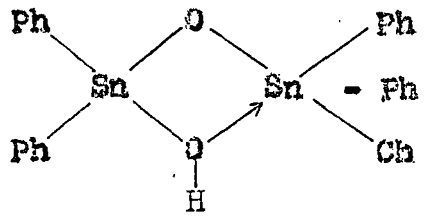
The compound has the following characteristics :

(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

$C_{34}H_{27}O_4NSn_2$: 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.

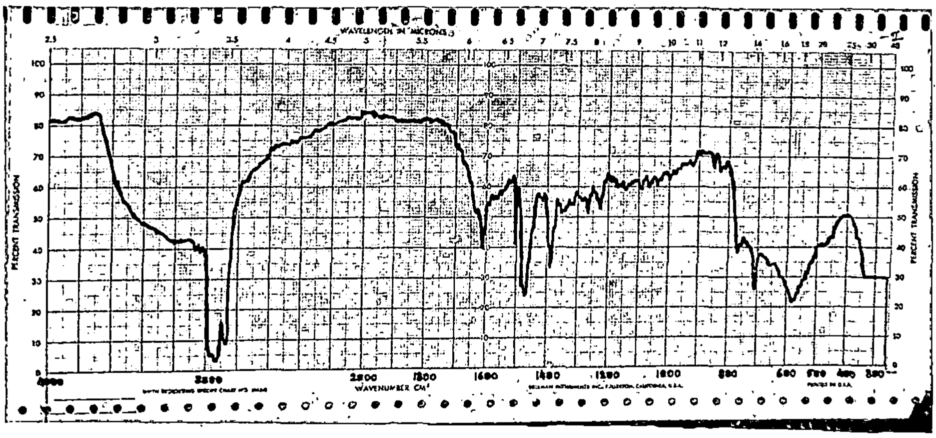


Figure - 18 : Infra red spectrum of (XLV)

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 evaporation to dryness gave unreacted 1-nitroso-2-napthol.

Identification of 14A

The compound has the following characteristics :

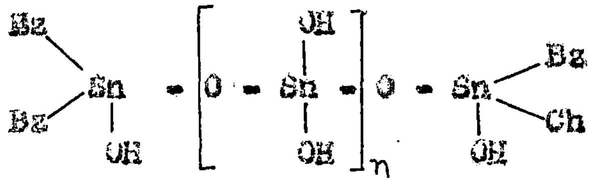
(i) The compound is infusible up to 360°

(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 ;



$$\mathrm{(Bz)_2Sn(OH)-[O-Sn(OH)_2]_n-O-Sn(OH)(Bz)(Ch)}$$

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 :

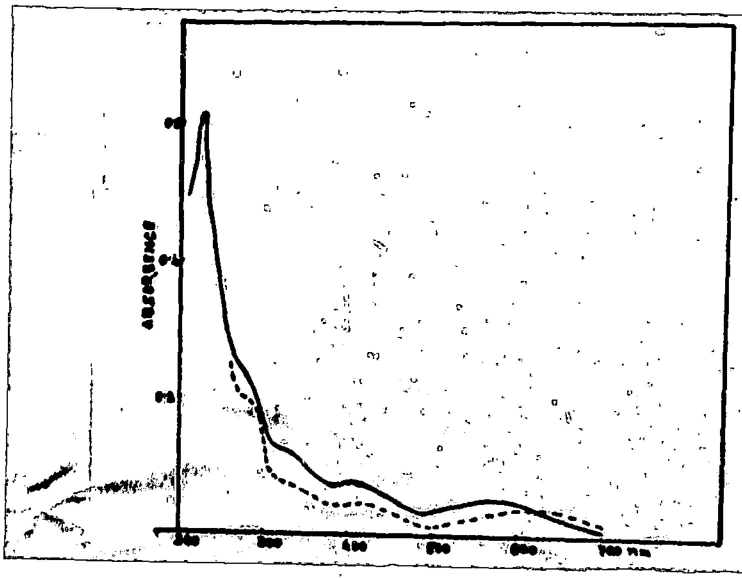


Figure - 19 : Electronic absorption spectra of

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

Methanol : ————————

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

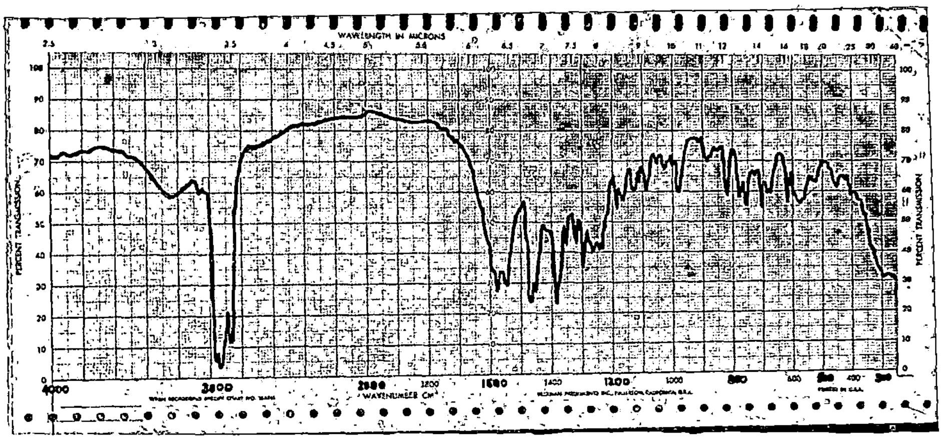


Figure - 20 : Infra red spectrum of $Bu_{10}(Ch)_2(OH)_2O_5Sn_6$ (XLVI)

(i) The compound is infusible upto 360°.

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

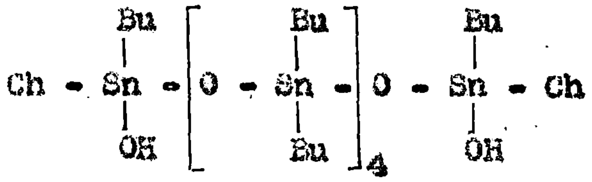
(iii) UV visible spectrum :

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

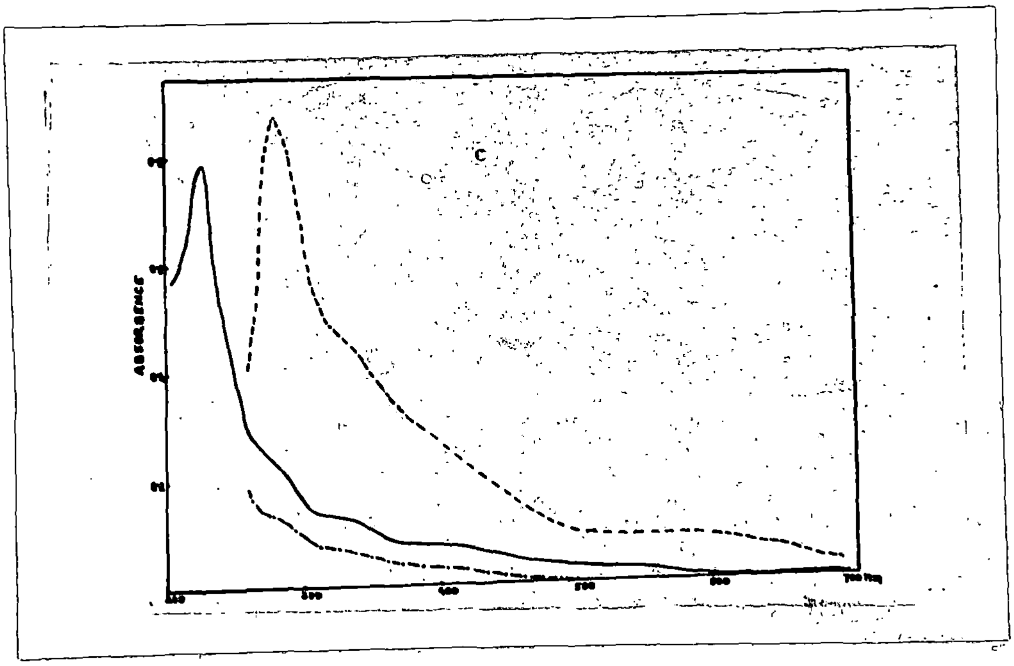


Figure - 21 : Electronic absorption spectrum of $[(C_4H_9)_2ChSn]_2O$

(XLVII) in

Methanol : ————————

DMSO : – – – – – – – – –

CCl$_4$: —·—·—·—

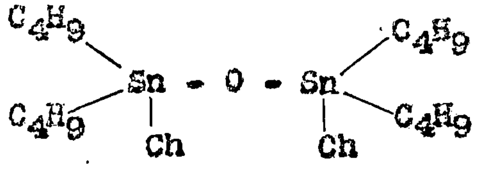
shoulders at 280 nm and 330 nm. The pattern of absorption is similar to 1-nitroso-2-napthol and those of yellow compounds obtained in the present study. Moreover the position of absorption bands remains unchanged in DMSO indicating strong co-ordination with the tin atom. The electronic spectra is shown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

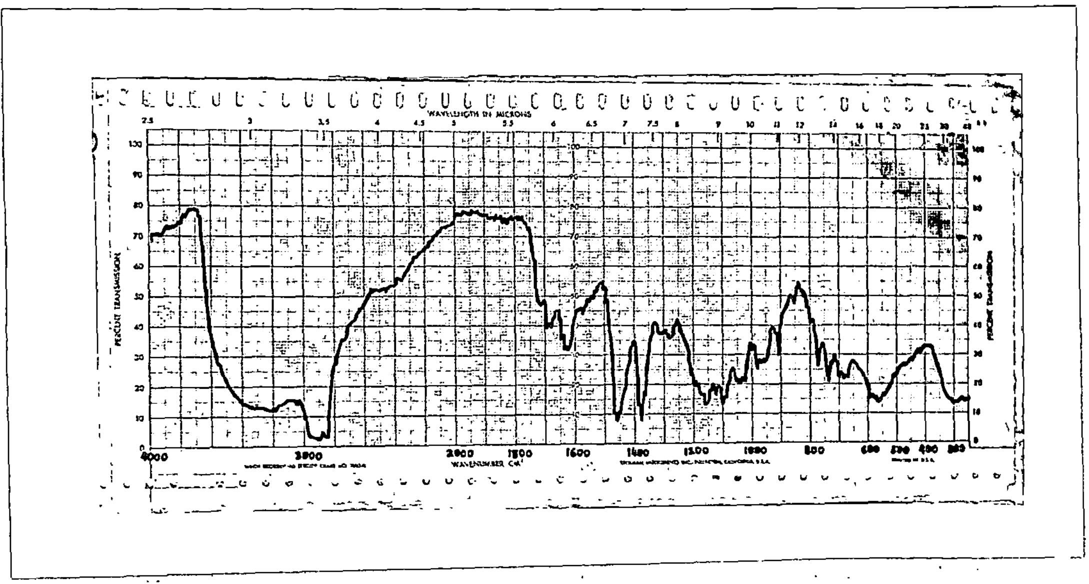


Figure - 22 : Infra red spectrum of (XLVIII)

(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 :

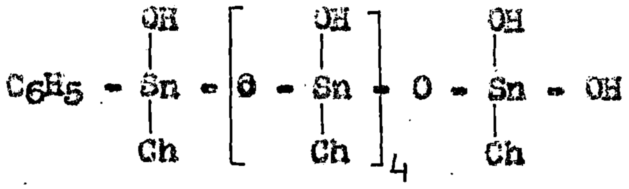
(i) It is infusible upto 360°.

(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.



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

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

(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) <u>Reaction of triphenyl tin acetate with diacetyl mono oxime</u>

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

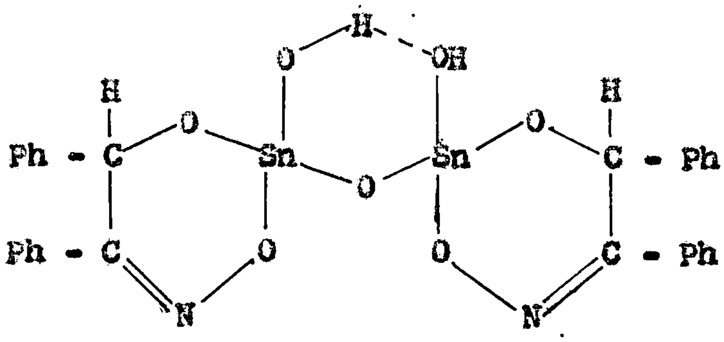
The compound has the following characteristics :

(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

$C_{28} H_{24} O_7 N_2 Sn_2$: 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

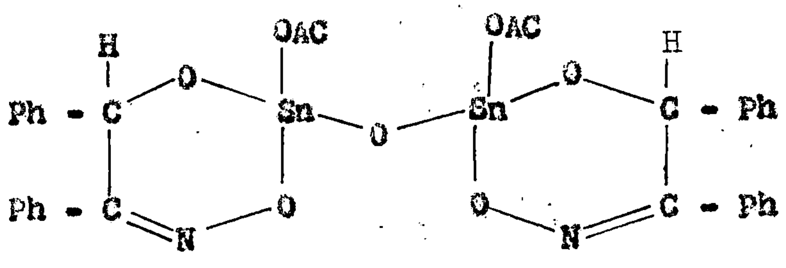
The compound exhibits following characteristics :

(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 = 45·75% ; H = 3·57% ; Sn = 28·28%

BIBLIOGRAPHY

1. K.Ramajah and D.F.Martin, Chem.Commun., 130 (1965

2. D.Blake, G.E.Coate and J.M.Tate, J.Chem.Soc., 756 (1961)

3. L.Ronucci, G.Faraglia and R.Barbieri, J.Organometal.Chem., 1(1964)427

4. T.Tanaka, M.Komura, Y.Kawasaki and R.Okawara, J.Organometal.Chem., 1(1964)484

5. P.P.Singh and S.B.Sharma, J.Indian.Chem.Soc.,LII(7)(1975)617

6. M.Wada, M.Shindo and R.Okawara, J.Organometal.Chem., 1(1963)95

7. F.Bonati, G.Minghetti and S.Cenini, Inorg.Chim.Acta, 2(1968)1

8. F.Bonati, S.Cenini,R.Ugo, Instituto.Lombardo.Rend.Sci., A,99(1965)825; Indem, J. Organometal.Chem., 9(1967)395, Ibid 10(1967) 257

9. E.L.Muetterties and C.M.Wright, J.Amer.Chem.Soc., 86 (1964)5132

10. W.N.Aldridge and J.E.Cremer, Analyst (London),82(1957)37

11. H.Irving and J.J.Cox, J.Chem.Soc, (1961) 1470

12. T.Tanaka, M.Komura, Y.Kawasaki and R.Okawara, J.Organometal.Chem, 1(1964)484

13. D.L.Alleston and A.G.Davis, J.Chem.Soc., (1962) 2050

14. I.R.Beattie and G.P.Quillan, J.Chem.Soc.,(1963) 1519

15. M.J.Yasuda and R.S.Tobias, Inorg.Chem, 2(1963) 207

16. R.C.Mehrotra and V.D.Gupta, J.Organometal.Chem.,4(1965)237

17. R.Ueeda,Y.Kawasaki, T.Tanaka and R.Okawara, J.Organometal.Chem 5(1966)294

18. B.P.Bachlas and R.R.Jain, J.Organometal.Chem.,82(1974)359

19. A.Singh,V.D.Gupta, G. Srivastava and R.C.Mehrotra and reference therein, J.Organometal.Chem.,64(1974)145

20. P.G.Harrison and J.J. Zuckerman, Inorg.Chem,9(1970)175

21. G.Weissenberger, U.S.Pat.,3232672, 1966, through CA 66(1967) 28891

22. K.C.Pande, Fr.Pat., 1506186, 1967, through CA., 69(1968) 106878.

23. P.G.Harrison and J.J. Zuckerman, Inorg.Nucl.Chem.Lett.,6(1970)5.

24. A.G.Farbenfabriken Bayer, Brit.Pat., 945068, 1963, through CA., 60(1964) 12051

25. G.Weissenberger, U.S.Pat., 3275659, 1966, through CA., 65(1966)20164.

26. G.Weissenberger, U.S.Pat., 3282672, 1966, through CA., 66(1967) 22391

27. M.Nakanishi and S. Inamasu, Jap.Pat., 6724573, 1967, through CA., 69(1968)44022

28. M.Nakanishi and S. Inamasu, Jap.Pat., 6726296, 1967, through CA., 69(1968) 52304

29. A.Singh, V.D.Gupta,G. Srivastava and R.C. Mehrotra, J.Organometal.Chem., 64(1974)145

30. P.G.Harrison, J.Organometal.Chem., 38(1972)C5

31. G.P.Mack and F.Parker, U.S.Pat., 2727917, 1955, through CA., 50(1956)10761

32. H.Koehler, U.Lange and B.Eichler, J.Organometal.Chem., 35(1972)C17

33. P.G.Harrison, Inorg.Chem 12(1973)1545

34. A.Singh,A.K.Rai, and R.C.Mehrotra, J.Chem.Soc.,(1972); quoted in 19

35. A.Singh, and R.C. Mehrotra, quoted in 19

36. A.Singh, A.K.Rai, and R.C.Mehrotra, J.Organometal.Chem., 57(1973)301

37. V.D.Gupta,G.Srivastava, and R.C.Mehrotra, Reviews Si,Ge,Sn and Pb compounds, Freund publishing house, Tel-Aviv, 1973.

38. T.J.King, and P.G.Harison, J.Chem.Soc.Commun.,815(1972)

39. R.Okawara, and M.Wada, Advan.Organometal.Chem.,5,151(1967).

40. D.L.Alleston, A.G. Davies, M.H.Hancock, and R.F.M. White, J.Chem.Soc., 5469(1963

41. A.C.Chapman, A.G.Davis, P.G.Harrison, and McFarlane, J.Chem.Soc C, 821(1970)

42. G.B.Deacon, Organometal.Chem.Rev,Sect, A5, 355(1970

43. Toshio,Tanaka,Rynheike, Masanori,Wada and R. Okawara, Bull.Chem.Soc.Japan, 37(10)(1904)1954-55

44. R.C.Mehrotra and B.P. Bachlas, J.Organometal.Chem. 22(1970)129-137

45. A.Burawoy, M.Cais,J.T. Chamberlain, F.Liversedge and A.R.Thompson, J.Chem.Soc.3727(1955)

46. A text book of practical organic chemistry : A.I.Vogel,Longmans,London (1961)

47. Chemistry of Organometallic Compounds : E.Rochow, D.T.Hurd and R.N.Lewis, John Willy and Sons, Inc.(1957) New York.

48. J.H.Van Rij, (N.V.Philips Gloeilampen fabricken) Neth.105,821(1953),CA.60,14539(1964)

49. Handbook of Organometallic compounds : H.C.Kaufman, D.Van Nostrand company, Inc.New Jersey,1961

50. O.Schmitz - Dumont and Bungard : Angew Chem.67,208(1955)

51. B.F.E.Ford,B.V.Liengme and J.R.Sams : J.Organometal Chem.,19,53(1969)

52. M.C.Henry and J.G.Noltes: J.Amer.Chem.Soc.82(1966)55

53. R.Okawara and M.Wada, Advan.Organometal.Chem.19(1969)53.

54. R.C.Poller, J.Inorg.Nucl.Chem,24,593(1962)

55. R.A.Cummins, Australian.J.Chem., 18,98(1965)

56. B.Kushlefsky,L.Simmons and A.Ross, Inorg.Chem.,2,187(1963)

57. S.Nagakura and A.Kuboyama, J.Am.Chem.Soc.,76(1954)

58. A.H.Westlake and D.F.Martin, J.Inorg.Nucl.Chem., 27(1965)1579

59. W.H.Nelson and D.F.Martin, J.Inorg.Nucl.Chem., 27(1965)89.

60. D.Dutta, B.Majee and A.K.Ghosh, J.Organometal.Chem., 84(1975) 231 - 238

61. D.Dutta, Ph.D. Thesis, North Bengal University, India.

62. Introduction to Infrared and Raman Spectroscopy, N.B.Colthup, L.H.Daly and S.E.Wiberley., Academic Press (1964) New York and London, page number 275, 232

63. B.G.Gowenlock and W.Luttke, Quart.Rev.12,321(1958)

64. B.G.Gowenlock, H.Spedding,L. Trotman and D.H.Whiffen J.Chem.Soc., 1957,3927

65. W.Lüttke, J.Phys.Radium., 15,633(1954)

66. W.Lüttke, Z.Elecktrochem.61,302(1957)

67. J.Mason and J.Dunderdale, J.Chem.Soc.,1956,754

68. Infrared spectra of inorganic and coordination compounds, Kazuo Nakamoto., John Wiley & Sons, Inc., New York and London (1963), Page number 223

CHAPTER - IV

On preparation of organotin carboxylates by the reaction of organotin hydroxides with esters.

IV A Introduction :

Despite the tremendous amount of work already done on organotin carboxylates, interest in compounds containing - $OCOSnR_3$ group still continues. This is partly due to the growing importance of diffent types of organotin carboxylates in the industry and agriculture, and partly due to the variety of structural features found in organotin carboxylates.

Organotin carboxylates are generally prepared by the reaction of organotin oxides or hydroxides with carboxylic acids and their anhydrides (1-10) :

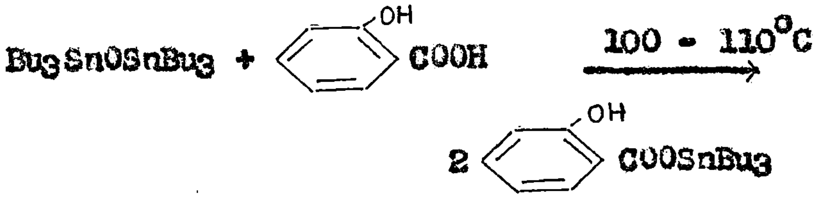
$$R_3SnOSnR_3 + 2R'COOH \rightarrow 2R_3SnOCOR' + H_2O \qquad (1)$$

$$R_3SnOSnR_3 + (R'CO)_2O \rightarrow 2R_3SnOCOR' \qquad (2)$$

$$R_2SnO + 2\,R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \qquad (3)$$

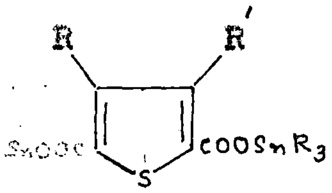
The water produced in these reactions is removed usually be azeotropic distillation or alternatively by refluxing at higher temperature

(II)

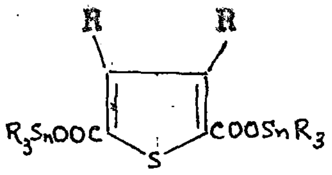


(4)

Recently a number of tin thiophene carboxylates (35) of the type I and II have been prepared from thiophene carboxylic acids and R_3SnOH or $(R_3Sn)_2O$.



(Ia)



(Ib)

R = Ph, H;
R' = Bu,Me etc.

Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halide with the alkali metal or silver salt of carboxylic acids either by stirring the reactants in mixtures of organic/ aqueous medium at room temperature or by refluxing the mixture (9,12-14). This method represented as

$$R_3SnX + R'COOM \longrightarrow R_3SnOCOR' + MX \qquad (5)$$

M = Na, K, Ag; X = Halogen

is frequently used for its simplicity.

The ability of carboxylic acids to cleave metal carbon bonds is the basis of yet another method for the preparation of organotin carboxylates (15,16)

$$R_4Sn + R'COOH \longrightarrow R_3SnOCOR' + RH \qquad (6)$$

The cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on temperature (17 - 19). Vinyl groups are cleaved more readily than normal alkyl groups but less readily than phenyl groups. $Pb(OAc)_4$ has also been used for acylation of R_3SnH, R_2SnH_2 ,$(R_3Sn)_2$, R_4Sn and $(R_3Sn)_2O$ (20).

Kuivila (21) showed that the reaction of organotin hydrides with carboxylic acids produces carboxylates according to following equations :

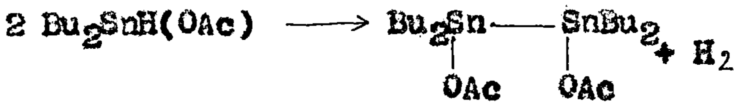
$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2 \qquad (7)$$

$$R_2SnH_2 + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2H_2 \qquad (8)$$

$$R_2Sn(OCOR')_2 + R_2SnH_2 \rightarrow 2R_2SnH(OCOR') \qquad (9)$$

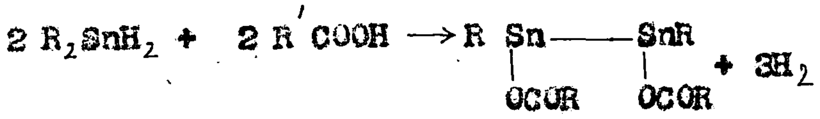
with di n - butyl tin dihydride, the intermediate hydride acetate decomposes to tetra n - butyl diacetate.

$$2\,Bu_2SnH_2 + 2\,CH_3COOH \longrightarrow 2\,Bu_2SnH(OAc) + 2H_2 \qquad (10)$$



$$2\,Bu_2SnH(OAc) \longrightarrow \underset{OAc}{\underset{|}{Bu_2Sn}}\!-\!\!-\!\!-\underset{OAc}{\underset{|}{SnBu_2}} + H_2 \qquad (11)$$

Using similar methods 1,2 dicarboxylates have been prepared (22 - 24)



$$2\,R_2SnH_2 + 2\,R'COOH \longrightarrow R\,\underset{OCOR}{\underset{|}{Sn}}\!-\!\!-\!\!-\underset{OCOR}{\underset{|}{SnR}} + 3H_2 \qquad (12)$$

The nature of the products sometimes depends on the carboxylic acid. Action of benzoyl peroxide on di-n-butyl tin dihydride also produces the 1,2 dibenzoate (25).

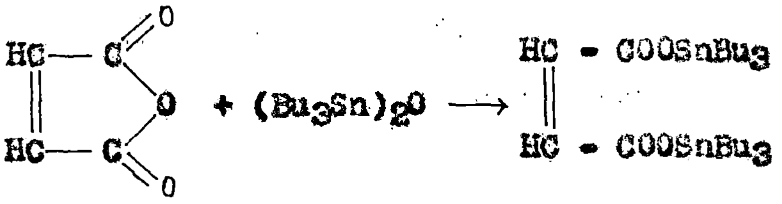
Halo carboxylate derivatives of organotin compounds are most conveniently prepared by heating equimolecular mixture of the dihalide and the carboxylate in an inert solvent (26,27)

$$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \rightarrow 2Bu_2SnBr(OAc) \qquad (13)$$

These may be prepared by the following reactions also (28,29)

$$Bu_2SnCl_2 + KOOCR' \rightarrow Bu_2SnCl(OCOR') + KCl \qquad (14)$$

Anhydrides of an unsaturated acid e.g. maleic anhydride forms disubstituted organotin esters when reacted with hexabutyl distannoxane (30)



(15)

A novel method of preparation of trialkyl tin acetate by electrochemical method using R_4Sn (where R = Me, Et, Pr, Bu) and Hg(1) acetate have been described by Tagliavini and his co-workers (31).

Tricarboxylates derivatives of the type $RSn(OCOR')_3$ are usually prepared from the corresponding trichloride by the action of silver salts of carboxylic acids (32).

Anderson (33) has shown that triethyltin carboxylates can be prepared in good yields by the following reaction :

$$(Et_3Sn)_2O + RCOOEt \longrightarrow Et_3SnOCOR + Et_3SnOEt \qquad (16)$$

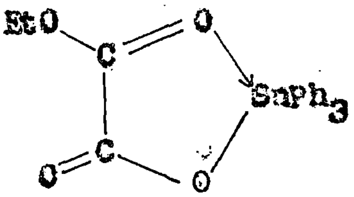
clearly, organotin hydroxides would undergo similar reaction according to the equation;

$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH \qquad (17)$$

Since the organotin hydroxides can be easily prepared from the corresponding halides by shaking an ethereal solution with aqueous sodium hydroxide, and since no drying of the product is necessary unlike $(R_3Sn)_2O$, it was decided to investigate the scope and suitability of the method for preparation of different types of organotin carboxylates. The results of this investigation are presented in this chapter.

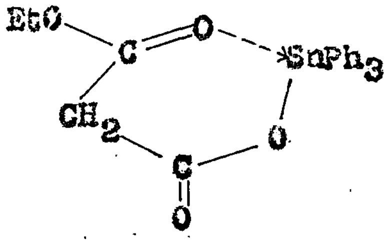
IV B Results and discussion

A summary of the reactions studied are given in table 1. As can be seen saturated carboxylates like formate and acetate are obtained in almost quantitative yield. With functionally substituted esters like $ClCH_2COOEt$ and $CNCH_2COOEt$ the yield are fairly high. Further, no side products or polymeric products are generally formed. The method is extremely suitable for the preparation of half esters of dicarboxylic acids of the type $R_3SnOCO(CH_2)_nCOOH$. Attempts to prepare $Ph_3SnOCOCOOH$ by the reaction of triphenyl tin chloride with sodium hydrogen oxalate (mono sodium derivative in 1:1 mole ratio) always led to the formation of $Ph_2Sn(OOC)_2H_2O$. Even, the reaction of Ph_3SnCl with $(COONa)_2$ in 1:1 mole ratio produced diphenyl tin oxalate through cleavage of Sn - Ph bond instead of the desired $Ph_3SnOOC.COONa$. However, the half ester $Ph_3SnOOC.COOEt$ could be easily prepared in good yield by stirring triphenyl tin hydroxide with diethyl oxalate with an excess of the latter. Half esters of diethyl malonate could also be obtained similarly. It is worth mentioning here that νas(OCO) of the ester group in (triphenyl tin) mono ethyl oxalate $Ph_3SnOCo.COOC_2H_5$ occurs at 1680 cm.$^{-1}$ This value is considerably lower than that observed in normal esters (1720 - 40 cm^{-1}). The lowering of νas(OCO) is indicative of co-ordination by the - C = O group of the ester. As such (triphenyl tin) mono ethyl oxalate is most probably intramolecularly co-ordinated as shown in structure II.



(II)

On the contrary, (triphenyl tin) mono ethyl malonate absorbs at 1730 cm^{-1} and 1550 cm^{-1} indicating the presence of unco-ordinated ester group probably intermolecularly bridged $\mathrm{Sn}-\mathrm{O}-\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}\rightarrow\mathrm{Sn}$ - as in triorganotin formates, acetates etc. where νas(OCO) occurs at about 1550 cm^{-1}. The reason for this difference between the molanate and the oxalate derivatives are not clear. However, it may be that the 5-membered Sn containing ring in structure II is probably more stable than 6-membered ring (III) which would be required to be formed in the malonate derivative if intramolecular co-ordination takes place. In that case inter molecular co-ordination may be more favourable in the malonate derivative.



III

The method however fails with benzoates and substituted benzoates. Thus no organotin derivative could be obtained with p - amino - or p - nitro benzoate. This is probably due to the facile hydrolysis of triphenyl tin benzoates by the water presnet with the organotin hydroxides.

It may be said in conclusion that the method seems to be preferable where pure derivatives are required, particularly when there is a tendency for the formation of polymeric products in the reaction between the organotin halides and the sodium or potassium carboxylates.

IV C Experimental

The summary of the reactions of organic esters with organotin hydroxides is given in the table-I

Table - I

Triorganotin hydroxides (1)	Esters of carboxylic acids (2)	Conditions of reaction (3)	Products formed (4)	Melting point °C (5)	Yield of the products (6)
Ph_3SnOH	$HCOOC_2H_5$	Stirred at room temperature for eight hours	$HCOOSnPh_3$	202°	Almost quantitative
Ph_3SnOH	$CH_3COOC_2H_5$	Stirred for eight hours at room temperature	$CH_3COOSnPh_3$	121°	Almost quantitative
Ph_3SnOH	$CH_3COOC_4H_9$	Stirred at room temperature for eight hours	$CH_3COOSnPh_3$	121°	Almost quantitative
Ph_3SnOH	$ClCH_2COOC_2H_5$	Refluxed for 5 hours in benzene	$ClCH_2COOSnPh_3$	135°	Almost quantitative

Table - I Contd.

(1)	(2)	(3)	(4)	(5)	(6)
Ph_3SnOH	$CNCH_2COOC_2H_5$	Refluxed for five hours in benzene	$CNCH_2COOSnPh_3$	141°	60%
Ph_3SnOH	$C_2H_5OCOCOOC_2H_5$	Refluxed for five hours in benzene	$C_2H_5OCOCOOSnPh_3$	127°	80%
Ph_3SnOH	$C_2H_5OCOCH_2COOC_2H_5$	Refluxed for five hours in benzene	$C_2H_5OCOCH_2\text{-}COOSnPh_3$	139°	Almost quantitative
Bu_3SnOH	$CH_3COOC_2H_5$	Refluxed for five hours	$CH_3COOSnBu_3$	80-81°	Almost Quantitative
Bu_3SnOH	$HCOOC_2H_5$	Refluxed for five hours	$HCOOSnBu_3$	127-30°/ 3mm	Almost quantitative
Bu_3SnOH	$CH_2{=}CHCOOCH_3$	Strried at room temperature for eight hours	$CH_2{=}CHCOOSnBu_3$	63°	Almost quantitative
Ph_3SnOH	$C_6H_5COOC_2H_5$	No easter formed			
Ph_3SnOH	p-$NH_2C_6H_4COOC_2H_5$	No easter formed			
Ph_3SnOH	p-$NO_2C_6H_4COOC_2H_5$	No easter formed			

Ph - C_6H_6 - ; Bu - C_4H_9 -

(1) Purification of ethyl formate, ethyl acetate, butyl acetate, diethyl oxalate and diethyl malonate : The esters, ethyl formate (b.p.53°), ethyl acetate (b.p. 76 - 77°), butyl acetate (b.p. 125°), diethyl oxalate (b.p. 182°) and diethyl malonate (b.p. 198°)

were thoroughly washed first with saturated sodium bicarbonate solution and then repeatedly with water. They were dried over anhydrous $MgSO_4$ and finally distilled. The last two esters were distilled under reduced pressure.

(2) Preparation of ethyl chloro acetate :

Ethyl chloro acetate was prepared by refluxing chloroacetic acid with ethyl alcohol in presence of concentrated sulphuric acid. The water produced in this reaction was removed by azeotropic distillation, the residue left in the distilling flask was added to water when the ester separated as an oily layer. The layer was separated, washed with saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and finally distilled when pure ethyl chloro acetate, b.p. 141°, was obtained.

(3) Preparation of ethyl cyano acetate :

Ethyl cyano acetate was prepared according to the method described by Vogel (34)

(4) Preparation of tri phenyl tin hydroxide :

Ph_3SnOH was prepared by shaking an ethereal solution of tri phenyl tin chloride with 2N aqueous solution of sodium hydroxide. The white solid precipitated was filtered and washed thoroughly with water to remove sodium hydroxide and then with ether to remove any unchanged triphenyltin chloride or bis (triphenyl tin) oxide, which may be formed during the reaction Ph_3SnOH was dried in air.

(5) Preparation of tributyl tin hydroxide :

Bu_3SnOH was prepared by shaking tributyl tin chloride in ethereal solution with 2N aqueous NaOH. The ethereal solution was washed thoroughly with water. This solution was used in the reactions with esters after drying over anhydrous calcium chloride.

(6) Reaction of triphenyl tin hydroxide with ethyl formate 3.6 gms of triphenyl tin hydroxide was stirred in 10 ml ethyl formate for eight hours. Addition of excess of petroleum ether to the solution precipitated 0.5 gms of a white solid. The filtrate furnished 3.3 gms of the same compound on evaporation nearly to dryness and cooling. The product was crystallised from petroleum ether (m.p 201°), and identified as triphenyl tin formate by mixed melting point and IR spectrum.

(7) Reaction of tributyl tin hydroxide with ethyl formate :

8.2 gms of tributyl tin chloride was converted to tributyl tin hydroxide. The ethereal solution of the latter was refluxed with 15 ml of ethyl formate for five hours. Unreacted ethyl formate was evaporated off, the residue was treated with petroleum ether and filtered. The petroleum ether was evaporated off and the liquid was purified by distillation under reduced pressure (B.P. 127°-30°/3 mm). The distillate was identified as tributyl tin formate by comparison of IR spectrum with that of an authentic sample.

(8) Reaction of triphenyl tin hydroxide with ethyl acetate :

3.6 gms of triphenyl tin hydroxide was stirred in 10 ml ethyl acetate for eight hours. The solution was evaporated nearly to dryness when 3.95 gm of a white crystalline compound separated. The compound was purified by recrystallisation from petroleum ether (m.p 121°). The compound was identified as triphenyl tin acetate by mixed melting point and IR spectrum.

(9) Reaction of tributyl tin hydroxide with ethyl acetate :

3.2 gms of tributyl tin chloride was converted to tributyl tin hydroxide. The ethereal solution of the latter was refluxed with 15 CC ethyl acetate for five hours. The solution on evaporation furnished 3.3 gms of the crude product. On recrystallisation from petroleum ether pure tributyl tin acetate, m.p. 80-81° was obtained. The product was identified by mixed melting point with authentic sample.

(10) Reaction of triphenyl tin hydroxide with butyl acetate :

3.6 gms of triphenyl tin hydroxide was stirred with 10 ml butyl acetate. The solution was evaporated to dryness when 3.9 gms of a white solid was obtained which was recrystallised twice from petroleum ether to furnish pure triphenyl tin acetate, m.p. 121 -122°.

(11) Reaction of triphenyl tin hydroxide with ethyl mono chloro acetate.

3.6 gms of triphenyl tin hydroxide was refluxed with 2 ml carefully purified ethyl mono chloro acetate for 5 hours in 15 ml dry benzene.

The solution on concentration to a small volume and cooling in ice furnished 4.2 gms of a needle shaped crystalline solid. The solid was recrystallised twice from benzene petroleum ther mixture.

The compound was identified as triphenyl tin mono chloro acetate from its melting point (135°) and mixed melting point with authentic sample.

(12) Reaction of triphenyl tin hydroxide with ethyl cyano acetate :

3.6 gms of triphenyl tin hydroxide was refluxed with 3 ml of pure ethyl cyano acetate in 15 ml benzene for five hours. 0.72 gms of a white polymeric solid (m.p $>360^{\circ}$) was filtered off. The filtrate on concentration under reduced pressure furnished 1.1 gms of a polymeric compound (m.p $>360^{\circ}$) again. The filtrate was evaporated to dryness under reduced pressure then recrystallised from benzene when 2.3 gms of triphenyl tin cyano acetate (m.p.141°, no depression in mixed melting point determination) was obtained.

(13) Reaction of tributyl tin hydroxide with methyl acrylate :

1.5 gms of tributyl tin chloride was converted to tributyl tin hydroxide. Theethereal solution of the latter was stirred with 10 ml of methyl acrylate for eight hours. A small amount of white solid formed was filtered off. The filtrate on concentration gave a semi-solid mass which furnished 1.3 gms of a crystalline solid by cooling in ice. The solid was crystallised twice from petroleum ether when pure tributyl tin methacrylate (m.p. 63°, lit. value 63°) was obtained.

(14) Reaction of triphenyl tin hydroxide with diethyl oxalate :

3.6 gms of triphenyl tin hydroxide was refluxed with 4ml of purified diethyl oxalate in 15 ml of benzene for five hours. The insoluble polymeric solid (m.p >360°) was filtered off. The filtrate was evaporated nearly to dryness when 3.5 gms of a white compound crystallised out. It was purified by recrystallization twice from benzene - petroleum ther mixture (m.p. 127°)

Identification of the compound :

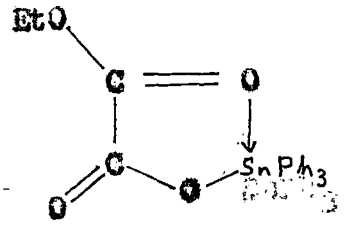
(i) Elemental analysis corresponds to (triphenyl tin) mono ethyl oxalate, $C_2H_5OCO.CO.OSnPh_3$

Analysis found : C = 55.42% ; H = 4.18% ; Sn = 24.39%

Calculated for

$C_{22}H_{20}O_4Sn$: C = 56.56% ; H = 3.86% ; Sn = 25.43%

(ii) The presence of two non equivalent - COO groups in the molecule is shown by ν as(OCO) absorptions at 1680 cm^{-1} and 1610 cm^{-1}. The 1610 cm^{-1} absorption can be attributed to - $COOSnR_3$ while the 1680 cm^{-1} absorption is certainly due to the - COOEt group. However, the lowering of νas(OCO) in the tin derivative compared to its position in normal esters (~ 1720 - 40 cm^{-1}) is indicative of intramolecular co-ordination as shown below :



(15) Reaction of triphenyl tin hydroxide with diethyl malonate:

3.6 gms of triphenyl tin hydroxide and 4 ml of diethyl malonate was refluxed in 15 ml benzene for five hours. The solution was heated to evaporate off benzene and the unreacted diethyl malonate was distilled off at 83-85° under reduced pressure. The residue (4.9 gm) was recrystallised from benzene when a white solid, m.p.139° was obtained.

Identification of the solid :

(i) Elemental analysis corresponds to (triphenyl tin mono ethyl malonate, $Ph_3SnOCO.CH_2COOC_2H_5$.

Analysis found : C = 57.26% ; H = 4.75% ; Sn = 24.38%

Calculated for

$C_{23}H_{22}O_4Sn$: C = 57.42% ; H = 4.5% ; Sn = 24.70%

(ii) IR spectrum shows the presence of $-COOC_2H_5$ group (1730cm^{-1}) and a carboxy group bonded to tin (1550 cm^{-1}). Unlike the oxalate derivative, no lowering of νas(OCO) of the ester group is observed here indicating the absence of co-ordination by the $-COOC_2H_5$ group.

BIBLIOGRAPHY

1. Jem-Hsi cho, Hau-Sheng Hsu, Hsu-Yu Cheng, Chang Lich Fan, Uan MuO and Chih Fu,	Chem.Abst. 65 (1966) 13733e
2. P.Duun and T.Norris,	Report No.269, Australian Defence Scientific Service, Defence Standard Laboratories (1964)
3. M.Vilarem and J.C.Maire,	Compt.Rend,262(1966)480
4. Japanese Patent,	Chem.Abstr., 65(1966)2298g
5. Japanese Patent,	Chem.Abstr., 65(1966)12240e
6. Japanese Patent,	Chem.Abstr., 69(1968)87136
7. Polish Patent,	Chem.Abstr., 68(1968)49776
8. U.S.Patent,	Chem.Abstr., 65(1966)12240b
9. B.F.E.Ford and J.R.Sams,	J.Organometal.Chem.,31(1971)47
10. R.C.Poller, J.M.R.Ruddick, B.Taylor and D.L.B.Toley,	J.Organometal.Chem.,24(1970)341
11. French Patent,	Chem.Abstr., 62(1965)16296a
12. M.Frenkel,D.Gertner, D.Wagner and A.Zilkha	J.Organometal.Chem.,9(1967)83
13. B.F.E.Ford, B.V.Léiengme and J.R.Sams,	J.Organometal.Chem.,19(1969)53
14. T.N.Srivastava,S.K.Tandon,	J.Prakt.Chem.,311(5)(1969)878.

15. H.C.Clark, R.J.O Brien and A.L.Pickard, J.Organometal.Chem.,4(1965)43

16. V.Peruzzo, G.Plazzogna and G.Tagliavini, J.Organometal.Chem.,40(1972)121

17. H.H.Anderson, Inorg.Chem.,1(1962)647

18. A.Henderson and A.K.Holliday, J.Organometal.Chem.,4(1965)377

19. E.Wiberg and Behringer, Z.Anorg.Allgen.Chem., (1964)290,328

20. Udo Christen and W.P. Neumann, J.Organometal.Chem.,39(1972)C58

21. H.G.Kuivila, Adv.Organometal.Chem.,1(1964)82.

22. R.E.Hester, J.Organometal.Chem.,23(1970)123

23. A.K.Sawyer and H.G.Kuivila, J.Org.Chem.,27(1962)610

24. A.K.Sawyer and H.G.Kuivila, J.Org.Chem.,27(1962)837

25. N.S.Vyazankin and V.T.Bychkov, Zhur.Obschehei Khim., 35(1965)634

26. D.L.Alleston and A.G.Davies, J.Chem.,Soc.,(1962)2050

27. A.K.Sawyer and H.G.Kuivila, Chem.and Ind.,(1961)260

28. A.S.Mufti and R.C.Poller, J.Chem.Soc(c)(1967)1362;1767

29. R.Okawara and E.G.Rochow, J.Am.Chem.Soc.,82(1960)3285

30. Z.M.Rzaev and Kochkin, Dokl.Akad.Nauk(English translation) consultants Bureau, Vol.172,No.103, January (1967)

31. G.Plazzogna, V.Peruzzo and G.Tagliavini, J.Organometal.Chem.,16(1969)500

32. H.H.Anderson, Inorg.Chem.,3(1963)912

33. H.H.Anderson, J.Org.Chem.,19(1954)1766

34. A text book of practical organic chemistry, A.I.Vogel, Longmans, London (1961)

35. M & T International, B.V. Neth Appl, Chem.Abstr., 81(1974)91732b