INTERACTION OF ORGANOSTANNOXANES WITH SOME KETO ACIDS.

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

By
Hiranmay Biswas

DEPARTMENT OF CHEMISTRY
University of North Bengal
Raja Rammohunpur, Darjeeling, Pin – 734430, India.
1995

ST - VERF

North Bengal University Library,
Call No. .....
Acc. No. .....

STOCK TAKING - 2011

Ref.
547.037
B623i

112557
19 DEC 1995

DEDICATED TO THE MEMORY OF MY FATHER

ACKNOWLEDGEMENT

This thesis embodies the results of the investigations undertaken by the author at the Department of Chemistry, North Bengal University, Dist. Darjeeling, W.B., India, under the invaluable guidance and active supervision of Professor B.Majee and the author deems it a proud privilege to convey his deepest sense of gratitude to Prof. Majee at the very first opportunity.

The author gratefully acknowledges the help received from Dr. P. Bandopadhyay, Lecturer, Department of Chemistry, NBU, at the various stages of the work.

The author expresses his indebtedness to Dr.T.K.Chatterjee, Registrar, NBU, Dr. B. Basu, Dept. of Chemistry, NBU, Dr. K. K. Das, Dept. of Chemistry, Jadavpur University, Dr. T. S. BasuBaul, RSIC, NEHU and Sri D. Banerjee, Dept. of Chemistry, Berhampore Women's College for their kind help.

The author thankfully acknoledges the help and encouragement received from Dr.S.K.Saha, Dr.S.K.Sarkar, Dr.D.P.Boot, Dr.P.K.Mondal and Sri A.K.Roy, all of North Bengal University, during the progress of the work.

The author wishes to extend his warmest thanks to all his fellow workers, specially to Dr.A.K.Kumar. Dr.Subhasish Mitra and Dr.(Miss) Rupa Bhowmik for their help in experimental work.

The author takes this opportunity to extend his heartiest thanks to all the teachers and staff members of the Department of Chemistry and also to the authorities of North Bengal University. Special thanks are due to the staff members of the university library for their cooperation.

Thanks are also extended to the authorities of CDRI, Lucknow and RSIC, NEHU for help in analytical and spectroscopic work.

The author expresses his gratitude to the UGC for awarding a Teacher Fellowship and the authorities of A. C. College, Jalpaiguri, for granting study leave, which enabled him to undertake the research work.

Above all, the encouragements received from his family members and their sacrifices in relieving him, albeit temporarily, from his duties and responsibilities towards them, are gratefully remembered by the author.

Hiranmay Biswas

(HIRANMAY BISWAS)

Dept. of Chemistry,
A. C. College, Jalpaiguri,
PIN-735101, INDIA.

PREFACE.

Along with the tremendous growth in the industrial, agricultural and other applications of organotin carboxylates, theoretical and structural interests in this class of compounds have continued to grow during the last few decades. It has also been suggested that their practical applications are significantly connected with their structures and great interest for the study of organotin carboxylates has evinced among organotin chemists.

In almost all organotin carboxylates, unless dictated by steric factors, the solid state structure consists of carboxylate bridged polymers. However, a bonding mode alternative to carboxyl bridging, leading to either intra- or intermolecularly coordinated structure, may become possible if the carboxyl moiety contains a substituent carrying a suitably placed donor atom. This possibility has, in recent times, generated tremendous interest in the solid state structure of organotin derivatives of carboxylic acids containing an additional potential donor site. Among many such organotin carboxylates the derivatives of substituted benzoic acids, pyridine carboxylic acids and some amino acids have received much attention. But keto carboxylic acids, though apparently capable of forming intramolecularly chelated ring structure, have not received adequate attention. This has prompted

us to attempt the synthesis of the organotin derivatives of α-keto carboxylic acids and to investigate their spectral properties.

The methods employed for the preparation of the organotin keto carboxylates are (i) reaction of the Na-salts of the acids with organotin halides and (ii) reaction of the free acids with organotin oxides. While the reaction (i) proceeded as expected giving organotin carboxylates, the reaction (ii) produced a unique class of addition compounds, in addition to the carboxylates, depending on the reaction condition.

The results of these investigations preceded by a comprehensive survey of organotin chemistry, are presented in this thesis.

In Chapter-I a brief review of the organotin chemistry, with special emphasis on both the donor and acceptor behaviour of the organotin compounds has been presented. The formation of addition complexes through donor-acceptor interactions has been discussed in some detail.

The Chapter-II consists of a review on organotin carboxylates, emphasis being given on the structural aspects. The various structural possibilities have been highlighted citing extensive examples from the literature.

The synthesis and characterisation of a number of new

organotin α-keto carboxylates [$R_nSn(OCOCOR')_{4-n}$, n = 3, R = n-Bu, Ph, $PhCH_2$ and n = 2, R = Me, n-Bu, n-Oct; R' = CH_3, Ph, $PhCH_2$] constitute the subject matter of Chapter-III. On the basis of spectroscopic data the tin atom, in some of the organotin α-keto carboxylates, has been shown to have attained a coordination number of six through involvement of the carboxyl moiety in both inter- and intramolecular coordination. The formation of a few carboxylato diorganotin hydroxides [$R_2Sn(OCOCOR')OH$, R = Me, n-BU, n-Oct, Ph and R' = CH_3, $PhCH_2$] are also reported in this chapter.

In the last chapter, the isolation and transformation of a few carboxylic acid adducts of the general formula $R_3SnOH.R'COCOOH$ [R = n-Bu, Ph, $PhCH_2$; R' = CH_3 and R = n-Bu, R' = $PhCh_2$], formed with organostannoxanes/ triorganotin hydroxides, are reported. The isolation of these unique compounds is the most significant feature of this work, since an understanding of the formation and structure of these compounds may pave the way to design new carboxylate ligands, with which one can, possibly, isolate the intermediate complexes believed to be the first step in the reaction between the stannoxanes and carboxylic acids.

CONTENTS.

CHAPTER-I

DONOR-ACCEPTOR CHARACTER OF TIN COMPOUNDS.

Donor -Acceptor Character of Tin Compounds .

I.1 *Introduction :*

During the last three decades the coordination chemistry of organotin compounds has experienced tremendous growth and still continues to grow, due mainly, to theoretical and structural interests as well as due to the role of these coordinated species as intermediates in various synthetic reactions and interesting biocidal properties in many of these compounds. The concept of organotin compounds as Lewis acids is of fundamental importance to an understanding of many problems of structure and reactivity.

The acceptor strength of the group IVB elements follows the sequence Sn >> Ge >Si. Tin compounds form complexes with Lewis bases much more readily, though to a lesser extent in the lower oxidation states, than Si and Ge, which behave as acceptors only when four strongly electronegative substituents are bonded to the metal atoms. The remarkable Lewis acidity of tin is attributed primarily to the availability of d-orbitals of sufficiently low energy, compared to the lighter group IVB elements. Addition complexes containing both tetravalent and divalent tin as acceptors are well characterised. Some of the important features of these compounds are discussed here in brief. Addition complexes of tin halides, though not organotin compounds in the strict sense

of the term, are also included in the discussion for the shake of completeness and comparison.

Beside the dominating acceptor character, organotin compounds often behave as interesting donors, an aspect not so well recognised.

In the bivalent state, tin should be capable of showing donor properties, at least in principle, due to the presence of the 5s-lone pair. However, the σ-donor strength of the 5s-lone pair in Tin (II) should be small, because the ability of an atom, possessing a lone pair, to act as donor, decreases with the increase in atomic number. Tin (IV), on the other hand, is devoid of any lone pair and as such the donor property in Tin(IV) compounds arises from M.O.'s delocalised over two or more atom centres. A short review on the donor abilities of organotin compounds is also presented here.

I.2.1. *Tin (IV) Compounds as Acceptors* :

I.2.1A. Relative Acceptor Strength :-

In the most familiar tetravalent state tin almost invariably behaves as a hard acid or class A acceptor[1,2] because of its small size, high positive charge, absence of any outer electron easily excitable to higher states and presence of empty

5d orbitals. The d-orbitals are of sufficiently low energy for them to be frequently used in bonding so that tin can readily expand its coordination number above four. Consequently, detailed studies regarding the acceptor properties of Sn(IV) compounds have been made with R_nSnX_{4-n} (where, n = 0,1,2,3,4; R = alkyl/aryl groups, and X = halogen, pseudo halogen, AcO, NO_3 etc.) and a large number of their complexes with N and O containing ligands are known[9-15].

It is well known that the tin tetrahalides have a marked tendency to form thermodynamically stable six coordinate adducts. As the halogen atoms are successively replaced by less electronegative organic groups the acceptor strength of tin declines, but in general, the stability of organotin complexes seems to indicate that tin retains its class A character[9]. Using the difference between the dipole moments in dioxan and hexane as a measure of complex forming ability, the following sequence for acceptor strengths was obtained[11].

$$SnCl_4 > PhSnCl_3 > Ph_2SnCl_2 > Ph_3SnCl > Bu_3SnCl.$$

The same sequence has also been found from both potentiometric and conductometric studies of penta-coordinated anionic complexes in acetonitrile[12].

The coordinative bond strength in complexes between several alkyltin chlorides and 2,2'-bipyridyl, as derived from

thermodynamic data is found to decrease in the order[11] :

$$SnCl_4 > n\text{-}BuSnCl_3 > (CH_3)_2SnCl_2 \simeq (C_2H_5)_2SnCl_2 > (n\text{-}Bu)_2SnCl_2.$$

The acidity constant of $SnCl_4$[11] on substitution of one chlorine by an organic substituent is decreased by a factor of

$$4x10^3(n\text{-}Bu) > 1.6x10^3(Me) > 5x10^2(Ph).$$

The same trend is observed in the stability of the hexa-coordinate organotin anions[11] , where the sequence

$$SnCl_6^{-2} > RSnCl_5^{-2} > R_2SnCl_4^{-2} >> R_3SnCl_3^{-2}$$

is observed and there are no reports on the existence of $R_4SnCl_2^{-2}$ ions. Anionic chloride or bromide complexes are also obtained more easily with PhSn(IV) than with MeSn(IV)[11]. The quantitative relative acceptor strength of three organotin trichlorides and $SnCl_4$ vs aniline bases[11] was found to be

$$SnCl_4(670) > PhSnCl_3(12) > MeSnCl_3(?) > n\text{-}BuSnCl_3(1).$$

For the tintetrachlorides it was found that complexes were formed with decreasing strength as the halide changed, in the sequence[11] F > Cl > Br > I. The quadrupole splitting in the Mossbauer spectra of Me_3SnX compounds with a series of donors was also interpreted in terms of the acceptor strength of the Me_3SnX moiety and showed that the nature of the X-substituent influenced this strength in the order[11] $F^- > Cl^- > Br^- > OH^-$. The tendency for complex formation by organotin halide systems was also studied by paper electrophoresis and anion exchange paper chromatography. The

results indicated decreasing complex stability as a function of the halogen substituents[11] : $F^- >> Cl^- > Br^- > > Br^- > I^-$

On the basis of the foregoing observations, the variation in the acceptor strength of the R_nSnX_{4-n} compounds can be represented conveniently by the following tabular form[16] :

Decreasing acceptor strength of R_4SnX_{4-n} →

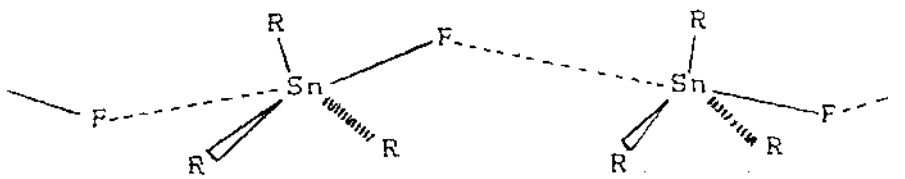
X	NCS F >> Cl > Br > I
R	Ph > Me > Et > Pr > Bu
n ↓	SnX_4 > $RSnX_3$ > R_2SnX_2 > R_3SnX > R_4Sn

I.2.1.B. Consequences Of Acceptor Character :-

(i) Intermolecular association :

As a manifestation of this remarkable acceptor property, tin increases its coordination number above four in solid organotin halides and pseudohalides by extensive intermolecular association[17,18]. These compounds are monomeric with tetrahedral tin atoms, only in the vapour phase or in dilute solutions in non-conducting solvents[17].

X-ray and Mossbauer studies have shown that triorganotin fluorides consist of planar organic groups and fluorine atoms arranged alternately, with non-linear asymmetric Sn—F----Sn bridges [I][16].



I

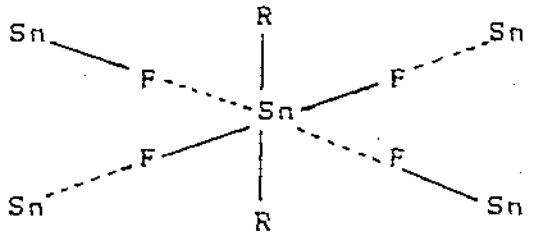
The lower alkyltin chlorides also have similar structures whereas, triphenyltin chloride contains discrete monomeric species with four coordinate tin. ^{35}Cl NQR data suggest that triorganotin chlorides with larger alkyl and aryl groups undergo phase change to associated structures at lower temperatures[15].

Due to their weak Lewis acidity and large size of the halogen, triorganotin bromides and iodides favour a monomeric tetrahedral structure in the solid state. ^{119}Sn Mossbauer spectroscopy indicates that at $80^{o}K$ the lower trialkyl tin bromides and iodides adopt associated structures containing penta-coordinate tin[16].

In the solid triorganotin pseudohalides, the pseudohalogen group bridges planar R_3Sn units to form infinite linear or zig-zag chains[16]. Even R_3SnX compounds (where X = ClO_4^-, NO_3^-, BF_4^-, AsF_6^-), which may be thought as being ionic in the solid state are bridged polymers according to I.R. data[12].The sterically hindered triorganotin halides and pseudohalides having bulky organic groups are monomeric with tetrahedral tin atoms.

Diorganotin difluorides consist of infinite two dimensional

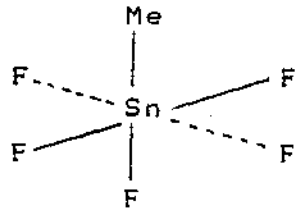
sheets of tin and fluorine atoms, with each tin linearly bridged to its four neighbours and having trans-octahedral tin atom configuration [II][16].



II

In other dialkyltin dihalides and pseudohalides the intermolecular association is weaker and the tin atom has distorted trans-R_2SnX environment[16]. Ph_2SnCl_2 contains distorted tetrahedral molecular species with weak or no intermolecular association[19].

The I.R. and Raman spectra of methyl tin trifluoride are indicative of both bridging and terminal halogen and a polymeric structure [III] containing octahedral tin in the solid phase[20].



III

The vibrational and NQR (^{35}Cl and ^{81}Br)[16] spectra of the other

$MeSnX_3$ (X = Cl,Br,I) compounds are indicative of similar associated structures in the solid state.

(ii) Solvation :-

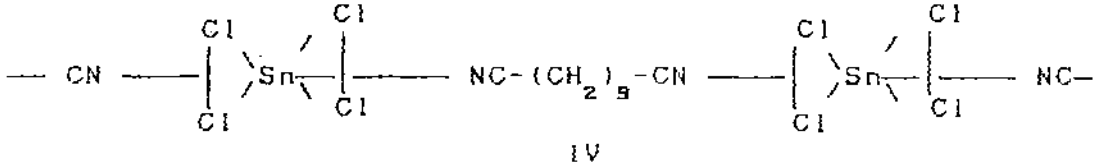
Addition of solvents to the R_nSnX_{4-n} compounds usually destroy their polymeric structures and produces solvated organometallic complexes. The ability of the coordinating solvents to act as ligands has been studied mainly by PMR and Mossbauer spectroscopy. In the NMR data, the increase of the tin-proton coupling constants $J\ ^{117/119}_{Sn-C-H}$ was thought to be related to the changes in the hybridisation around tin on changing from the tetrahedral sp^3 state in the pure organotin compound to a trigonal bipyramidal configuration in the penta-coordinated tin complexes and to an octahedral configuration in the hexa-coordinated tin compounds[11]. The relative nucleophilic character for a series thus established is : DMSO ~ DMF > HOH > Py > MeOH > MeCOMe ~ MeCOOMe > Dioxan > MeCN ~ MeCOOH > $MeNO_2$ > PhCl ~ CCl_4. It should be noted that O- or N-donor solvents solvate organotin compounds more efficiently than S- and P-donors, e.g., Et_2S < Et_2O ; DMTA < DMA ; HMTAPT < HMPTA ; Bu_3P < Py etc. This behaviour is typical for hard Lewis acids.

The quadrupole splitting observed in ^{119}Sn Mossbauer studies of the interaction between n-Bu_2SnCl_2 and a number of organic coordinating solvents yielded the following sequence for their

relative nucleophilicity : DMSO > DMF > HMTAP > DME > THF > DEF > Et_2O[11].

(iii) Formation of addition complexes :-

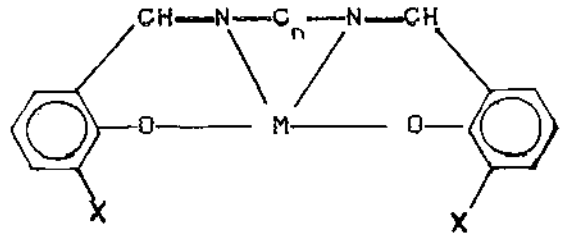
The tin tetrahalides form both ionic and neutral adducts with an enormous range of monodentate ligands and most of these have the composition $SnX_4.2L$, though 1:1 adducts have also been reported[21]. The 1:2 complexes have octahedral geometry[22], whereas, 1:1 complexes are trigonal bipyramidal. With some monodentate ligands both 1:2 and 1:1 complexes may be obtained, e.g. $SnX_4.2PBu_3$ and $SnX_4.PBu_3$[23,24]. Bidentate ligands generally form 1:1 complexes having octahedral tin atom geometry[25-30]. A bidentate ligand can also act as a bridge between SnX_4 units [IV][31].



IV

However, some bidentate ligands, e.g. o-amino benzonitrile[32], or amide derivatives of hydroxybenzoic and anthranilic acids[33], give $SnX_4.2L$ complexes as well as $SnX_4.L$ complexes. Many bidentate Schiff-bases act uniformly as monodentate ligands forming $SnX_4.2L$ type complexes[26b,34,35]. Transition metal derivatives of polydentate Schiff-bases [V] may act as bidentate ligands and add on to tin tetrachloride producing bimetallic complexes as 1:1

addition products[95,96].



[where, M = Cu, Ni ; C_n = $-CH_2-CH_2-$, X = H , -COOH.

C_n = $-C_6H_4-$, X =H.]

V

In the intra molecularly coordinated complex dichloro bis (ethyl 3-oxo butanoato)tin(IV) [$Cl_2Sn(CH_3COCH_2COOEt)$], the β-keto ester acts as a bidentate ligand coordinating through the carbonyl O-atoms and the environment around tin is slightly distorted octahedral[97]. Pyrazole derivatives behaving as tridentate ligands can react with SnX_4 producing compounds of the type $Sn(L)X_3$ [where, L = tris-(3,5 dimethyl poly pyrazolyl)borate ; X = Cl, Br] having hexacoordinated tin atoms[98a,b].

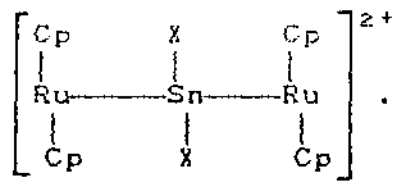
Acetate and haloacetate esters can act as monodentate ligand and add on to $SnCl_4$ giving trigonal bipyramidal as well as octahedral (both cis and trans) complexes[44].

In crown ether derivatives, such as, $SnCl_4(18\text{-crown-}6).2H_2O$, X-ray studies have shown that the tin atom environment consists of

octahedral $SnCl_4(H_2O)_2$ units and the ether molecule is only hydrogen bonded to the water molecule[40-42]. Additional water or other solvent molecules may be associated through hydrogen bonding[41].However, Atwood et.al. have interpreted X-ray data suggesting that the ether acts as a bidentate ligand[43].

In ionic adducts the tin:ligand ratio may be other than 1:2 or 1:1,[23,45-48] e.g., 2 $SnCl_3.PBu_3$[23] or $(Cp)_2Ru.1.5\ SnX_4$ (where, Cp = cyclopentadiene and X = Cl,Br)[45], because these complexes contain both tetrahedral and trigonal bipyramidal tin moieties, one in the cationic and the other in the anionic part [VI,VII].

$[SnCl_3(PBu_3)]^+(SnCl_5)^-$;



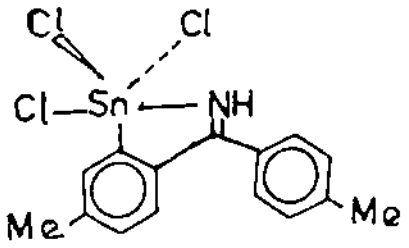
$. 2(SnX_5)^-$.

VI VII

The compounds $4XeF_6.3SnF_4$ and $3XeF_6.4SnF_4$ are intermediate compounds with both $Xe_2F_{11}^+$ and XeF_5^+ cations present[49].

Mono-organotin compounds, $RSnX_3$ also show a marked tendency to increase their coordination number from 4 to 6 or even 7, the lowering in the acceptor strength of tin becoming striking only when weak donors are involved, such as alkyl sulfides, which gives adducts with $SnCl_4$ but not with $PhSnCl_3$. With monodentate ligands there are few examples of five coordinate 1:1 complexes of the

type $RSnX_3.L$, containing a trigonal bipyramidal tin atom[50,51,62,69,104a], although these are far less common than the octahedral adducts $RSnX_3.L_2$ (L = monodentate donor). $MeSnBr_3.DMF$ [50] and $(Ph_4As)^+(MeSnCl_4)^-$ [51] are examples of 1:1 complexes having trigonal bipyramidal structure with Me groups occupying an equatorial site. A similar geometry was also found in the intra molecularly penta coordinate ketiminotin trichloride [VIII][52] and ester tin trichlorides, $ROCO(CH_2)_2SnCl_3$ (R = H,Me,Et,Bu, Ph)[59].



VIII

The six-coordinate complexes may be anionic, e.g., $RSnX_5^{-2}$ or neutral, e.g., $RSnX_3.bipy$ and are readily formed with a wide range of ligands[25,40,54-62,64], both mono and bidentate.

In some intra molecularly coordinated mono organotin complexes, such as $PhSnT_3$ (T = tropolonate) [65], $BuSn(OCOR)_3$ (R = Me,Et)[66], $MeSn(SCSNEt_2)_3$[67], $BuSn(OX)_3$ (OX = oxinate) and $MeSn(NO_3)$[68], involving potentially polydentate ligands, the coordination number of tin is seven. In intra molecularly coordinated poly pyrazolyl

borate derivatives $RSn[(pz)_3BH]X_2$ [where, pz = pyrazolyl moiety , and X = halogen or pseudohalogen], however, only coordination number six is attained[38,69] , the ligand behaving as a tridentate one (though, potentially hexadentate in this case).

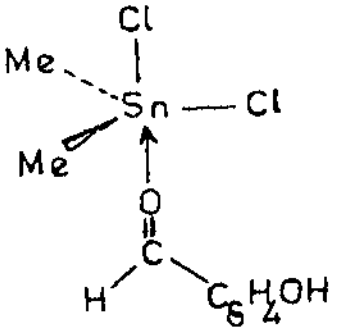
No example of mono-organotin trihalide or pseudohalide adducts with a higher coordination number than six have been demonstrated by X-ray crystallography, although a number of 1:4 adducts ,such as, $MeSnI_3.4py$[8] or $PhSnCl_3.4$(morpholine)[70] have been synthesised.

The R_2SnX_2 compounds are able to form complexes having five, six or seven-coordinate tin atoms. Generally, coordination saturation at tin is reached at six, as $R_2SnX_2.L_2$ (L = monodentate ligand, L_2 = bidentate ligand, X = Cl, Br, I, NCS, AcO, CF_3CO_2) forming octahedral complexes with a wide range of organic donors, the R groups being usually trans to each other[25,54,64,71-84]. Mossbauer spectroscopy has indicated that certain octahedral R_2SnX_2 adducts, e.g., R_2SnX_2.bipy [where X = Cl, Br, R = furyl, thienyl[85]; X = Cl, R = p-tolyl [69]; X = NCS, R = Ph[86]], Ph_2SnCl_2.(2-amino methyl pyridine)[87] contain a cis disposition of the R groups.

However, the formation of $R_2SnX_2.L_2$ complexes must a priori proceed via a five coordinate $R_2SnX_2.L$ species[88] and the existence of a number of penta-coordinated complexes having a cis $R_2SnX_2.L$

geometry have been demonstrated by X-ray crystallography. The anion in quinolinium dimethyl trichlorostannate $(C_9H_8N)^+(Me_2SnCl_3)^-$ contain a distorted trigonal bipyramidal tin atom with the two Me groups occupying equatorial positions[89]. Salicylaldehyde forms a 1:1 complex with Me_2SnCl_2, where X-ray studies revealed a similar tin atom geometry, with two Me groups occupying equatorial positions of a trigonal bipyramid [IX][90]. With some ligands both the penta-coordinated (1:1) and hexa-coordinated (1:2) complexes of diorganotin dihalides have been isolated[76,91-98].

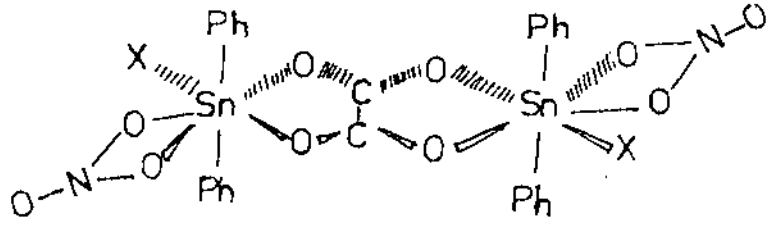
Dimethyltin diisothiocyanate forms a 1:1 adduct with terpyridyl, in which the tin atom is occupying a seven coordinate



IX

pentagonal bipyramidal geometry with trans organic groups ; the five nitrogen atoms, two from the NCS groups and three from the

tridentate ligand are situated in the equatorial plane[94]. X-ray diffraction studies have shown that $Ph_2Sn(NO_3)_2.L.CHCl_3$ (where, L = cis-$Ph_2P(O)CH=CHP(O)Ph_2$) have a pentagonal bipyramidal structure. However, trans-$PH_2P(O)CH=CHP(O)Ph_2$ acts as a bidentate bridging ligand joining two six-coordinate tin atoms in $[Ph_2Sn(NO_3)_2]_2.L.2H_2O$[95]. $[Ph_2Sn(NO_3)(X)]_2C_2O_4$ (where, X = Ph_3AsO, Pr^n_2SO), obtained by the addition of X, at room temperature under nitrogen, to an acetone-chloroform solution of $Ph_2Sn(NO_3)_2$, also have been indicated by X-ray studies, to contain a seven coordinated tin atom having a slightly distorted pentagonal bipyramidal geometry with two Ph rings in axial position and the nitrate, oxalate and X in the equatorial plane [X][96,97].



X

X = Ph_3AsO, Pr^n_2SO.

Although the pyrazole derived ligands [$RB(pz)_n$], (where R = H or a non coordinating substituent, pz = pyrazole or its C-substituted derivative and n = 2-4) are potentially polydentate, (tetra-, hexa- or octa-dentate depending on the value of n), the tin atom in their di organotin derivatives, $R_2Sn(L)X$[38], is only hexa

112557

13 DEC 1995

NORTH BENGAL
University Library
Raja Rammohunpur

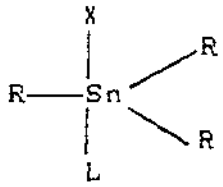
coordinated. Similar intra molecularly hexa coordinated diorganotin complexes are also formed by trihalo β-diketones[99]. Diphenyltin diisocyanate is unusual in that it forms a 2:1 adduct $[Ph_2Sn(NCO)_2]_2$.bipy with bipyridyl. It is believed to contain a bridging bipyridyl group and pentacoordinated tin atoms[98].

Although organotin carboxylates unlike organotin halides or pseudohalides are reluctant to form addition complexes, diorganotin dicarboxylates are known to form 1:1 adducts in solution[100]. A few well authenticated examples of hydrate adducts of diorganotin dicarboxylates have been reported in recent years[101,102]. Lockhart et.al. have reported an ionic acetate adduct of dimethyl tin di acetate[103]. In these complexes[101-103] the tin atom is seven coordinate with pentagonal bipyramidal environment.

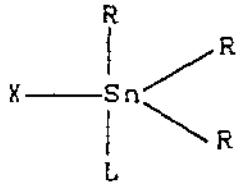
The R_3SnX compounds show marked difference from their mono- and di-organotin analogues in that 1:1 adducts are formed. The generally weak acceptor strength of R_3SnX favours an increase in coordination number of the tin atom to five, by reaction with a monodentate ligand to form a trigonal bipyramidal complex in which the three organic groups are situated in the equatorial plane. X-ray studies of several $R_3SnX.L$ compounds [where X = NO_3, L = Ph_3PO, Ph_3AsO, PyO[105,106]; X = Br, L = QuinO, Ph_3PO[107,108]; X =

Cl, L = LutO, $(Me_2N)_2CO$[109,92]) have shown the tin atom to have the trigonal bipyramidal geometry [XI]. The tri organotin pseudo halides also behave like their halide analogues, producing 1:1 adducts with monodentate ligands[110]

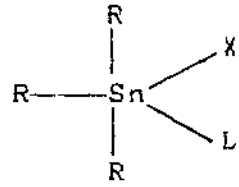
With potentially bidentate ligands the tri organotin halides still prefer to form five coordinate adducts[57,80-82,87,111,112], utilising only one of the donor groups as in $Ph_3SnCl.Ph_2P(O)CH=CHP(O)Ph_2$[113]. However, in some $R_3SnX.L$ complexes involving bidentate ligands X-ray studies suggest chelation and cis-geometry [XII] around the tin atom[114-116]. A third structural possibility i.e. the meridional structure XIII has been suggested for the cationic complexes $[R_3Sn(Ch)]^+[BPh_4]^-$, (where Ch is a chelating ligand) on the basis of Mossbauer studies[117].



XI



XII



XIII

The triorgano tin isocyanates and isothiocyanates are stronger Lewis acids than their halide counterparts and the IR spectra of $Ph_3SnNCX.DMO$ (where X = O,S and DMO = dimethyl oxamide)[118] and $Me_3SnNCS.phen$[119] are indicative of octahedral tin atom configuration in these complexes. The 1:1 adducts of Me_3SnCl with

2,2'bipyridyl is also believed to contain 6-coordinate tin on the basis of IR spectra[119]. However, no example of octahedral triorgano tin halide or pseudohalide complex has yet been demonstrated crystallographically. Triethyl tin chloride is known to form the unusual $2Et_3SnCl.L$ complexes with dimethyl-,diethyl- and trimethyl amine, though the normal 1:1 adducts are also formed with the first two ligands[120].

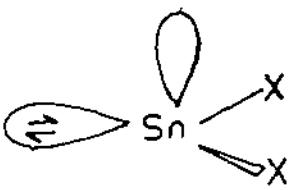
Both mono and bidentate ligands have been reported to form five coordinate adducts with triphenyl tin trihalo acetates[121,122]. X-ray data for the polymeric adduct, triphenyl tin(IV) 8-quinolyloxyacetate hydrate[123] also suggest a distorted trigonal bipyramidal tin atom geometry involving coordinated water molecule.

Tetralkyl tin compounds show no tendency to increase their coordination number owing to their weak Lewis acidity, conferred by the four electron releasing alkyl groups. However, Beattie has indicated that besides the electronegativity of the groups attached to tin other factors may affect the acceptor properties[4] and it seems possible that compounds with four perfluoro-organic groups joined to tin, would interact with suitable donors, since it is known that the electronegativities of the CF_3 and C_6F_5 groups are comparable with that of bromine[124,125]. A coordination

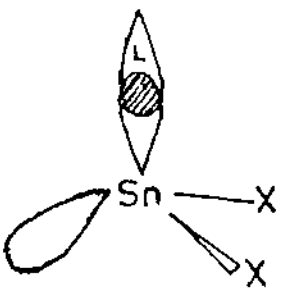
stage has been proposed for the abnormal halide ion-catalised hydrolysis of $R_{4-n}Sn(C_6H_5)_n$ compounds[126], as also for the acid mediated additions of alkenyl tributyl stannane to aldehydes and substituted aldehydes[127-131]. It has been claimed that trimethyl(trifluoro methyl)tin forms a 1:1 adduct with hexamethyl phosphoric triamide (HMPTA) and that this may be isolated in the solid state[132]. The addition of Sn_2Me_6 to alkenes and alkynes in the presence of $Pd(PPh_3)_4$[158,159] is also most likely to involve initial donation from the π-bonding orbital of the hydrocarbons followed by cleavage of the Sn-Sn bond. The reactions of $R_3Sn\text{-}SnR_3$ with Li-metal, alkyllithium, grignard reagents and NaOR are also instances of the electron acceptor ability of the σ(Sn-Sn) bond[135].

1.2.2. Sn(II) *Compounds as Acceptors* :

Covalent SnX_2 compounds, having essentially sp^2 hybridisation, have an empty p-orbital, of similar energy to those used in bonding, at right angles to the plane of the molecule [XIVa], and should act as monofunctional acceptor towards suitable monodentate ligands to form compounds of the type $SnX_2.L$, by the overlap of lone pair orbitals on the ligand with the empty p-orbital of the Sn-compound, causing a distortion towards sp^3 hybridisation [XIVb].



XIVa



XIVb

This acceptor tendency makes most Sn(II) compounds polymeric. Structures of the oxide, sulfide, selenide, chloride and sulfate reveal this[196]. Although many monomeric organotin(II) compounds have been reported in the older literature, the R_2Sn compounds exist only as unstable intermediates which self react to form cyclic oligomers, unless the R group is π-cyclopentadienyl or strongly sterically hindering[16]. The polymerisation is caused by the overlap of the lone pair orbital on a monomer with the empty p-orbital of an adjacent tin atom.

The stannous ion with empty 5p and 5d orbitals can also act as an acceptor towards certain ligands. The complexes would be formed by overlap of lone pair orbitals on the ligands with the empty hybrid orbitals on tin. In view of the small energy separation between the s and p orbitals in the stannous ion all p orbitals should be included in the hybridisation and the sp^3

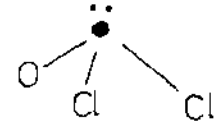
hybrid configuration should be very stable. The involvement of d-orbital in the hybridisation would appear to be less likely due to greater s-d energy separation.

Most of the available evidence does suggest that the stannous ion is a class A acceptor and the order of stability of the complexes formed with halide ligands is $F^- >> Cl^- > Br^- > I^-$. The trifluorostannate(II) ion has been shown to be a very stable species[196], and to be the strongest tin(II) halide complex. IR and Raman spectra suggest that the trihalostannate(II) ions have a pyramidal structure based on sp^3 hybridisation of the tin(II) orbitals[197,198].

For ligands other than halides, the order of stability of complexes formed by type A acceptors $OH^- > NH_3 > RS^- > H_2O$ etc. may not be exactly followed by the stannous ion, because of the probability[196] that the lone pair 5s orbital is strongly antibonding with respect to certain ligands such as NH_3, H_2O, and the CN^- ion. A spectroscopic study of the tin(II) thiocyanate complexes has shown that the nitrogen atom of thiocyanate is the donor atom and this provides further evidence for the A type acceptor behaviour of the stannous ion[196].

A number of adducts of tin(II) compounds with monodentate oxygen and nitrogen donors, such as, water, acetic acid, dioxan, sulfoxides, DMF, NH_3, py, amines, amine-N-oxides etc. are

known[136,139,140]. Spectroscopic study of dihalo bis-(p-toluidine) tin(II) compounds has suggested that the tin-nitrogen bonds are relatively weak[136]. Beside the usual 1:1 addition compounds, some of these ligands may form complexes with varying tin to ligand ratio, e.g. in NH_3 adducts of SnX_2 (X = Cl,Br,I) the mole ratio may be as high as 1:9[136]. In the 1:1 complexes the tin atom acts as a monofunctional acceptor making use of the empty p-orbital in its valence shell in complex formation. Often, the first material to be precipitated from the solution of a tin(II) compound in a donor solvent is a polysolvated material,from which the 1:1 complex can usually be obtained[136]. This suggests that the tin is acting primarily as a monofunctional acceptor and that further donor molecules are taken up mainly for lattice packing purposes. The crystal structue of tin(II)chloride dihydrate shows that only one of the solvent molecules is bonded directly to the tin atom having a pyramidal environment [XV][136].



XV

The second water molecule in the structure forms hydrogen bond

with the water molecule bonded to the tin atom and can be removed by careful dehydration at $80^{o}c$[136]. Other 1:1 complexes are believed to have similar structures[139,140].

The only known addition compounds formed with sulfur ligands are the thiourea and tetramethyl thiourea adducts[136]. From X-ray studies, diacetato bis-(thiourea)tin(II) has been shown to have a square-pyramidal structure, the tin atom being bonded to two thiourea S atoms and two carboxylate O atoms,whereas, in tetrabromo pentathiourea ditin(II)dihydrate, $(SnBr_2)_2[S=C(NH_2)_2]_5.2H_2O$ both the tin sites have trigonal pyramidal configuration[141]. A tin(II)fluoride-hydrofluoric acid complex, $SnF_2.2HF$, containing a halogen donor is known[136].

4 coordinated complexes of the type $SnX_2.L_2$ (where L = monodentate and L_2 = bidentate ligand) are frequently formed by $Sn(SO_3Cl)_2$[142], tin halides and isothiocyanate[104b,140,143-146]. 1:1 complexes with many bidentate Schiff's bases, semicarbazones and thiosemicarbazones with $SnCl_2$ are also known[147-149]. But their structures are not very well authenticated.

In the 2:1 addition product of $SnCl_2$ with 18-crown-6 ether formulated as $[SnCl(L)][SnCl_3]$ and in $[SnCl(L)][ClO_4]$[150], X-ray crystallography has revealed that the tin in the cationic moiety occupies a hexagonal pyramidal site, being bonded to all six crown ether oxygens and the chlorine atom in an axial position.

In the pyruvic acid thiosemicarbazone (HL) derivative $Sn^{II}(L)Cl$[151], the tin atom is five coordinate due to intra molecular coordination by the tetradentate ligand. The tin(II) poly(1-pyrazolyl)borates $[(pz)_{4-n}BR]_mSnCl_{2-m}$ (where, Hpz = pyrazole or its C-substituted derivative ; R = non coordinating substituent ; n = 0-2 and m = 1,2)[152] are interesting due to the fact that in these compounds the effective coordination number of Sn(II), assigned on the basis of ^1H NMR data, can be five, six or even seven, obviously through the involvement in intra molecular coordination, of the N atoms of the pyrazolyl moiety.

I.3 *Donor Property Of Tin Compounds :*

From the forgoing discussion it is apparent that tin compounds almost universally behave as acceptors, unless the substituents bonded to tin atom are donors themselves. As for example, the π-orbital of the cyclopentadienyl part in bis-(cyclopentadienyl)tin(II)[153] acts as donor, forming charge-transfer complexes with acceptors like TCNE (= tetracyano ethylene) and TCNQ (= tetracyano quinodimethane), the complexes being similar to those of iron cyclopentadienyls[154]. Organotin bases such as tetrakis-(2-cyanoethyl)tin(IV) [XVI], or triphenyl[2-(4'-pyridyl)ethyl]tin(IV) [XVII] have been used to form adducts with compounds of tin and other metals. Thus, XVI

forms 1:1 complexes with stannic chloride and bromide, $SnX_4.L$[155] and XVII forms stable adducts with organotin and other halides, e.g., $Ph_2SnCl_2.2L$, $Ph_3SnCl.L$, $ZnCl_2.2L$, $CoCl_2.4L$, $NiCl_2.4L$ and $CuCl.L$[156].

$(NCCH_2CH_2)_4Sn$

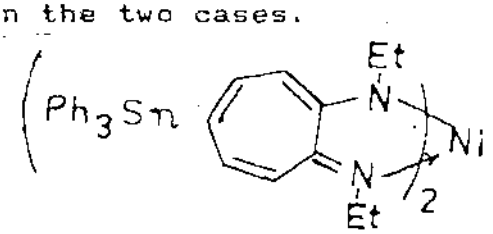
XVI

$Ph_3SnCH_2CH_2$–(pyridine N)

XVII

A Ni-complex of structure XVIII is also known[156]. But the donor abilities of such compounds are almost solely the property of the organic moiety, because the tin atom is too far apart from the donor atom to modify their donor strength in any way.

These compounds are, therefore, of very little interest in the discussion of the donor properties of organotin compounds. However, not only quite a few Sn(II) molecules and complex ions containing sterically active lone pairs behave as donors[136], but also, a number of tin(IV) compounds, notably the tin tetraalkyls are known to form complexes with acceptors, although the analogous unsubstituted alkanes do not show any such tendency. In the latter compounds, the donor activity of the molecules is a direct consequence of substitution by tin, although tin(IV) itself, is not the donor. The donor properties of Sn(II) and Sn(IV) compounds are now discussed separately, because of the totally different role of the tin atoms in the two cases.



XVIII

1.3.1. Sn(II) *Compounds as Donors* :

In Sn(II) compounds the donor property is masked because of the predominating acceptor tendency of the vacant hybrid orbital. These compounds exhibit donor property only when the vacant orbitals have been used in forming dative bonds with Lewis bases such as halide ions and the anionic halogen complexes of the type SnX_3^- possess sufficient donor strength to form a variety of complexes with suitable acceptors, particularly the platinum metal acceptors[196]. The lone pair orbital of the pyramidal trihalostannate(II) ion must be responsible for the σ-donor properties of the group. The donor ability of the SnX_3^- ions, in contrast to the other Sn(II) complexes is presumably due to the lowering of 5s ionisation potential in the anionic species. This is supported by the absence of donor tendency in SnF^+, $SnCl^+$ and $SnBr^+$, where the 5s lone pair is expected to be more difficult to ionise[196]. Similar donation by a pyramidal monosolvated tin(II) halide results in the formation of neutral complexes in some nonaqueous solutions[196]. Examples where SnX_3^- ions act as donors include $PtCl_2(SnCl_3)_2^-$; $Pt(SnX_3)_5^{-3}$ (where X = Cl,Br); $Pt_3Sn_8Cl_{20}^{-4}$; $Pd_2Cl_2(SnCl_3)_4^{-4}$; $Ir_2Cl_6(SnCl_3)_4^{-4}$; $OsCl_2(SnCl_3)_4^{-4}$; $RuCl_2(SnCl_3)_2^{-2}$; $Rh(SnCl_3)_4^{-3}$; $Rh_2Cl_2(SnCl_3)_4^{-4}$; $RhCl(CO)(SnCl_3)_2^{-2}$ etc.[196]. Evidence for the presence of the trichlorostannate(II) ligand in $Pt_3Sn_8Cl_{20}^{-4}$ ion comes from the

strong IR band in its spectrum at 330 cm^{-1}, which is characteristic of σ-bonded $SnCl_3^-$ [136]. The best confirmatory evidence for the existence of tin(II) donor atoms in the complexes formed with the platinum metals comes from ligand replacement reaction involving the tin(II) species. The $SnCl_3^-$ ion can be replaced from anions containing it by strong π-bonding ligands such as py, p-toluidine, PPh_3 and CO, e.g.,

$$RuCl_2(SnCl_3)_2^{-2} + 4py \longrightarrow (py)_4RuCl_2 \text{ ------[1]}$$

Similarly the trichlorostannate(II) ion can replace weaker π-bonding ligands such as chloride, mesityl oxide etc.

$$PtCl_4^{-2} + 2SnCl_3^- \longrightarrow PtCl_2(SnCl_3)_2^{-2} \text{ -----[2]}$$

Many such replacement reactions in organic solvents result in the formation of neutral complexes crystallisable from solution, e.g., $(Ph_3P)_2Pt(SnCl_3)$, $(Ph_3P)_3Pt_3(SnCl_3)_2$ etc.[136].

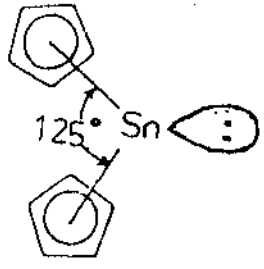
Though SnX_3^- ion is a weak σ-donor, it exhibits a large trans-effect because of its ability to form strong $d\pi$-$d\pi$ bonds with Pt-group metals. The π-acceptor property of SnX_3^- ion is in fact comparable to those of the two most powerful π-acceptor ligands NCS^- and CN^- [136]. The $SnCl_3^-$ ion appears to have empty d orbitals of the correct size and symmetry to form strong π-bonds with the filled d orbitals on the platinum metals.

The trichlorostannate ion in $(Et_3NH)(SnCl_3)$ acts as σ-donor towards acceptor molecules such as TCNE and TCNQ forming 1:1

complexes. The formation of the complexes of tin(II) halides with TCNE and TCBQ (= tetrachloro benzoquinone) and of bis-(β-ketoenolato)tin(II) with TCNE, TCNQ and TCBQ, also involves σ-donation from the tin(II) atom. But in the process TCNE and TCBQ completely oxidise the metal in the tin(II) halide and bis-(β-ketoenolato)tin(II) to the quadrivalent state. The TCNQ complexes of bis-(β-ketoenolato)tin(II) exhibited resonance due to both Sn(II) and SN(IV)[159]. Similar oxidative additions are also undergone by Sn(II) derivatives of 1,2-diols[158,159].

Although the π-acceptor properties of SnX_3^- ion play an important part in its donor ability, the BX_3 complexes can only involve the σ-donor properties of the ion. The formation of $Cl_3SnBF_3^-$ and $Cl_3SnBCl_3^-$ has been accounted for by σ-donation from the lone pair of the $SnCl_3^-$ ion to the empty acceptor orbital of the BX_3[160].

Electron diffraction and X-ray crystallography has shown that the two rings in bis-(cyclopentadienyl)tin(II) are non parallel [X]X] and the bonding can be described in terms of sp^2-hybridised tin with two orbitals involved in bonding to the cyclopentadienyl rings and the third containing unshared pair of electrons[161-163]. This unshared pair can coordinate to a Lewis acid such as BF_3.



XIX

The addition of BF_3-etherate to a THF solution of stannocene [XIX] precipitated the complex $(\eta^5\text{-}C_5H_5)_2Sn{:}\!\longrightarrow\!BF_3$[164]. Stannocene also forms 1:1 complexes with Lewis acids such as $AlCl_3$ and $AlBr_3$[165]. The Mossbauer spectra of these adducts are very similar to that of stannocene indicating that the complexation of the tin lone pair does not significantly affect the 5s electron density at the tin atom. However, the stannocene complex $(\eta^5\text{-}C_5H_5)_2Sn{:}\!\longrightarrow\!BF_3$ has recently been shown to contain the units $[BF_4]^-$, $(\eta^5\text{-}C_5H_5)_2Sn$, $[\eta^5\text{-}C_5H_5Sn]^+$ and THF by Zuckerman et.al. from X-ray crystallographic measurements[166].

The bonding in organostannylene complexes such as $[CH(SiMe_3)_2]_2Sn.M(CO)_5$ (M = Cr,Mo) or $Cp_2Sn.M(CO)_5$ (M = Cr,Mo, W)[165b,167,168] and bis-naphthyl $Sn^{II}.W(CO)_5$[169] can be interpreted as involving σ-donation from the lone pair of the tin atom to the transition metal and back donation from the later to the empty p

or d orbitals of the former. Base stabilised terminal complexes such as $R_2Sn(B).Cr(CO)_5$ (R = CH_3, t-Bu; B = py, THF)[170] involve coordination of the tin to only one metal atom but the vacant p orbital on Sn additionally coordinates a molecule of the base.

I.3.2. *Tin(IV) compounds as Donors :*

As already mentioned, the donor property of Sn(IV) compounds arises from delocalised M.O.'s involving the metal atom and its neighbours. Bond polarity and inductive effect play important role in the ability of tin atom to modify the donor activity of the substituent bonded to it. The Sn—X bonds in molecules of the type R_nSnX_{4-n} (where X = a monovalent atom or group, such as H, OH, OR, NR_2, halogen; n = 1-4) acquire a large polarity due to the low electronegativity of tin as compared to the common ligands. Addition reactions of alkyltins to aldehydes and ketones demonstrate the polarity of Sn—C bond.

Closely related with this is the inductive effect which the tin atoms or stannyl groups exert on their surroundings. The bond polarisation, $Sn^{\delta+}—X^{\delta-}$, which is there in principle, may be changed by substitution at X as well as at tin. NMR data on organotin compounds[171,172] and semi empirical calculations of Majee and Gupta [173] emphasise this. Studies of the relative rates of acid cleavage of the compounds $p\text{-}Me_3MCH_2C_6H_4SnMe_3$ (M = Si, Ge,

Sn)[174] and the rates of alkaline hydrolysis of $R_3M(CH_2)_nCOOEt$ (R = Me, Et; n = 1-3; M = Si, Ge, Sn)[175], as also, IR and NMR measurements on $(Me_3Si)_2N(MMe_3)$ (M = Si, Ge, Sn, Pb)[176] and IR studies on esters of the type $MeCOOMMe_3$ (M = C,Si,Ge)[177] have established that the R_3M groups have a +I effect and the order of electron release is Me_3Pb > Me_3Sn > Me_3Ge > Me_3Si. The drift of electrons from the metal to its partner in the Sn—X bond, therefore, makes the atom X quite rich in electron density. Unless there is back bonding between the filled orbitals of X and empty 5d orbitals of Sn, a possibility of electron donation through X arises. Although there are controversies regarding the extent of $d\pi$—$p\pi$ back bonding in Sn(IV) compounds, it is now broadly agreed that such bonding is generally absent except in compounds having sp^2 C—Sn bonds[178] There is evidence that the π-character in the M—X bonds decreases as we go down the group IVB. Thus Si—O or Si—N bonds have appreciable π-character, whereas, IR and Raman studies of compounds $R_3SnXSnR_3$ (X = O,S) indicated that there is no π-contribution to the Sn—O and Sn—S bonds[178]. It is expected that the much diffused nature of 5d orbitals on Sn (as compared to the 3d orbitals on Si) would be unsuitable for back bonding with filled $p\pi$ orbitals on the more electronegative atoms.

Depending on the nature of the substituents two types of donors may be encountered:

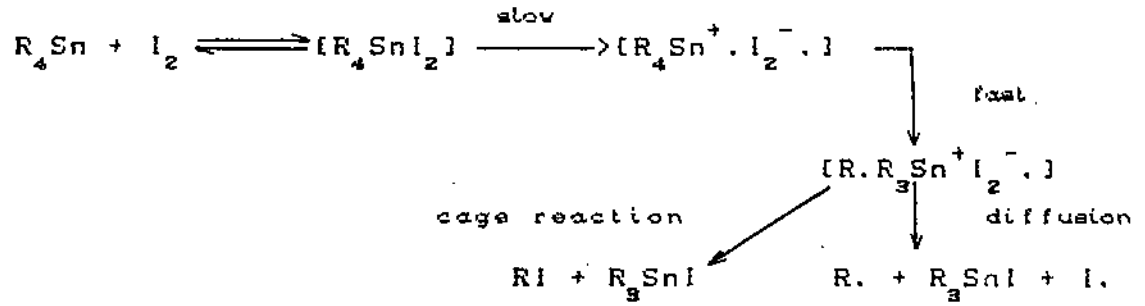
(i) Type A : Compounds in which the substituent X is not an electron pair donor, e.g., tetraalkyl tin compounds. The comparatively low energy of the σ-M.O. corresponding to the Sn—X bond and its polarity makes this class of compounds weak donors.
(ii) Type B : Compounds in which the sbstituent is an electron pair donor, e.g., $(R_3Sn)_2O$. Although the donor orbital is almost localised on the substituent in these compounds, the adjacent tin atom often profoudly modifies their donor strength through inductive effect and in some case even through σ—π conjugation.

In addition some triorgano tin(arylazo)benzoates have been shown to form 1:1 molecular complexes of weak donor acceptor type with almost any type of molecules including unsubstituted alkanes[179]. Electronic absorption spectral studies show the organotin molecules to be the donor. However, the role of the tin atom in these case is not yet fully understood and these compounds have been excluded from the purview of the present discussion. The above two types of Sn(IV) donors are now discussed in some details.

I.3.2.A. Type A Tin(IV) Donors :

The unsubstituted alkanes do not usually possess any donor or acceptor property, presumably, due to the absence of any low lying M.O. in them. However, substitution of a hydrogen by tin

results in a relatively high energy HOMO (low I.P.) and because of this lowering in I.P., the tetraalkyl tin compounds can act as weak σ-donors[180]. Group IVB metal alkyls have been found by Kochi et.al.[181-186] to form weak charge-transfer complexes with acceptors such as TCNE, I_2, $HgCl_2$ etc. in CCl_4 and CH_2Cl_2. These authors have interpreted the iodinolysis of R_4Sn as involving electron transfer within the charge-transfer complex as shown below[185].



In CT complexes of benzyl organotin derivatives, e.g., $PhCH_2SnPh_3$, $PhCH_2SnMe_3$, $C_6H_4(CH_2)_2SnPh_2$ etc. with TCNE[187,188], the organotin group is found to exert a large activity on the aromatic ring through σ-π conjugation. The magnitude of the decrease of the CT frequency in the stannyl derivatives compared to that in the corresponding carbon compounds show that the donor ability of the $\rangle Sn—CH_2-$ group is comparable to that of $—NR_2$ group[187].

The metal alkyls have also been found to undergo electron transfer reactions with oxidants like $IrCl_6^{-2}$, $Fe(dipy)_3^{+3}$ and $Fe(Phen)_3^{+3}$. In molecular contact complexes, reported to exist in

solutions of NbF_5, MoF_6, WF_6 and WF_5OMe in the tetraalkyls of Ge, Sn and Pb[189], electron transition from the σ-M.O. of the M—C bond in R_4M to the empty antibonding M.O. of the penta/hexavalent metal is believed to take place.

The cleavage of Sn—C bonds of R_4Sn compounds by metal halides such as SnX_2, SnX_4, BX_3, PX_5, CuX_2, PdX_2 and HgX_2 are well known[190,191]. The disproportionation between R_4Sn and $SnCl_4$ is the basis of the Kocheshkov preparation of alkyltin chlorides, R_nSnCl_{4-n}. These reactions involve donation from the σ-M.O. of the Sn—C bond to the electrophiles, nucleophilic assistance being provided at the tin centre.

Although homopolar, the σ(Sn—Sn) bond in hexaorgano distannanes can act as σ-donor due to its low energy. Thus oxidative cleavage R_3SnSnR_3, by various π-acceptors, e.g., TCNE TCNQ, TCBQ, 1,4-Benzoquinone etc. gives CT complexes like $[R_3SnSnR_3]^+[TCNE\ ]^-$ and $[Ph_3SnSnPh_3]^+[TCNQ\ ]^-$ as well as free radicals R_3Sn-TCNE., R_3Sn-TCNQ., [R_3Sn-(1,4-benzoquinone).], as shown by ESR studies[192,193]. Stable free radicals like R_3Sn-TCNQ. (R = Me, n-Pr, n-Bu) and $Me_2Sn(TCNQ.)_2$ are also obtained by the reactions of the Li-salt of TCNQ with organotin(IV) chlorides[192]. Oxidative cleavage of the Sn—Sn bond by electrophiles, e.g., halogens, O_2 etc. has also been studied[135]. These cleavage reactions take place through electron transfer from the σ(Sn-Sn)

bond. Complexes of polysilanes, hexamethyl disilanes and hexamethyl germane with TCNE and TCNQ also form in a similar way through σ-electron transfer to the π-acids[194,195].

1.3.2.B. Type B Tin(IV) Donors :

The Lewis basicity of compounds such as $(R_3M)_nX$, where X is an electron donor such as N, O, S etc. and M is a group IVB element, have been evaluated from the shift caused in ν(C-D), due to C—D ----X hydrogen bonding, in their IR spectra in $CDCl_3$. Values for the relative donor strength of some of these organometallic bases measured as $\Delta\nu$ (cm^{-1}) for ν(C-D) of 'free' and 'H-bonded' states in $CDCl_3$, are illustrated in the table-1.1. below[196]:

Table:-1.1.

Relative Donor Strength of $(R_3M)_nX$. [as $\Delta\nu$ cm^{-1}].

M	$(Me_3M)_3N$	$(Me_3M)_2O$	$(Me_3M)_2S$
C	100	33	40
Si	0	13	29
Ge	72	55	38
Sn	106	84	43

The data in the table reflect differences both in the inductive effects of the group IVB elements and also their capacity to form

$p\pi$-$d\pi$ bonds with N, O or S. The absence of interaction between $(Me_3Si)_3N$ and $CDCl_3$ implies complete involvement of the nitrogen lone pair in π-bonding in contrast to the strongly basic $(Me_3Sn)_3N$, which is pyramidal, and in which N—>Sn multiple bonding, if present at all, does little to offset the electron releasing properties of the Me_3Sn group. As a result, the trimethyl stannyl amine is found to be more basic than the organic amine[197]. The proton acceptor abilities of the chlorine atom in group IVB organometallic chlorides as measured by the shift of ν(OH) of phenol in CCl_4 in presence of the chlorides[198] also indicate the same trend. Organotin azides and organotin acylates (R_3SnCOR') also have been found to be stronger bases than their carbon analogues[199-201].

In compounds such as R_3MOMR_3 and $R_nM(OR')_{4-n}$ (where n = 1-3, M = Group IVB metal), the following sequence of basicity for the oxygen atom has been assigned on the basis of IR frequency shifts $\Delta\nu$(OH) of methanol or $\Delta\nu$(NH) of pyrole due to hydrogen bonding with the oxygen atoms of these compounds in methanol or pyrole solution[202].

increasing basicity →

increasing basicity ↓

$SiOSi < Si(OC)_3 < Si(OC)_2 < SiOC$

$Ge(OC)_3 < Ge(OC)_2 < GeOC < GeOGe$

$Sn(OC)_2 < SnOC < SnOSn$

The increased basicity of the oxygen atom in alkyl or aryl stannoxanes has been confirmed by the isolation of 1:1 and 1:2 adducts of μ-oxo-bis[triphenyltin(IV)] with $TiCl_4$; of $R_3SnOSnR_3$ (R = n-Pr, n-Bu) with $TiCl_4$ and $SnCl_4$; and 1:1 adducts of μ-oxo-bis[triphenyltin(IV)] with $SbCl_5$, as well as, adducts of di n-butyltin oxide with $TiCl_4$, $SnCl_4$ and $SbCl_5$[203a,204]. μ-oxo-bis[tri n-butyltin(IV)] also react with MX_2 (where M = Cu(II), Mn(II),Ni(II), Co(II); X = Cl^-, Br^-, I^-, NCS^- and NO_3^-) to form compounds of general composition $MX_2.L_4$. Compounds of the type $M(ClO_4)_2.L_6$ also have been reported for M = Ni(II), Cu(II) and Mn(II)[205,206]. $(R_3Sn)_2O$ (R = n-Pr, n-Bu, Ph) forms complexes of stoichiometries $NiCl_2.L.EtOH$ and $Ni_2Cl_4.L.3EtOH$ with $NiCl_2$ in absolute alcohol[203b]. Amongst these oxoorganotin compounds the donor strength varies as -

$$(Ph_3Sn)_2O < (Pr_3Sn)_2O < (Bu_3Sn)_2O.$$

The IR spectra of all these addition products show that the $\nu_{as.}$(SnOSn) band of the free stannoxane which appears around 780 cm^{-1} suffers considerable negative shift, thereby indicating that, in all these products the organo stannoxane is coordinated to the metal through oxygen atom[203a,205,206].

Beside these adducts with metal halides, organotin oxides and hydroxides are known to combine with organotin halides, R_2SnIOH and $R_2Sn(OAC)_2$ to form a large number of addition

products in which the oxides or hydroxides donate through the oxygen atom[5,209a]. Some of these compounds are listed in table-1.2.

The nucleophilicity of the oxygen bonded to tin is important in the addition reactions of the Sn—O bond. Trialkyltin oxides and alkoxides [XX], (X = SnR_3 and R' respectively) often combine with a variety of multiply-bonded acceptors (A=B) to give 1:1 adducts.

$$R_3Sn\text{-}OX + A{=}B \underset{3(b)}{\overset{3(a)}{\rightleftharpoons}} R_3Sn\text{-}A\text{-}B\text{-}OX \quad \text{-----[3]}$$

XX

Tributyltin oxide and methoxide which are regarded as model compounds for their respective classes, add on to acceptors, such as, aldehydes and ketones, CO_2, carbodiimides (RN=C=NR), isocyanates (RNCO), CS_2, isothiocyanates (RNCS), SO_2, sulfodiimides (RNSNR), sulfinylamines (RNSO), imines (RNCR), nitriles (RCN), ketenes (CH_2=CO) etc. to give 1:1 adducts[207,208], examples of which are shown in the table-1.3.

Most of the additions shown in the table-1.3. occur exothermally at room temperature. The reactions are reversible and the adducts dissociate upon heating. However, the decomposition can proceed by a route other than simple retrogression [eqn. 3(b)] particularly, where oxide adducts are concerned.

Table:-I.2.

Addition compounds of organotin oxides and hydroxides with organotin halides and acetates:

Compound type	R	R'	X
$R_2SnO.R'_2SnX_2$	Me	Et,n-Pr	Br, I
	Et	Me	I
		Et	Cl, Br, I
		n-Pr	Br
	n-Pr	Et	Br
		n-Pr	Cl, Br
$(R_2SnO)_2.R'_2SnX_2$	Me	Me	Cl
$R_2SnO.R'_2SnIOH$	Me, Et,	R'=R	-
	iso-Pr,	,,	-
	iso-Bu,	,,	-
	iso-Pent	,,	-
$R_2SnO.R'_2Sn(OAC)_2$	Me	Me	-
$H(R_2SnO)_9OH.R'_2SnX_2$	Me	Me	Br, I
	Et	Me	I
		Et	Cl.Br, I
	n-Pr	n-Pr	I
$R'(R_2SnO)_9OR'.R_2SnX_2$	Me	Me, Et,	Br, I
		n-Pr, n-Bu	I
	Et	Et	Cl, Br, I
	n-Pr	Et, n-Pr	I
$(R_3Sn)_2O.R'_3SnX$	Me	Me	Br, I
$(R_3Sn)_2O.R'_2SnX_2$	n-Bu	Et	Cl
$(R_3Sn)_2O.R'SnX_3$	n-Bu	Et	Cl
$R_3SnOH.R'_3SnX.H_2O$	Me	Me	Cl, Br, I
$(R_3SnOH)_2.R'_3SnX$	Me	Me	Cl, Br, I
	Et	Et	Br

$$R_3Sn.O.SnR_3 + A{=}B \rightleftharpoons R_3Sn.A.B.OSnR_3 \rightleftharpoons R_3Sn.A.SnR_3 + O{=}B$$

XXI -----[4]

Clearly, the product XXI formed by addition of $R_3Sn.O.SnR_3$ to A=B could equally arise from addition of $R_3Sn.A.SnR_3$ to O=B.

The multiple bond of the acceptor being polar, the tributyltin group is attached to the negative end of the dipole $A^{\delta-} = B^{\delta+}$. Hence, structural alterations within a given class of acceptors which increase the electrophilicity of B increase their reactivity. Thus, for carbonyl compounds the acceptor strength changes in the sequence-

$CCl_3CHO > CBr_3CHO > MeCHO > PrCHO \sim$ iso-$BuCHO >> PhCHO$ etc.

The relative power of tin-oxygen bonded compounds to act as addenda by equation 3(a) above, decreases in the sequence-

$R_3SnOMe > R_3SnOSnR_3 > R_3SnOPh$ etc.

these suggest that the principal process governing the reactivity is the nucleophilic attack by the oxygen bonded to tin upon the positive end of the dipole and that the electrophilic attack of tin upon the negative end is relatively unimportant[207].

Dialkyltin dialkoxides undergo similar reactions[207]. Dialkyltin oxide and alkyltin trialkoxides are expected to undergo similar reaction, but have not yet been investigated.

Liquid SO_3 in CCl_4 reacts with μ-oxo-bis[triphenyl tin(IV)] in dichloromethane at -20^oc to give a 1:1 adduct. In the IR spectrum of the adduct[209] the ν_{as}(SnOSn) appears at 650 and 630

Table:-1.3.

Products of the reaction between Bu_3SnOX and A=B :

A=B	$Bu_3Sn.A.B.OX$	
	X = Me	X = $SnBu_3$
O=CH.CCl_3	$Bu_3Sn.O.CH(CCl_3).OMe$	$Bu_3Sn.O.CH(CCl_3).OSnBu_3$
O=C:O	$Bu_3Sn.O.CO.OMe$	$Bu_3Sn.O.CO.OSnBu_3$
NpN=C:NNp	$Bu_3Sn.N.Np.C(:NNp).OMe$	$Bu_3Sn.NNp.C(:NNp).OSnBu_3$
MeN=C:O	$Bu_3Sn.NMe.CO.OMe$	$Bu_3Sn.NMe.CO.OSnBu_3$
O=S:O	$Bu_3Sn.O.SO.OMe$	$Bu_3Sn.O.SO.OSnBu_3$
Tol.N=S:N.Tol	No reaction	[$Bu_3Sn.NTol.SO(=NTol).SnBu_3$]
Ar.N=S:O	[$Bu_3Sn.NAr.SO.OMe$][a]	b
S=C:S	[$Bu_3Sn.S.CS.OMe$]	c
S=C:NPh	$Bu_3Sn.S.C(:NPh).OMe$	d
SO_2TolN=CHCCl$_3$	[$Bu_3Sn.N(SO_2Tol)CH(CCl_3)OMe$]	[$Bu_3SnN(SO_2Tol)CH(CCl_3)OSnBu_3$]
N C.CCl_3	[$Bu_3Sn.N:C(CCl_3)OMe$]	$Bu_3Sn.N:C(CCl_3).OSnBu_3$
H_2C=C:O	[$Bu_3Sn.CH_2.CO.OMe$]	[$Bu_3Sn.CH_2.CO.OSnBu_3$]

Notes: Np = 1-naphthyl, Tol = p-tolyl, Ar = p-$NO_2C_6H_4$.

a- The 1:1 adduct only exist in equilibrium with its precursors.

b- A 1:1 mixture of $Bu_3Sn.O.SO.OSnBu_3$ and $Bu_3Sn.NAr.SO.NAr.SnBu_3$ is obtained.

c- $Bu_3Sn.S.SnBu_3$ and $Bu_3Sn.O.CO.OSnBu_3$ are obtained.

d- oxygen-sulfur exchange occurs giving $Bu_3Sn.S.SnBu_3$ and $Bu_3Sn.NPh.CO.OSnBU_3$.

[ ]Compounds in parenthesis have not been obtained analytically pure.

cm^{-1}, thereby suggesting that it is formed by donor-acceptor interaction between the O atom of the stannoxane and the S atom of SO_3, the former being the donor. Subsequently, on being refluxed in dry CCl_4 for 1-2 hours the adduct undergoes imtramolecular rearrangement to give bis[triphenyl tin(IV)]sulfate[209] [eqn. 5], which can also be prepared by reacting either the organotin halide with Ag_2SO_4[210] or the oxide with H_2SO_4[16].

$$(Ph_3Sn)_2O + SO_3 \xrightarrow[\text{at } -20^{\circ}C]{\text{under } N_2} (Ph_3Sn)_2O{:}\!\longrightarrow SO_3 \xrightarrow[\text{for 1-2 hours.}]{\text{refluxed in } CCl_4}$$

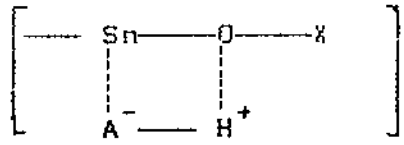
$$(Ph_3Sn)_2SO_4 \quad \text{----[5]}$$

Therefore, it is evident that the adduct is formed as an intermediate in the formation of bis-[triphenyl tin(IV)] sulfate from the reaction of $(Ph_3Sn)_2O$ with SO_3. However, no such intermediate could be detected when $(R_3Sn)_2O$ (where R = n-Pr and n-Bu) and di-n-butyltin oxide reacted with liquid SO_3 and the corresponding sulfates were obtained directly[209,211].

It should be stressed that the formation of an intermediate may help a reaction by substantially decreasing the energy of the transition state, even if the intermediate is too unstable to be detected[212].

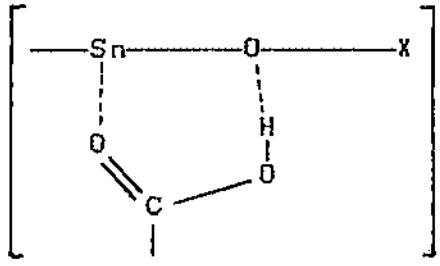
The reaction between organotin oxides/hydroxides and organic or inorganic acids, universally used for the preparation of

organotin esters, is also believed to proceed through an intermediate donor-acceptor transition state, similar to [XXII] proposed for the reaction of siloxanes with $AlCl_3$[212] and the reaction between $(Ph_3Sn)_2O$ and HgX_2[213].



XXII

The transition state involving organotin oxides/hydroxides and carboxylic acids in non-ionising solvents may be represented by



X = SnR_3, H.

XXIII

Such a cyclic intermediate is expected to be most favourable, because the nucleophilic attack of the oxygen bonded to tin upon the H-atom and the electrophilic attack by the tin centre upon the O-atom of the carboxylic acid assist each other. Although no evidence in favour of such an intermediate, is available so far, its stability (if it does exist at all) is likely to be enhanced with the increase in the electronegativity of RCO_2^- group of the

acid. Thus, if the reaction is assumed to proceed through the formation of the cyclic intermediate, the presence of strongly electron withdrawing group and additional potential donor atom capable of forming a chelate ring, both most effective if present on the α-carbon atom within R, can create a situation conducive to the realisation of such intermediate in the isolated state.

Bibliography.

1. Ahrland S., Chatt J. and Davies N.R., *Quart. Rev.*, 1958, 12, 265.
2. Pearson R.G., *J. Am. Chem. Soc.*, 1963, 85, 3553.
3. Poller R.C., *The Chemistry Of Organotin Compounds.*, Logos Press, U.K., 1970, Ch-11.
4. Beattie I.R., *Quart. Rev.*, 1960, 17, 382.
5. Ingham R.K., Rosenberg S.D. and Gilman H., *Chem. Rev.*, 1960, 60, 459.
6. Satchell D.P.N. and Wardell J.L., *Proc. Chem. Soc.*, 1963, 86.
7. Nyher J.J. and Russel K.E., *Can. J. Chem.*, 1964, 42, 1555.
8. Poller R.C., *J. Organomet. Chem.*, 1965, 3, 321.
9. Geilen M. and Sprecher N., *Organomet. Chem. Rev.*, 1966, 1, 455.
10. Wardell J.L., *J. Organomet. Chem.*, 1967, 9, 89.
11. van Der Kelen G.P., van Der Berghe E.V. and Verdonek L., *Organotin Compoinds.*, A.K.Sawyer Ed., M.Dekker, N.Y., 1971, P-118 and references cited therein.
12. Belatskaya I.P., Butin K.P., Ryabtsev A.N. and Reutov O.A., *J. Organomet. Chem.*, 1973, 59, 1.
13. Petrosyan V.S., Yashina N.S. and Reutov O.A., *J. Organomet. Chem.*, 1973, 52, 307, 315, 321, 333.
14. Petrosyan V.S., Yashina N.S. and Reutov O.A., *Adv. in Organometallic Chem.*, F.G.A.Stone and R.West Ed., Acad.Press, N.Y., 1976, Vol.-14.
15. Nicholson J.W., Douak J.A. and Crowe A.J., *J. Organomet. Chem.*, 1981, 219, 309.

16. Davies A.G. and Smith P.J.,*Comprehensive Organometallic Chemistry*. G.Wilkinson, F.G.A.Stone and E.W.Abel Ed., Pergamon Press.,U.S.A., 1982, Ch-11, P-562 and references cited therein.

17. Zubieta J.A. and Zuckerman J.J., *Prog.Inorg.Chem.*, 1978, 24 ,251.

18. Cusack P.A., Smith P.J., Donaldson J.D. and Grimes S.M., *A Bibliography of X-Ray Crystal Structures of Tin Compounds.*, I.T.R.I.,London, 1981,(Publication no-588).

19. Greene P.T. and Bryan R.F., *J.Chem.Soc.(A)*, 1971, 2549.

20. Levchuk L.E., Sams J.R. and Aubke F.,*Inorg.Chem.*, 1972, 11 ,43.

21. Lasses J. and Brown T.L., *Inorg.Chem.*, 1964, 3 ,148.

22. Tudela D. Khan M.A. and Zuckerman J.J., *J.Chem.Soc.Dalton Trans.*, 1991(4), 999.

23. Yashina N.S., Gefel E.I., Petrosyan N.S. and Reutov O.A., *Koord.Khim.*, 1985, 11(12), 1639.

24. Feshin V.P., Dolgushin G.V., Lazarev I.M. and Voronkov M.G., *Koord.Khim.*, 1990, 16(9), 1215.

25. Rivarola E., Silvestri A., Alonzo G., Barbieri R. and Huber R.H., *Inorg.Chim.Acta.*, 1985, 99(1), 87.

26. Arquero A., Souza P., Garcia-Vazquez J.A. and Masaguer J.R., *Transition Met.Chem.(Weinheim, Ger.)*, (a) 1985, 10(11), 424.
(b) 1986, 11(6), 229.

27. Drew M.G.B., Kisenyi J.M., Willey G.R. and Wandiga S.O., *J.Chem.Soc.Dalton Trans.*, 1984,(8), 1717.

28. Pery D.L., Margrave J.L. and Bonnell D.W.; *Inorg. Chim. Acta.*, 1985, 101(1), L_1.

29. Agarwal R.K., Kaushik S.D. and Rawat H.K., *Proc. Natl. Acad. Sci., India, Sec. A.*, 1986, 56(1), 101.

30. Zakharov V.N., Yatshenko A.V., Kamyshnyi A.L. and Aslanov L.A., *Koord. Khim.*, 1991, 17(6), 789.

31. Liu Ling Kang, *Bull. Inst. Chem. Acad. Sin.*, 1985, 32, 45.

32. Dolgova N.A. and Litvyak I.G., *Izv. Acad. Nauk. Kaz. SSR., Ser. Khim.*, 1986, 5, 23.

33. Slavinskaya R.A., Kovaleva T.A. and Dolgova N.A., *Koord. Khim.*, 1990, 16(8), 1028.

34. Sing R.P. and Gupta V.D., *Spectrochim. Acta. Part A.*, 1984, 40A(5), 407.

35. Biradar N.S., Divakar M.C. and Aminabhavi T.M., *Ind. J. Chem.*, (a) 1984, 23A, 586 ; (b) 1986, 25A, 283.

36. Cunningham D., Fitzgerald J. and Mark L., *J. Chem. Soc. Dalton Trans.*, 1987(9), 2261.

37. Angenault J., Mondi C. and Rimsky A., *Inorg. Chim. Acta.*, 1979, 37(2), 145.

38(a). Gioia L.G., Bonati F., Cecchi P., Lorenzotti A. and Pettinari C., *J. Organomet. Chem.*, 1991, 403(3), 317.

(b). Lobbia G.G., Zamponi S., Marassi R., Berrettoni M., Stizza S. and Cecchi P., *Gazzetta Chimica Italiana.*, 1993, 123(10), 589.

39. Channareddy S. and Gupta V.D., *Synth. React. Inorg. Met.-Org. Chem.*, 1988, 18(1), 29.

40. Russo U., Cassol A. and Silvestri A., *J. Organomet. Chem.*, 1984, 260(1), 69.

41. Cusack P.A., Patel B.N., Smith P.J., Allen D.W. and Nowell I.W., *J. Chem. Soc. Dalton Trans.*, 1984(6), 1239.

42. Hough E., Nicholson D.G. and Vasudevan A.K., *J. Chem. Soc. Dalton Trans.*, 1988(11), 2335.

43. Bott S.G., Prinz H., Alvanipour A. and Atwood J.L., *J. Coord. Chem.*, 1987, 16(3), 303.

44. Feshin V.P., Dolgushin G.V., Lazarev I.M. and Voronkov M.G., *Zh. Obshch. Khim.*, 1988, 58(10), 2267.

45. Mann K.R., Morrison W.H.(Jr) and Hendrickson D.N., *Inorg. Chem.*, 1974, 13(5), 1180.

46. Ginzburg A.G., Bokyi N.G., Yanovsky A.I., Struchkov Yu.T., Setkina V.N. and Kursanov D.N., ITRI Abstract., 1980, P29, 569.

47. Watnabe M., Motoyama I. and Sano H., *Chem. Lett.*, 1988(10), 1699.

48. Watnabe M., Motoyama I. and sano H., *Bull. Chem. Soc. Jpn.*, 1986, 59(7), 2109.

49. Zemva B. and Jesih A., *J. Fluorine Chem.*, 1984, 24(3), 281.

50. Aslanov L.A., Ionov V.M., Attiya W.M. and Perumin A.B., *J. Struct. Chem.(Engl. Transl.)*, 1978, 19 ,269.

51. Webster M., Mudd K.R. and Taylor D.J., *Inorg. Chim. Acta.*, 1976, 20, 231.

52. Fitzsimmonds B.W., Othen D.G., Shearer H.M.M., Wade K. and Whitehead G., *J. Chem. Soc., Chem. Commun.*, 1977, 215.

53. Hutton R.E., Burby J.W. and Oakes V., *J. Organomet. Chem.*, 1978, 156, 369.

54. Saraswat B.S., Srivastava G. and Mehrotra R.C., *Rev. Silicon, Germenium, Tin, Lead Compds.*, 1982, 6(3), 171.

55. Paseshnichenko K.A., Aslanov L.A., Yatsenko A.V.and Medvedev S.V., *Koord. Khim.*, 1984, 10(9), 1279.

56. Paseshnichenko K.A., Aslanov L.A.. Yatsenko A.V.and Medvedev S.V., *J. Organomet. Chem.*, 1985, 284(2), 181.

57. Medvedev S.V., Yatsenko A.V. and Aslanov L.A., *Zh. Neorg. Chim.*, 1987, 32(6), 1518.

58. Tursina A.I., Aslanov L.A., Yatsenko A.V. and Medvedev S.V., *Koord. Khim.*, 1985, 11(3), 417.

59. Yasina N.S., Gefel E.I., Petrosyan N.S. and Reutov O.A., *Dokl. Akad. Nauk. SSSR.*, 1985, 283(3), 654.

60. Bonire J.J., *Chem. Chron.*, 1986, 15(1), 3.

61. Bozimo H.T. and Bonire J.J., *Polyhedron.*, 1987, 6(3), 393.

62. Ray C. and Dainis D., *Inorg. Chim. Acta.*, 1988, 143(2), 151.

63. Yoder C.H., Coley S.M., Grushow A., Enders B.G., Kreizys S.F. and Spencer J.N., *J. Organomet. Chem.*, 1988, 346(2), 165.

64. Kumar A.K., Chattopadhyay T.K. and Rivarola E., *Ind. J. Chem. Sect. A*, 1988, 27A(10), 912.

65. Muetterties E.L. and Wright C.M., *J. Am. Chem. Soc.*, 1964, 86 ,5132.

66. Anderson H.H., *Inorg Chem.*, 1964, 3 ,912.

67. Thevet F., Nguyen H.D. and Dagron C., *C.R. Acad. Sci. Ser.*, 1972, C275 ,1279.

68. Ruddick J.N.R. and Sams J.R., *J. Chem. Soc. Dalton Trans.*, 1974,470.

69. Jung O.K.S., Jeong J.H. and Sohn Y.S., *J. Organomet. Chem.*, 1990, 399(3), 235.

70. Goodman B.A., Greenwood N.A., Jaura K.L. and Sharma K.K., *J. Chem. Soc. (A).*, 1971, 1865.

71. Huber F., Enders M. and Kaiser R., *Z. NturForsch. B.*, 1966, 21 ,83.

72. Tanaka T., Matsumura Y., Okawara R., Musya Y. and Kinumaki S., *Bull. Chem. Soc. Jpn.*, 1968, 41 ,1497.

73. Srivastava T.N. and Agarwal M.P., *J. Inorg. Nucl. Chem.*, 1970, 32, 3416.

74. Alleston D.L. and Davies A.G., *Chem. Ind. (London).*, 1961, 551.

75. Midha A. and Verma R.D., *J. Ind. Chem. Soc.*, 1985, 62(6), 421.

76. Miller J.M., Mondal H., Wharf I. and Onyszchuk M., *J. Organomet. chem.*, 1986, 306(2), 193.

77. Tursina A.I., Aslanov L.A., Chernyshev V.V., Medvedev S.V. and Yatsenko A.V., *Koord. Khim.*, 1985, 11(10), 1420.

78. Rheingold A.L., Ng S.W. and Zuckerman J.J., *Inorg. Chim. Acta.*, 1984, 86(3), 179.

79. Srivastava T.N. and Chauhan A.K.S., *J. Inorg. Nucl. Chem.*, 1977, 39 ,371.

80. Sanchi R., Bansal R.K. and Mehrotra R.C., *J.Organomet.Chem.*, 1986, 303(3), 351.

81. Gopinathan S., Degaonkar M.P. and Gopinathan C., *Ind.J.Chem.Sect.A.* 1990, 29A(10), 971.

82. Nath M., Sharma N. and Sharma C.L., *Synth.React.Inorg.Met.-Org. Chem.*, 1991, 21(1), 51.

83. Zubieta J.A. and Zuckerman J.J., *Prog.Inorg.Chem.*, 1978, 24 ,251.

84. Smith P.J., *J.Organomet.Chem.Library.*, 1981, 12 ,97.

85 Allen D.W., Derbyshire D.J., Brooks J.S., Blunden S.J. and Smith P.J., *J.Chem.Soc. Dalton Trans.*, 1984(9), 1889.

86. Mullins M.A. and Curran C., *Inorg.Chem.*, 1966, 7 ,2584.

87. Crowe A.J., Hill R., Smith P.J., KumarDas V.G. and Brooks J.S., *J.Organomet.Chem.*, 1979, 182(3), 345.

88. Harrison P.G. and Molloy K.C., *J.Organomet.Chem.*, 1978, 152 ,63.

89. Buttenshaw A.J., Duchene M. and Webster M., *J.Chem.Soc. Dalton Trans.*, 1975, 2230.

90. Cunningham D., Douek I., Frazer M.J., McPartlin M.and Mathews J.D. *J.Organomet.Chem.*, 1975, 90 ,C-23.

91. Lycka A. and Holecek J., *Inorg.Chim.Acta.*, 1986, 122(1), 15.

92. Calogero S., Valle G.and Russo U.,*Organometallics.*,1984,3(8),1205.

93. Ray C. and Dainis D., *Inorg.Chim.Acta.*, 1988, 148(1), 31.

94. Naik D.V. and Scheidt W., *Inorg.Chem.*, 1973, 12 ,272.

95. Dondi S., Nardelli M., Pelizzi C., Pelizi G. and Predieri G., *J.Chem.Soc. Dalton Trans.*, 1985(3), 487.

96. Mangia A., Pelizzi C. and Pelizzi G., *J.Chem.Soc. Dalton Trans.*, 1973, 2557.

97. Tarasconi P., Pelizzi C. and Pelizzi G., *J.Chem.Soc. Dalton Trans.*, 1983(12), 2689.

98. Mufti A.S. and Poller R.C., *J.Organomet.Chem.*, 1965, 3 ,99.

99. KumarDas V.G., Chen W., Yap C.K. and Mak T.C.W., *J.Organomet.Chem.*, 1986, 299 ,41.

100. Graddon D.P. and Rana B.A., *J.Organomet.Chem.*, 1977, 136 ,19.

101. Huber F., Preut H., Hoffman E. and Gielen M., *Acta.Crystallogr. Sect.C: Cryst.Struct.Commun.*, 1989, C45(1), 39.

102. Ng S.W., Chen W.,Zainudin A., KumarDas V.G., Yip W.H., Wand R.J. and Mak T.C.W., *J.Crystallogr.Spectrosc.Res.*, 1991, 21(1), 39.

103. Lockhart T.P., Calabrese J.C. and Davidson F., *Organometallics.*, 1987, 6 ,2479.

104. (a) Fregona D., Guo Z.J., Faraglia G.and Sitran S., *J.Coord.Chem.*, 1993, 28(1 Pt.-A), 73.

(b) Fregona D., Faraglia G.and Sitran S., *J.Coord.Chem.* 1993, 30(3-4), 221.

105. Nardelli M., Pelizzi C. and Pelizzi G., *J.Organomet.Chem.*, 1976, 112 ,263 ; 1977, 125 ,161.

106. Tarasconi P., Pelizzi C. and Pelizzi G., *J.Organomet.Chem.*, 1977, 124 ,151.

107. KumarDas V.G., Yap C.K., Ng S.W., Chen W. and Mak T.C.W., *J.Organomet.chem.*, 1986,311(3), 289, and references cited therein.

108. Allen D.W., Derbyshire D.J., Nowell I.W. and Brooks J.S., *J.Organomet.Chem.*, 1984, 260(3), 263.

109. Rheingold A.L., Ng S.W. and Zuckerman J.J., *Organometallics.*, 1984, 3(2), 233.

110. Wharf I., Pichler L., Sailofsky B.M., Onyszchuk M.and Simard M.G., *Can.J.Chem.*, 1987, 65(3), 639.

111. Graddon D.P. and Rana B.A., *J.Organomet.Chem.*, 1976, 105 ,51.

112. George E., McKinney-Forbes P.K., Richie K.L. and Nguyen V.V., *J.Organomet.Chem.*, 1986, 310(3), 285.

113. Pelizzi C. and Pelizzi G., *Inorg.Nucl.Chem.Lett.*, 1980, 16 ,451.

114. Harrison P.G., Lambert K., King T.J. and Majee B., *J.Chem.Soc. Dalton Trans.*, 1983, 363, and references cited therein.

115. Swisher R.G., Vollano J.F.,Chandrashekhar V., Day R.O. and Holmes R.R., *Inorg.Chem.*, 1984, 23 ,3147.

116. Vollano J.F., Day R.O., Rau D.N. Chandrashekhar V. and Holmes R.R.. *Inorg.Chem.*, 1984, 23 ,3153.

117. Bancroft G.M., KumarDas V.G., Sham T.K. and Clark M.G., *J.Chem.Soc. Dalton Trans.*, 1976, 643.

118. Rupainwar R.(Mrs.) and Pandey B.D., *Ind.J.Chem.*, 1984, 23A(1), 75.

119. Holloway J.H., McQuillan G.P. and Ross D.S., *J.Chem.Soc.(A)*., 1969, 2505.

120. Joshi K.K. and Waytt P.A.H., *J.Chem.Soc.*, 1959, 2825.

121. Srivastava T.N., Siddiqui M.A., Sing J.D. and Srivastava S., *Ind.J.Chem.*, 1987, 26A(2), 158.

122. Alcock N.W. and Rose S.M., *J.Chem.Soc.Dalton Trans.*, 1988(8),1589.

123. KumarDas V.G., Chen W., Ng S.W. and Mak T.C.W., *J.Organomet.Chem.*, 1987, 322(1), 33.

124. Holmes J.M., Peacock R.D.and Tatlow J.C., *Proc.Chem.Soc.*,1963,108.

125. Lagowski J.J., *Quart.Rev.*, 1959, 13 ,233.

126. Chambers R.D. and Chivers T., *Proc.Chem.Soc.*, 1963, 208.

127. Pratt A.J.and Thomas E.J., *J.Chem.Soc. Chem.Commun.*,1982(19),1115.

128. Yamamoto Y., Komatsu T. and Maruyama K., *J.Chem.Soc. Chem.Commun.*, 1983(4), 191.

129. Yamamoto Y., Maeda N. and Maruyama K., *J.Chem.soc, Chem.Commun.*, 1983(13), 742 ; 1983(14), 774.

130. Keck G.E. and Boden E.P., *Tetrahedron Lett.*, 1984, 25 ,265 ; 1879.

131. Keck G.E. and Abbott D.E., *Tetrahedron Lett.*, 1984, 25 ,1883.

132. Petrosyan V.S. and Reutov O.A., *Pure.Appl.Chem.*, 1974, 37 ,147.

133. Killing H. and Mitchell T.N., *Organometallics.*, 1984, 3(8), 1318.

134. Killing H., Mitchell T.N., Amamria A. and Rutschow D., *J.Organomet.Chem.*, 1983, 241(3), C 45-47.

135. Kobayashi K.(nee Kuno), Kawanisi M., Kozima S., Hitomi T., Iwamura H. and Sugawara T., *J.Organomet.Chem.*, 1981, 217 ,315 and references cited therein.

136. Donaldson J.D., *Prog.Inorg.Chem.*, F.A.Cotton Ed., Interscience Publishers, N.Y., 1967, Vol-8, 287 and references cited therein.

137. Woodward L.A. and Taylor M.J., *J.Chem.Soc.*, 1962, 407.

138. Donaldson J.D., Knifton J.F., O'Donoghue J.D. and Ross S.D., *Spectrochim.Acta.*, 1966, 22 ,1173.

139. Morrison J.S. and Haendler H.M., *J.Inorg.Nucl.Chem.*, 1967, 29 ,393.

140. Srivastava T.N. and Dwivedi B.K., *J.Ind.Chem.Soc.*, 1985, 62(3), 244.

141. Calogero S., Russo U., Valle G., Grimes S., Donaldson J.D. and Smith P.J., *Inorg.Chim.Acta.*, 1984, 84(2), 173.

142. Zaidi S.A.A., Yamin M., Shakir M., Zaidi S.R.A. and Siddiqui Z.A., *Ind.J.Chem.*, 1985, 24A(9), 788.

143. Srivastava T.N. and Dwivedi B.K., *J.Ind.Chem.Soc.*, 1985, 62(3), 246.

144. Dwivedi B.K., Bhatnagar K. and Srivastava A.K., *Synth.React.Inorg. Met.-Org.Chem.*, 1986, 16 , 715 ; 841.

145. Dwivedi B.K., Bhatnagar K.and Sing R.D., *Acta.Ciene.Indica, Chem.*, 1985, 11(2), 108.

146. Donaldson J.D. and Nicholson D.G., *J.Chem.Soc.(A).*, 1970, 145 and references cited therein.

147. Tandon J.P. and Varshney A., *Synth.React.Inorg.Met.-Org.Chem.*, 1986, 16(10), 1371.

148. Tandon J.P. and Varshney A., *Ind. J. Chem.*, 1985, 24A(1), 70; 1986, 25A(2), 191.

149. Tandon J.P. and Varshney A., *Proc. Ind. Acad. Sci., Chem. Sci.*, 1987, 96(4), 265.

150. Drew M.G.B. and Nicholson D.G., *J. Chem. Soc. Dalton Trans.*, 1986(8), 1543.

151. Burshtien I.F., Gerbelen N.V., Bologa O.A., Kon A.Yu. and Malinovskii T.I., *Metalloorg. Khim.*, 1990, 3(5), 1162.

152. Hansen M.N., Niedenzu K., Serwatowska J., Serwatowski J. and Woodrum K.R., *Inorg. Chem.*, 1991, 30(4), 866.

153. Cornwell A.B., Cornwell C.A. and Harrison P.G., *J. Chem. Soc. Dalton Trans.*, 1976(16), 1612.

154. Adman E., Rosenblum M., Sullivan S. and Margulis J.N., *J. Am. Chem. Soc.*, 1967, 89, 4540.

155. Reifenberg G.H. and Considine W,J., *J. Organomet. Chem.*, 1967, 10, 285.

156. Poller R.C. and Toley D.L.B., *J. Organomet. Chem.*, 1968, 14, 453.

157. Eaton D.R. and McClellan W.R., *Inorg. Chem.*, 1967, 6, 2134.

158. Mabrouk H.E. and Tuck D.G., *J. Chem. Soc. Dalton Trans.*, 1988(10), 2539.

159. Annan T.A., McGarvey B.R., Ozarowski A., Tuck D.G. and Chadha R.K., *J. Chem. Soc. Dalton trans.*, 1989(3), 439.

160. Johson M.P., Shriver D.F. and Shriver S.A., *J. Am. Chem. Soc.*, 1966, 88, 1568.

161. Almenningen A., Haaland A. and Motzfeld T., *J. Organomet. Chem.*, 1967, 7, 97.

162. Atwood J.L., Hunter W.E., Cowley A.H., Jones R.A. and Stewart C.A., *J. Chem. Soc. Chem. Commun.*, 1981, 925.

163. Jutzi P., Kohl F., Hofmann P., Kruger C. and Tsay Y.H., *Chem. Ber.*, 1980, 113, 757.

164. Harrison P.G. and Zuckerman J.J., *J. Am. Chem. Soc.*, 1970, 92, 2577.

165. Cornwell A.B., Harrison P.G. and Richards J.A., *J. Organomet. Chem.*, (a) 1974, 76, C26 ; (b) 1976, 108, 47.

166. Dory T.S., Zuckerman J.J. and Barnes C.L., *J. Organomet. Chem.*, 1985, 281(1), C1.

167. Cotton J.D., Davidson P.J. and Lappert M.F., *J. Chem. Soc. Dalton Trans.*, 1976, 2275.

168. Davidson P.J, and Lappert M.F., *J. Chem. Soc. Chem. Commun.*, 1973, P317.

169. Jastrzebski J.T.B.H., van der Schaaf P.A., Boersma J., van Koten G., Heijdenrijk D., Goubitz K. and de Ridder D.J.A., *J. Organomet. Chem.*, 1989, 367, 55.

170. Marks T.J. and Newman A.R., *J. Am. Chem. Soc.*, 1973, 95, 769.

171. Holmes J.R. and Kaesz H.D., *J. Am. Chem. Soc.*, 1961, 83, 3903.

172. Fliteroft N. and Kaesz H.D., *J. Am. Chem. Soc.*, 1963, 85, 1377.

173. Gupta R. and Majee B., *J. Organomet. Chem.*, 1971, 29, 419; 1971, 33, 169; 1972, 36, 71; 1972, 40, 97; 1973, 49, 191, 197, 203.

174. Bott R.W., Eaborn C. and Walton D.R.M., *J.Organomet.Chem.*, 1964, 2 ,154.

175. Rijkens F., Janssen M.J., Drenth W. and van der Kerk G.J.M., *J.Organomet.Chem.*, 1964, 2 ,347.

176. Scherer O.J. and Schmidt M., *J.Organomet.Chem.*, 1964, 1 ,490.

177. Srivastava T.N. and Onyszchuk M., *Can.J. Chem.*, 1963, 41 ,1244.

178. Poller R.C., *The Chemistry of Organotin Compounds.*, Logos Press, U.K., 1970, Ch-I.

179. Chattopadhyay T.K. and Majee B., *J.Ind.Chem.Soc.*, 1982, LIX ,219.

180. Fehlner T.P., Ullman J., Nugent C.W.A. and Kochi J.K., *Inorg. Chem.*, 1976, 15 ,2544.

181. Kochi J.K., *Organometallic Mechanisms and Catalysis.*, Acad.Press., N.Y.,1978.

182. Wong C.L. and Kochi J.K., *J.Am.Chem.Soc.*, 1979, 101 ,5593.

183. Fukuzumi S., Mochida K. and Kochi J.K., *J.Am.Chem.Soc.*, 1979, 101, 5961.

184. Fukuzumi S., Wong C.L.and Kochi J.K., *J.Am.Chem.Soc.*,1980,102,180.

185. Fukuzumi S. and Kochi J.K., *J.Am.Chem.Soc.*, 1980, 102 ,2141.

186. Fukuzumi S and Kochi J.K., *J.Phys.Chem.*, 1980, 84, 608; 617; 1981, 85 ,648.

187. Hanstien W, Berwin H.J. and Taylor T.G., *J.Am.Chem.Soc.*, 1970, 92 ,7476.

188. Reutov O.A.., Rosenberg V.I., Gavrilova G.V and Nikanorov V.A., *J.Organomet.Chem.*, 1979, 177 ,101.

189. Mclean R.R., Sharp D.W.A. and Winfield J.M., *J.Chem.Soc. Dalton Trans.*, 1972, 676.

190. Abraham M.H., *Electrophilic Substitution At A Saturated Carbon Atom.*, C.H.Bamford and C.F.H.Tipper Ed., Elsevier,Amsterdam, 1973.

191. Anderson H.H., *Inorg.Chem.*, 1962, 1 ,647.

192. Cornwell A.B., Harrison P.G. and Richards J.A., *J.Organomet.Chem.*, 1977, 140 ,273.

193. Kozima S., Fujita H., Hitomi T., Kobayashi K., Kobayashi K (nee Kuno), and Kawanisi M., *Bull.Chem.Soc.Jpn.*, 1980, 53 ,2953 and references cited therein.

194. Sakurai H., Kira M and Uchida T., *J.Am.Chem.Soc.*, 1973, 95 ,6826.

195. Traven F. and West R., *J.Am.Chem.Soc.*, 1973, 95 ,6824.

196. Coates G.E., Green M.L.H., Powell P. and Wade K., *Principles Of Organometallic Chemistry.*, Chapman and Hall, London, 1977, Ch-4.

197. Cotton F.A. and Wilkinson G., *Advanced Inorganic Chemistry.*, Wiley Eastern., New Delhi, 1977, Ch-19.

198. Jakoubkova M., Papouskova Z., Pola J. and Chvalovsky V., *Collect.Czech.Chem.Commun.*, 1977, 42(90), 2798.

199. Thayer J.S. and West R., *Inorg.Chem.*, 1965, 4 ,114.

200. Yates K. and Agolini F., *Can J.Chem.*, 1966, 44 ,2229.

201. Brook A.G., *Adv. in Organometallic Chem.*, F.G.A.Stone and R.West Ed., Acad.Press, N.Y.,1968, Vol.-7, P-96.

202. Marchand A., Mendelsohn J., Lebedeff M. and Valade J., *J.Organomet.Chem.*, 1969, 17 ,379.

203. Narula S.P. and Sharma R.K., *Ind.J.Chem.*, (a) 1979, 17A, 98 ; (b) 1980, 19A, 769.

204. Paul R.C., Mahajan V.K., Ahluwalia S.C., Sharma R.K. and Narula S.P., *Inorg.Nucl.Chem.Lett.*, 1973, 9 ,893.

205. Srivastava M.,Srivastava A.K. and Agarwal R.K., *Proc.Indian.Natl. Sci.Acad.,Part.A.*, 1984, 50(3), 249.

206. Srivastava M., Srivastava A.K. and Agarwal R.K., *J.Ind.Chem.Soc.*, 1985, 62(9), 639.

207. Bloodworth A.J. and Davies A.G., *Organotin Compounds.*, A.K.sawyer Ed., Mercel Dekker., N.Y., 1971, Vol.-I, P-227 and references cited therein.

208. Sisido K. and Kozima K.S., *J.Org.Chem.*, 1964, 29 ,907.

209. Paul R.C., Sharma R.K., Walia R. and Narula S.P., *Ind.J.Chem.*, 1978, 16A ,544.

210. Okawara R. and Ohara M., *Organotin Compounds.*, A.K.Sawyer Ed., Mercel Dekker., N.Y., 1971, Vol.-II, P-253.

211. Harber R.H. and Stapfer C.H., *Inorg,Nucl.Chem.Lett.*, 1971, 7 ,617.

212. Eaborn C., *Organosilicon Compounds.*, Butterworths, London, 1960, P-103.

213. Dutta D.R., Majee B.and Ghosh A.K., *J.Organomet.Chem.*, 1971, 29, 251.

CHAPTER-II

ORGANOTIN CARBOXYLATES : A BRIEF REVIEW.

ORGANOTIN CARBOXYLATES : A BRIEF REVIEW

II.1 *Introduction :*

Organotin carboxylates constitute one of the most important classes of compounds in the ever expanding field of organotin chemistry. Theoretical and structural interests in this class of compounds continue to grow along with the tremendous growth in their industrial, agricultural and other applications.

These compounds are derivatives of tin(IV) and may be of three general types, viz. $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$, where, the groups R and R' may either be the same or different. Many discussions on the chemistry of this group of organotin compounds with varying degrees of details are available[1-5] and as such only the more important aspects are presented here.

II.2. *Preparation :*

Organotin carboxylates are prepared through a number of routes, of which the most common and convenient one involves the reaction between organotin oxides (or hydroxides) and carboxylic acids or their anhydrides[6-14] as shown below :

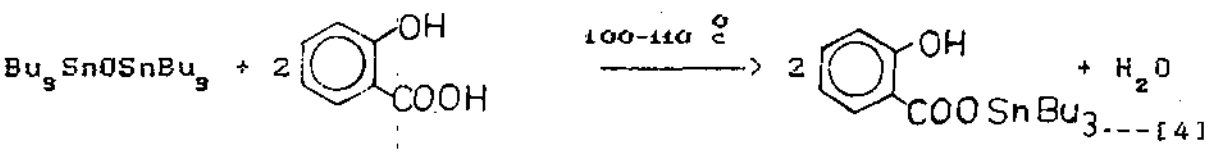
$$R_3SnOSnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O \text{ ------- [1]}$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \text{ ------[2]}$$

$$R_3SnOSnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR' \text{----------[3]}$$

The water produced in these reactions is removed, usually by

azeotropic distillation using a Dean and Stark separator or alternatively by refluxing at higher temperature[15] for example :



---[4]

Triphenyl tin carboxylates, such as, p-$ROC_6F_4COOSnPh_3$, (where, R = Me, Et), p-$(Ph_3SnOCO)_2C_6F_4.H_2O$ and o-$(Ph_3SnOCO)_2C_6F_4.H_2O$ have been prepared by the reaction of Ph_3SnOH with the appropriate polyfluoro carboxylic acids in MeOH[16].

Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halides with the alkali metal or silver salts of carboxylic acids either by stirring at room temperature or by refluxing the reactants in a suitable solvent[13,17-19].

$R_nSnX_{4-n} + (4-n)\ MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} + (4-n)\ MX$ ----[5]

(M = Na, K, Ag or Tl; X = halogen)

Another method for the preparation of organotin esters involves the cleavage of one or more organic groups of tetraorganotin compounds by carboxylic acids[20,21].

$R_4Sn + n\ R'COOH \longrightarrow R_{4-n}Sn(OCOR')_n + n\ RH$ -----[6]

In this acidolysis reaction, the cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on the temperature[22-24]. Vinyl groups are cleaved more readily than saturated alkyl radicals, but less readily than phenyl groups[25] and successive groups are lost with increasing

difficulty. Tetraalkyltin is more reactive than tetravinyltin[21].

A novel electrochemical method of preparation of trialkyltin carboxylates involving the cleavage of organic groups from R_4Sn (R = Me, Et, Pr, Bu) by Hg(I) carboxylates, has been described by Tagliavini et al[26]. Thus, tetramethyltin produces trimethyltin acetate when treated with Hg(I) acetate in MeOH at room temperature.

$$2Me_4Sn + Hg_2(OCOMe)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_2H_6 \quad \text{------[7]}$$

Organotin hydrides react with carboxylic acids to form the corresponding organotin esters[27,28] with evolution of hydrogen.

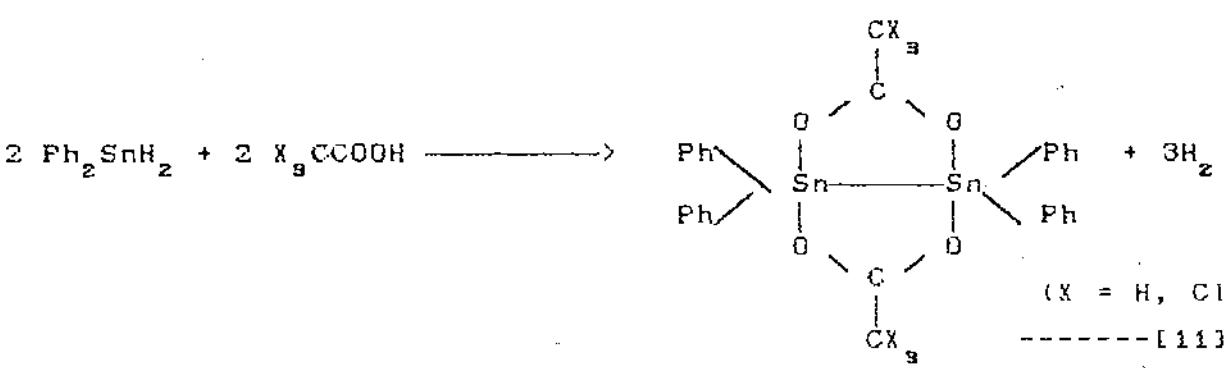
$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2 \quad \text{----------[8]}$$

$$R_2SnH_2 + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2H_2 \quad \text{---------[9]}$$

The initially formed dicarboxylate equilibrates with unreacted dihydride as follows[29].

$$R_2Sn(OCOR')_2 + R_2SnH_2 \rightleftharpoons 2R_2Sn(H)OCOR' \quad \text{----------[10]}$$

With di-n-butyltin dihydride the intermediate hydride carboxylate $Bu_2Sn(H)OCOR'$ decomposes to give distannane 1,2--dicarboxylates[27,90,91]. Using similar methods the acetato bridged compounds shown below have been prepared[92].



-------[11]

Halocarboxylate derivatives of organotin compounds are most conveniently synthesised by heating equimolecular mixtures of the diorganotin dicarboxylates and the diorganotin dihalides in an inert solvent[33,34].

$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \longrightarrow 2Bu_2Sn(Br)OAc$ ---------[12]

These compounds can also be prepared by the reaction of R'COOM (M = Na, K) with diorganotin dihalide as shown below[35,36].

$Bu_2SnCl_2 + KOCOR' \longrightarrow Bu_2Sn(Cl)OCOR' + KCl$ ----------[13]

At 100°C trimethyltin chloride reacts with carboxylic acids to give dimethylchlorotin carboxylate[37] which may also be prepared by the exchange reaction between dimethyltin dichloride and a triorganotin carboxylate in CCl_4 or C_6H_6 at room temperature[33] as shown below.

$Me_3SnCl + R'COOH \longrightarrow Me_2Sn(Cl)OCOR' + MeH$ ----------[14]

$R_2SnCl_2 + R''_3SnOCOR' \longrightarrow R_2Sn(Cl)OCOR' + R''_3SnCl$ --------[15]

A number of dialkylhalotin acetates have been synthesised using the following reactions[38] :

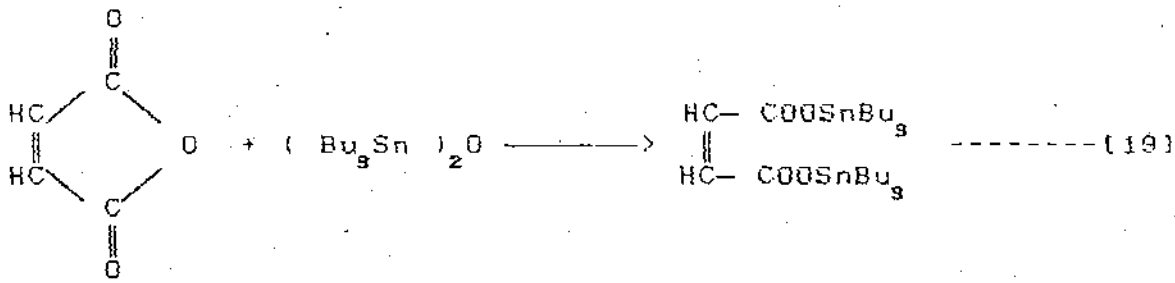
$(R_2SnCl)_2O + 2CH_3COOH \longrightarrow 2R_2(Cl)SnOCOCH + H_2O$ ------[16]

$(R_2SnCl)_2O + (CH_3CO)_2O \longrightarrow 2R_2(Cl)SnOCOCH_3$ ----------[17]

$R_2SnO + ClCOR' \longrightarrow R_2Sn(Cl)OCOR'$ ----------[18]

Anhydride of an unsaturated acid (e.g., maleic anhydride) when reacted with hexabutyl distannoxane produces disubstituted organotin esters[39].

Organotin carboxylates may also be prepared from the esters of carboxylic acids by the reactions [20] and [21][40,41], below.



$$(R_3Sn)_2O + R'COOEt \longrightarrow R_3SnOCOR' + R_3SnOEt \quad \text{----------(20)}$$

$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH \quad \text{----------(21)}$$

Tricarboxylate derivatives of the type $RSn(OCOR')_3$ are usually prepared from the corresponding trichlorides by the action of the silver salts of the carboxylic acids[42].

$$RSnCl_3 + 3R'COOAg \longrightarrow RSn(COCOR')_3 + AgCl \quad \text{----------(22)}$$

II.3 *Physical Properties of Organotin Carboxylates :*

The Sn— O bond in organotin carboxylates is essentially covalent, but undergoes polar reactions depending on the solvents and attacking groups. This is why the carboxylates with small organic groups are more soluble in alcohol, ether etc. than in water[2]. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric structures. Many of the carboxylates have low melting points indicating these to be covalent compounds.

The polymeric stannoic acids are colorless and infusible. A few of them are soluble in chloroform and carbon tetrachloride and are fairly stable towards hydrolysis. The melting/boiling points of some common organotin esters are listed in

table-II.1.[1,2,4,5,48].

Table:-II.1.

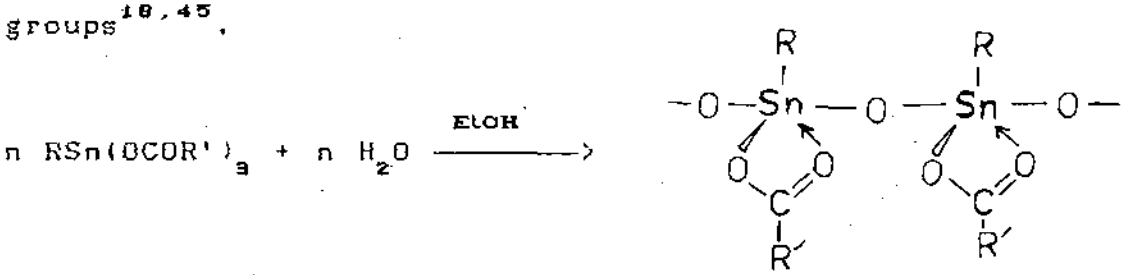
Mp./Bp. of Organotin Carboxylates :

Compound	Mp.(^{o}c) Bp.(^{o}c/mm Hg)	Compound	Mp.(^{o}c) Bp.(^{o}c/mm Hg)
$Me_3SnOCOMe$	196.5-197.5	$Bu_2Sn(OCOMe)_2$	144.5-145.5/10
$Ph_3SnOCOH$	202-203	$Ph_2Sn(OCOMe)_2$	116-117
$Ph_3SnOCOPh$	84-85.5	$Bu_2Sn(OCOCH=CHMe)_2$	34
$Bu_3SnOCOH$	120-125/0.7	$Bu_2Sn(OCOC_{11}H_{23}^{n})$	22-24
$Bu_3SnOCOMe$	85		
$Bu_3SnOCOPh$	166-168/1	$BuSn(OCOMe)_3$	46
$(Cy\text{-}hex)_3SnOCOMe$	62-63	$EtSn(OCOPh)_3$	185-188
$Ph_3SnOCOMe$	121-122	$PhSn(OCOMe)_3$	76
$Pr_3SnOCOMe$	99-100		
$Pr_3SnOCOCF_3$	88-90/1	$Et_2Sn(Cl)OCOMe$	94
$Et_3SnOCOMe$	134-135	$Bu_2Sn(Br)OCOMe$	67-68.5

II.4 *Chemical properties of Organotin Carboxylates :*

Most triorganotin carboxylates are hydrolytically stable, whereas the diorganotin derivatives undergo partial hydrolysis to produce the dimeric distannoxanes $R_2Sn(OCOR')OSnR_2(OCOR')$ and $R_2Sn(OCOR')OSnR_2OH$[4,44]. The monoorganotin tricarboxylates are readily hydrolysed in ethanol to form the monoorganotin oxycarboxylates[42] which exist as polymers or olygomers in the solid state with Sn— O— Sn bridges and chelating carboxyl

groups[18,45].



+ 2n R'COOH -----[23]

The most widely studied reactions of organotin carboxylates are decarboxylation and disproportionations. The thermal decarboxylation of triorganotin carboxylates[46] has been used for the preparation of trialkyltin hidrides[47] (equation 24), trialkyl-alkynyltins (equations 25,26)[48], triorgano cyanomethyltins (equation 27)[49] and polyfluorophenyl triphenyltins (equation 28)[16].

$$R_3SnOCHO \xrightarrow[(R = Pr,Bu)]{100\text{-}170^{o}C} R_3SnH + CO_2 \text{ ----------[24]}$$

$$R_3SnOCOC = COCOSnR_3 \xrightarrow[(R = Et,Pr,Bu)]{160^{o}C} R_3SnC = CSnR_3 + 2CO_2 \text{---[25]}$$

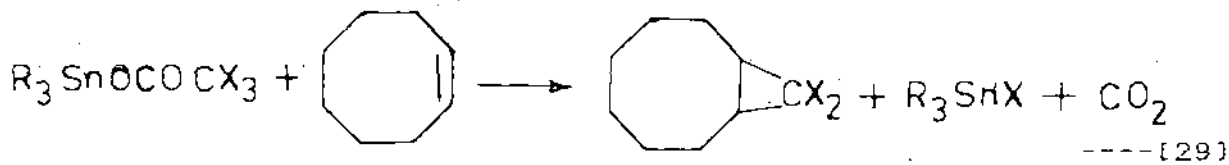
$$Bu_3SnOCOC{=}CPh \xrightarrow{60^{o}C} Bu_3SnC = CPh + CO_2 \text{ ---------[26]}$$

$$R_3SnOCOCH_2CN \xrightarrow[(R = Bu,Ph)]{140\text{-}150^{o}C} R_3SnCH_2CN + CO_2 \text{ ------[27]}$$

$$Ph_3SnOCOR \xrightarrow[(R = C_6F_5, C_6F_4OMe\text{-}4, C_6F_4OEt\text{-}4)]{\text{Boiling Py}} Ph_3SnR + CO_2 \text{ ----[28]}$$

The $Ph_3SnOCOR$ (R = C_6F_5, C_6F_4OMe-4, C_6F_4OEt-4) compounds undergo disproportionation reactions also, to form $Ph_2Sn(OCOR)_2$ and Ph_4Sn[16]. Seyferth et.al.[50] have successfully used the reaction of triorganotin carboxylates of halogen substituted carboxylic

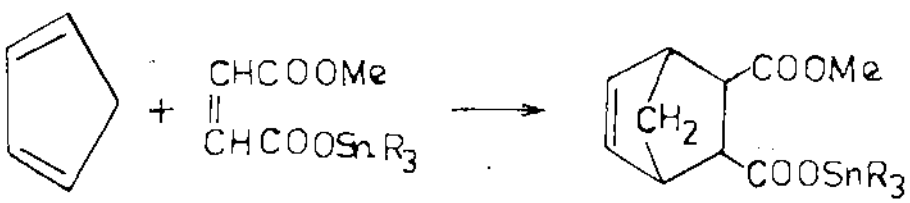
acids with cyclooctene as a carbene transfer reaction, although the reaction mechanism is not yet established.



----[29]

(R = Me, Ph; X = Cl, Br)

Diels-Alder type reactions have been carried out with organotin carboxylates and dienes[35,39].



---[30]

(R = Bu, Ph)

With thiols the following equilibrium is established and the reactions can be driven from left to right by removing the organic acid from the reaction mixtures[51].

$R_3SnOCOR' + R''SH \rightleftharpoons R_3SnSR'' + R'COOH$ ----------[31]

Action of alkoxy derivatives of metals and metalloids on organotin carboxylates produce metallostannoxanes[52,53] as shown below :

$Ph_3SnOAc + Ph_2Si(OEt)_2 \longrightarrow Ph_2Si(OSnPh_3)_2 + 2EtOAc$ ----[32]

$Bu_3SnOAc + Ti(OBu)_4 \longrightarrow Bu_3SnOTi(OBu)_3 + BuOAc$ ----------[33]

Organotin carboxylates readily undergo redistribution with other organotin compounds to form mixed organotin carboxylate derivatives (equations 10, 12, 15, 34)[4,54,55].

$$R_2Sn(OCOR')_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR')X \quad \text{----------[34]}$$

(X = hal.,OR,H,etc.)

In some cases carboxylate groups of the organotin ester may be exchanged with that of a free acid as shown below [17,56]:

$$AcOBu_2SnOSnBu_2OAc + 2Bu^tCOOH \longrightarrow (Bu^tCOO)Bu_2SnOSnBu_2(OOCBu^t) + 2AcOH \quad \text{-----[35]}$$

Oligomeric acetate is usually formed when a dialkyltin diacetate and a dialkyltin dialkoxide are heated at 180°C in water for 2 hours[57,58]. Oligomeric α-w diacetoxy stannoxanes are also obtained by the reaction[50]

$$Bu_2Sn(OAc)_2 + H_2O \xrightarrow{CH_2N_2} AcO(Bu_2SnO)_nSnBu_2OAc + MeOAc \quad \text{----[36]}$$

(n = 1,3,7,15)

Some triorganotin esters[60,61], most commonly the triorganotin acrylates or methacrylates, undergo polymerisation or copolymerisation under the influence of heat or free radical initiators.

$$n\ CH_2{=}\!=\!CR' \longrightarrow \left[-CH_2-CR'-\right]_n \quad \text{----[37]}$$
$$\qquad\qquad\quad CO_2SnR_3 \qquad\qquad\quad CO_2SnR_3$$

(R' = H or Me)

Generally, the organotin esters are weaker Lewis acids than organotin halides, so complex formation by esters is less extensive than by the halides. This weaker acidity appears to be essentially an inductive effect and may be related to the lower electron withdrawing power of the $ROCO^-$ group compared to the

halogen atom[62]. The presence of electron withdrawing groups attached to the tin and/or the $ROCO^-$ moiety[69] increases the Lewis acidity at tin and is expected to favour complex formation by the carboxylates. This explains why in the majority of the adducts of the di- and tri-organotin carboxylates with N, O and S containing ligands, reported so far[9,62,64-73], the organotin carboxylates are derivatives of halo carboxylic acids such as CF_3COOH or CCl_3COOH[65,66,69,72,73].

II.5. *Structure Of Organotin Carboxylates :*

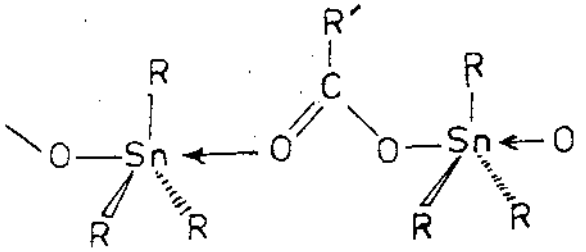
The commercial viability of organotin carboxylates has necessitated understanding of the bonding in these compounds to establish the relationship between their biocidal as well as non-biocidal activity with structure. Consequently, in recent years there has been an upsurge in the synthesis and structural elucidations of various organotin esters of well known carboxylic acids.

As early as 1961, Beattie and Gilson[74] suggested the structure involving intermolecular bridging through carboxyl oxygen atom, as an alternative to the ionic bonding previously postulated by Freeman[75] and Okawara[76]. Since then various physical methods like I.R., ^{119m}Sn Mossbauer, ^{119m}Sn NMR spectroscopy and X-ray diffraction studies have been utilised to deduce the structures of this class of compounds. The subject has been discussed and reviewed by several authors[1-5]. The salient

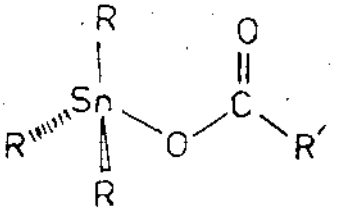
features of the structures of the three type of organotin carboxylates are discussed below.

II.5.A. Triorganotin carboxylates [$R_3SnOCOR'$] :

The triorganotin caboxylates are rich in structural possibilities. Generally, their solubilities in organic solvents are poor, because of their polymeric associated structure [1]. In the solid state the structure of trialkyltin carboxylates are polymeric involving bridging carboxylate groups and planner and near planner R_3Sn moieties[4], the geometry at the metal atom being trigonal bipyramidal [1].



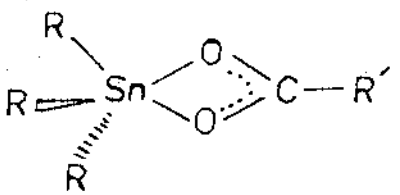
I



II

Thus IR spectrum of trimethylstannyl acetate in the solid state consist of ν_{as}(OCO) and ν_s(OCO) stretching frequencies at 1576 cm^{-1} and 1428 cm^{-1} respectively, indicating the presence of symmetrical carboxyl group as in $NaOCOCH_3$[77] . Appearance of a single Sn-C stretching band in $Me_3SnOCOMe$ is consistent with planner trimethyltin group. The associated polymeric chain

structure [I] has been demonstrated crystallographically for $Me_3SnOCOMe$, $Me_3SnOCOCF_3$[78], $Me_3SnOCOH$[9], Bz_3OCOMe[79], $(CH_2=CH)_3OCOCCl_3$[80] and $Me_3SnOCOC_4H_3S$[81].



III

On dissolving the compounds in nonpolar, noncoordinating solvents, the carboxylate absorption bands [ν_{as}(OCO) and ν_s(OCO)] are shifted to around 1650 cm^{-1} and 1300 cm^{-1} respectively, with the appearance of both ν_{as}(Sn-C) and ν_s(Sn-C) bands indicating the breakdown of polymeric structure [I] into monomers [II] with essentially tetrahedral tin atoms having ester-like carboxylate groups bonded to it. Molecular weights of the carboxylates in benzene and CCl_4 also support monomeric structure [II] in solution with the exception of trimethyltin formate. The insoluble form of the latter, when heated with cyclohexane in a sealed tube at 90^oc, is converted into a soluble form, which exists as an equilibrium of associated and unassociated forms in CCl, but monomeric in ethanol[82].

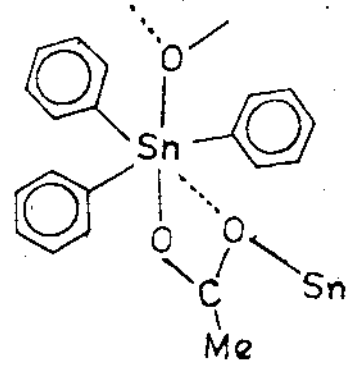
However, when the group R and/or R' is bulky or when there is branching at the carbon atom α to the tin atom (e.g., triphenyltin 2-ethyl hexoate) the compounds assume monomeric

ester-like structure [II] in the solid state, as a result of steric hindrance[18,83-87]. Thus, X-ray study on $Cy_3SnOCOMe$ showed the presence of discrete molecules, with the tin atom occupying a distorted tetrahedral geometry[85], although Majee et.al. have doubted such a representation[108]. Crystallographically authenticated claim in favour of structure [II] has also been made for tricyclohexylstannyl 1,3-indolyl acetate by Zuckerman et.al.[88]. Similar monomeric structures have been suggested for the sterically hindered trineophyltin formate and acetate on the basis of Mossbauer and I.R. spectroscopy[86,87].

In the structure of the bis-(trimethyl stannyl)ester of a dicarboxylic acid $Me_3SnOCOCH_2OCOSnMe_3$[89], each carboxyl group links planar Me_3Sn moieties intermolecularly to form a three dimensional polymeric network. In the derivatives of 2,6-pyridine dicarboxylic acids, structures [149] with trigonal bipyramidal tin atom environment involving unidentate carboxylate groups linking two different tin centres have been established recently.

Among the triphenyltin derivatives, $Ph_3SnOCOCHMe_2$ and $Ph_3SnOCOCH=CH_2$ are penta-coordinate one dimensional polymers possessing structure [I] in the solid state, whereas, $Ph_3SnOCOCMe_3$, $Ph_3SnOCOC(Me)=CH_2$, $Ph_3SnOCOCCl_3$[66,69,73] and $(p\text{-tolyl})_3SnOCOCCl_3$[90] are said to be tetra-coordinate monomers (structure [III]) in the solid state as well as in solution. The $\nu_{as}(OCO)$ band in the I.R. spectra of all these latter compounds appear above 1600 cm^{-1} both in the solid and solution state. While

the carboxylate bridged trans-C_3SnO_2 chain structure of triphenyltin carboxylates have been adequetly supported by X- ray analysis[91-95], the tetrahedral monomeric structure has been authenticated crystallographically only for a few compounds, such as the triphenyltin esters of anthranilic and salicylic acids[96,97] and the triphenyltin derivative of thiophene 2-carboxylic acid ($Ph_3SnOCOC_4H_3S$)[98]. However, triphenyltin acetate, on careful X-ray analysis appears to have a distorted six coordinate mer-Ph_3SnO_3 geometry at tin as shown below[99].



IV

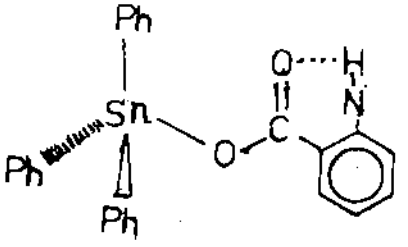
The intra molecularly chelated structure [III] involving bidentate carboxylic group has been assigned to some triorganotin esters of carboxylic acids, especially Ph_3Sn-derivatives of substituted benzoic acids, on the basis of I.R., NMR and Mossbauer spectroscopy[96,97,100-103,144]. The ν_{as}(OCO) mode in solid triphenyltin benzoate is found at 1620 cm^{-1} [104] and in

tri-n-propyl and tri-n-butyl tin benzoates, which are liquids, at 1565 cm^{-1} and 1640 cm^{-1} [105,106] respectively. Since the $\nu_{as}(OCO)$ mode is not shifted towards higher frequencies in solution, it is likely that, structures adopted in both states contain chelated benzoate groups[38]. However, examples of this geometry among trialkyl tin esters[100,101] are extremely rare, due probably, to the lower electronegativity of the alkyl than the phenyl group, which disfavours axial occupancy of the alkyl group in the trigonal bipyramidal structure.

Data for $Ph_3SnOCOC_6H_4X$ [where X = $2\text{-}NH_2$, $4\text{-}NH_2$, $2\text{-}NMe_2$, 2-OH, 4-SMe] have all been interpreted in terms of 5 coordinated structure [III], although this has been questioned[107]. From ^{119}Sn NMR and Mossbauer studies of $Ph_3SnOCOC_6H_4X$ [where X = H, 2-Me, $2\text{-}NH_2$, $2\text{-}NMe_2$, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 4-SMe, 2-OMe] in solution and in solid phases, Molloy et.al. have assigned a coordination number of four at tin in all the compounds in solution as well as in solid state with the exception of 2-Cl and 2-OH derivatives[107]. The 2-Cl and 2-OH derivatives are said to exhibit carboxylate/hydroxyl bridged polymeric structure.

On the basis of crystallographic data Holmes et.al assigned the intramolecularly five coordinate structure [III] to the 4-chloro- derivative[91], but Molloy et.al continues to prefer the tetrahedral monomeric structure[69]. The tetrahedral arrangement around tin in these compounds is supported by the X-ray diffraction studies on triphenyl tin esters of anthranilic and

salicylic acids[96,97], in which the carbonyl oxygen is only hydrogen bonded with the substituent at the ortho position of the benzene ring as shown below :



V

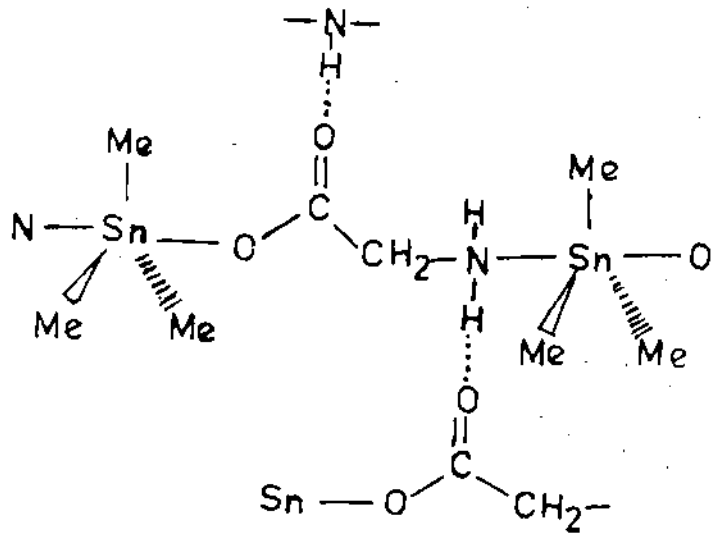
However, in the triphenyltin anthranilate and salicylate the geometry is distorted towards trigonal bipyramidal, because of the approach of oxygen of the $RCOO^-$ moiety at a tetrahedral face opposite one of the tin-phenyl groups and the Sn---O (carbonyl) distances (2.823 A^o in the anthranilate and 3.071 A^o in the salicylate) are indicative of weak interactions[96,97].

The only yet undisputed structure of type [III] has been demonstrated crystallographically for triphenyl tin o-(2-hydroxy-5-methyl phenyl azo)benzoate[108].

It should be noted here that among the $R_3SnOCOC_6H_4X$ compounds (where X is a donor group), there is no convincing evidence in favour of the involvement of the substituent X on the benzene ring in intramolecular coordination leading to chelate rings. On the other hand, there is evidence that the X group may be linked to a tin centre which is not at all carboxylated. Such

examples are provided by triorganotin derivatives of mercapto carboxylic acids[145]. However, examples of monomeric carboxylates in which the carboxylate group is part of a chelated ring formed by intramolecular coordination of N—>Sn have been provided by Majee et.al[109-111], for tri- and di-organotin derivatives of arylazo benzoic acids and arylazo phenoxy acetic acids.

Unlike the triorganotin carboxylates cited so far, the structure of trimethyl tin glycinate is unique in having lone pair donation through nitrogen giving a one dimensional amino bridged polymer and trigonal bipyramidal geometry at tin. There is hydrogen bonding between carbonyl oxygen and amino N— H between the chains[112].



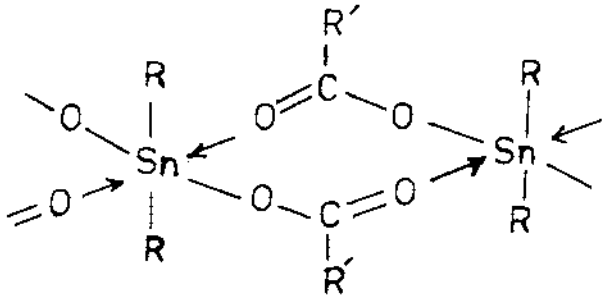
VI

This structure seems unusual since the affinity of tin for oxygen is greater, but the structure has been demonstrated crystallographically[112]. Similar structure has also been demonstrated for di-t-butyltin glycylglycinate monohydrate[146], with the exception that, the equatorial plane is composed of two Bu groups and one N atom of the tridentate ligand. The water molecule present contributes to the H-bonding net work.

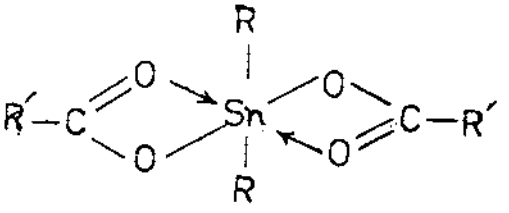
From the above observations it is apparent that in spite of accumulation of large amount of structural information on triorganotin carboxylates it is still not clear what properties of the R and R' groups determine which of the structures I, II, III is adopted in the solid state.

II.5.B. Diorganotin Dicarboxylates $[R_2Sn(OCOR')_2]$:

The structure of dialkyltin dicarboxylates was first suggested for dimethyltin diformate by Okawara[76] as consisting of a linear Me_2Sn cation and formate anion. Mossbauer[113,114] and I.R.[4,115] studies on a number of dialkyltin dicarboxylates suggest that in the neat liquid or solid states, these adopt a polymeric structure [VII] with intermolecularly bridging carboxylate groups and an octahedral trans-R_2SnX_4 tin atom geometry. X-ray crystallographic evidences in favour of this structure are, however, lacking. In solution, these compounds are monomeric and probably possess an octahedral intramolecularly chelated structure [VIII][4,115].



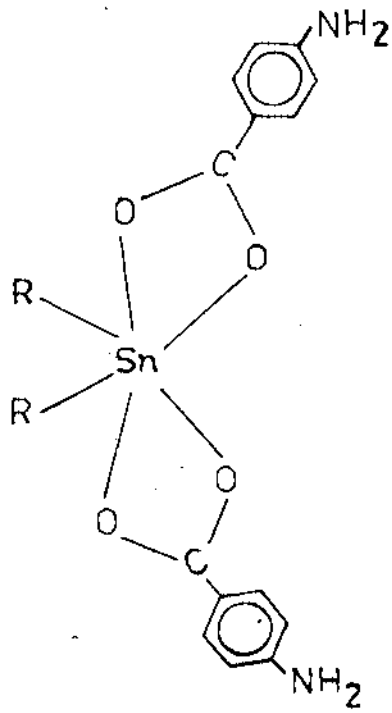
VII



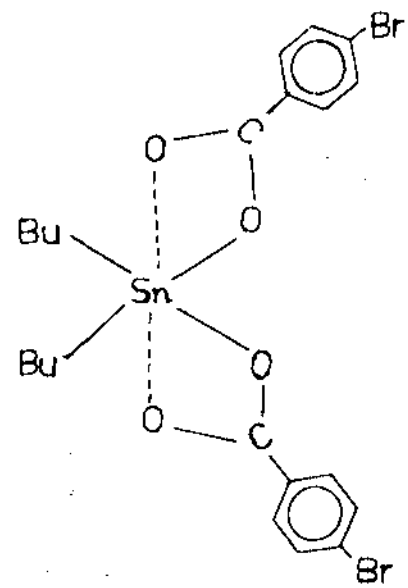
VIII

Recently, some dialkyltin dicarboxylates have been shown from crystallographic studies, to have monomeric structure in the solid state[116-119]. Thus from X-ray studies the mono nuclear $Me_2Sn(OCOC_6H_4\text{-}p\text{-}NH_2)_2$ has been assigned a distorted octahedral cis-R_2SnX_4 geometry around tin[116] as shown in structure IX. The structures of $^nBu_2Sn(OCOCH_2SC_6H_5)_2$[117], $^nBu_2Sn(OCOC_6H_4\text{-}p\text{-}Br)_2$[118], $Et_2Sn(OCOC_4H_3S)_2$[147] and $Pr_2Sn(OCOCH_2SPh)_2$[148] have been described as having a skew trapezoidal bipyramidal geometry at tin, also with a cis-R_2SnX_4 disposition as shown in figure (X). The $^nBu_2Sn(OCOC_6H_4\text{-}o\text{-}Br)_2$ has, however, been shown[120] to have, in the solid state, a distorted pentagonal bipyramidal geometry with trans Bu groups, due to dimerisation through weak interaction between a tin atom and a carboxylate-O atom linked to the other tin atom (XI). In solution the dimer dissociates.

In polymeric dimethyltin dipicolinate, where both carboxylate groups bridge successive atoms, tin is formally seven



IX

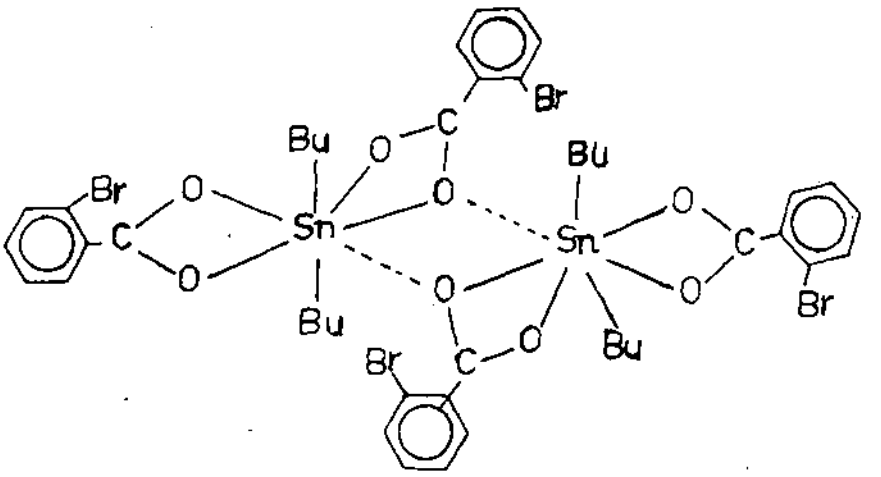


X

coordinate due to the formation of intramolecular tin-nitrogen bond[142]. Sandhu et.al. also have suggested the involvement of the N atom in intramolecular coordination in derivatives of picolinic acid [$R_2Sn(pic)_2$; where, R = Me, n-Bu, n-Oct and Bz.] on the basis of Mossbauer studies[149]. A distorted trans octahedral structure involving unidentate carboxylate groups has been suggested for these compounds. However, a weak C=O----Sn bridging interaction has not been ruled out in some compounds.

On the basis of IR, NMR, and ^{119}Sn Mossbauer studies, the intramolecularly chelated octahedral trans-R_2SnX_4 geometry around

tin [VIII] has been suggested for the diorganotin derivatives of 3-Benzoyl propionic acid[99], 2-Benzoyl benzoic acid[121] and some N-substituted amino acids[122-124].



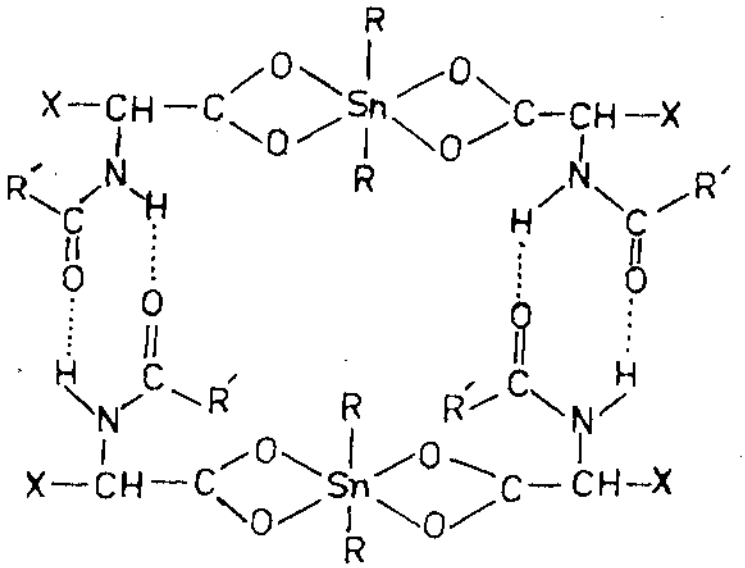
XI

The aminoacid derivatives dimerise due to H-bonding through the functional substituents on the amino N atom as shown below [XII][122,129]:

However, from X-ray studies, Sandhu et.al. have shown that [$Bu_2Sn(A)$] (where, HA = monochloro acetyl-L-phenyl alanine) has a monomeric structure with skew trapezoidal planar geometry around tin[150], instead of the octahedral geometry shown above [XII].

In addition to the 1:2 complexes shown above the aminoacids form similarly hydrogen bonded carboxy diorgano stannoxanes of the type $R_2(L)Sn\text{-}O\text{-}Sn(L)R_2$, where, the geometry around tin atom is trigonal bipyramidal trans-R_2SnX_3, involving chelating carboxylate groups[122-124,150].

In the diorganotin derivatives of mercapto carboxylic acids

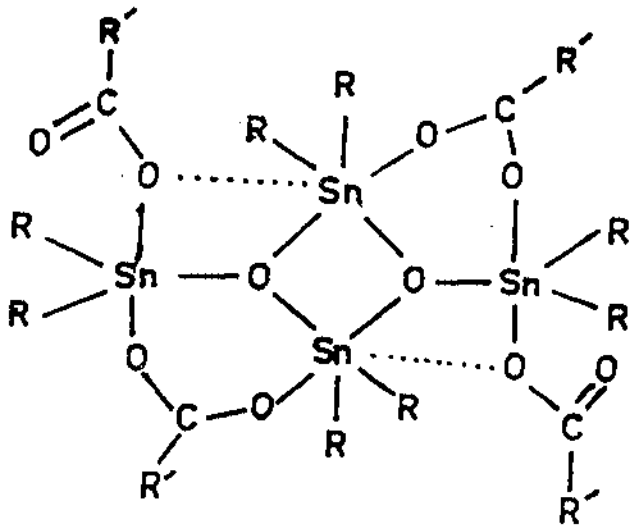


XII

also, Mossbauer[151] and X-ray[152] data indicate that the tin atom geometry is trigonal bipyramidal, nonlinear polymeric compounds being formed through the involvement of the S atom and bridging bidentate carboxylate groups.

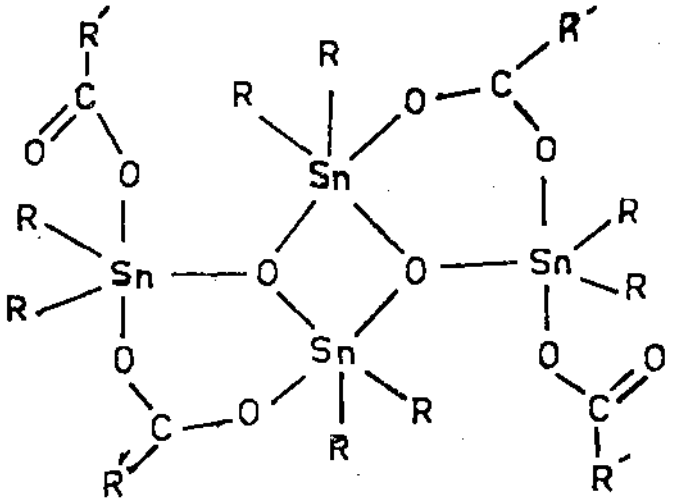
The reaction between diorganotin oxides and carboxylic acids often leads to the formation of carboxy diorgano stannoxanes, which are hydrolysed derivatives of the diorganotin carboxylates. A survey of the literature reveals that, diorganotin esters in general, and carboxy diorgano stannoxanes carrying ligands with functional substituents in particular, have not received attention commensurate with their structural possibilities[116,125-128]. As far back as in 1977, Tagliavini et.al. suggested the following dimeric structure [XIII] involving both monodentate and bidentate

carboxylate groups for tetrabutyl-1,3-trichloroacetoxy distannoxane $[(^{n}Bu_2SnOCOCCl_3)_2O]_2$ and similar compounds[125,129] in the solid state, as well as in CCl_4 solution, on the basis of IR spectra and X-ray studies. In more polar solvents like $CHCl_3$ the weak Sn----O bonds shown in structure XIII are broken and partial depolymerisation occurs and structure XIV and XV are supposed to be present[125].

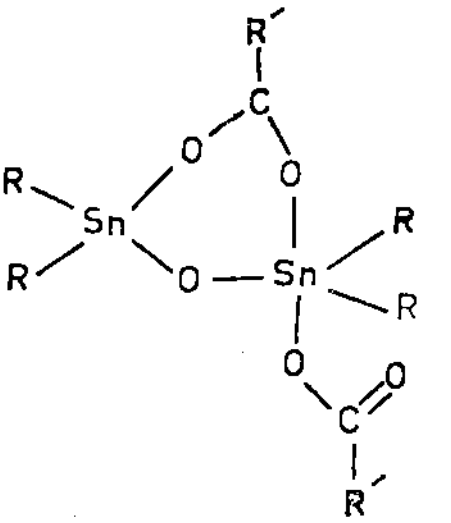


XIII

The distinctive features of these structures are the presence, in each, of two different tin atom geometries and two types of unique carboxylate groups, one of which bridges two tin centres, though weakly, via one oxygen atom only, the carbonyl oxygen remaining free. Further experimental support for the above structure XIII with a planar four membered Sn_2O_2 ring, of tetraalkyl dicarboxy



XIV

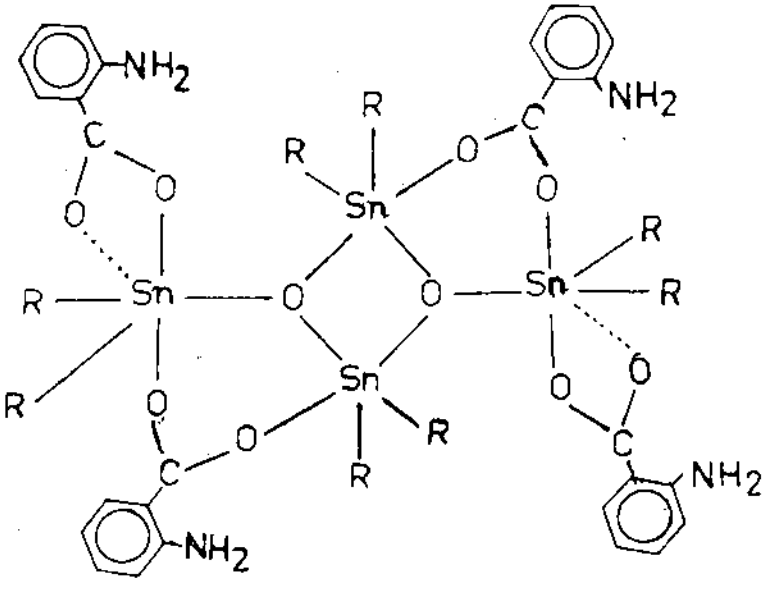


XV

distannoxane has only recently been provided from crystallographic studies of $[(Me_2SnOCOC_6H_4\text{-}o\text{-}NH_2)_2O]_2$[116], $[(^nBu_2SnOCOC_6H_4\text{-}o\text{-}NH_2)_2O]_2$[128], $[(^nBu_2SnOCOC_6H_4\text{-}o\text{-}OMe)_2O]_2$[119], $[(Bu_2SnOCOC_4H_3S)_2O]_2$[153] and other compounds[148]. However, the structure assigned to these compounds [XVI] differs slightly from structure XIII due to the involvement of the carbonyl oxygen in weak Sn----O interaction, thus rendering both the endocyclic and exocyclic tin atoms six-coordinate[116].

The tetraorgano stannoxane structure suggested for $[Me_2SnOCOC_6H_4\text{-}p\text{-}NH_2)_2O]_2$[116] differs considerably from both structures XIII and XVI in having two different tin atom geometries, but only one type of essentially monodentate carboxylate group, one oxygen atom of which bridges two tin centres through weak Sn----O interaction [XVII] . The other oxygen

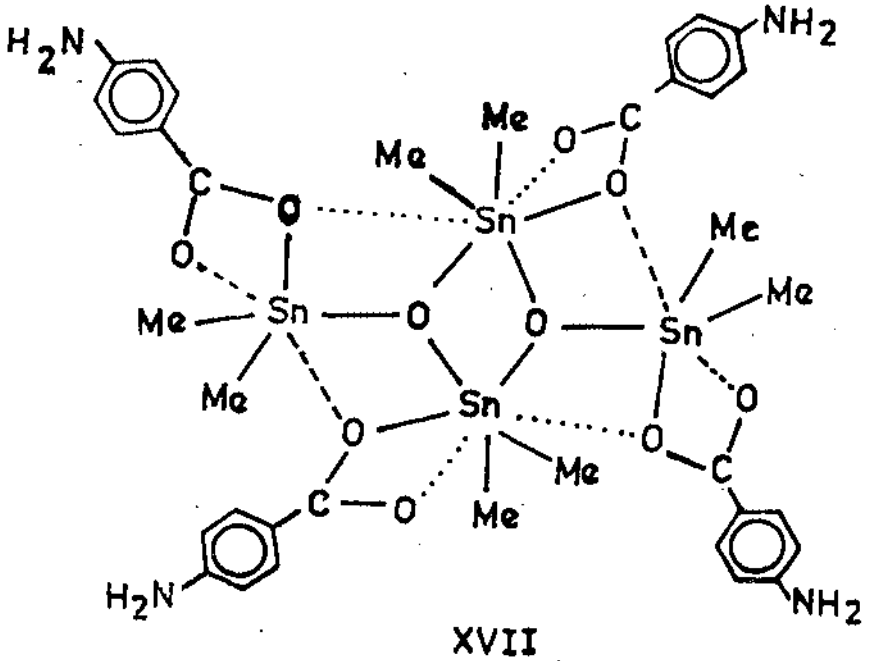
atom is also involved in weak Sn----O interaction.



XVI

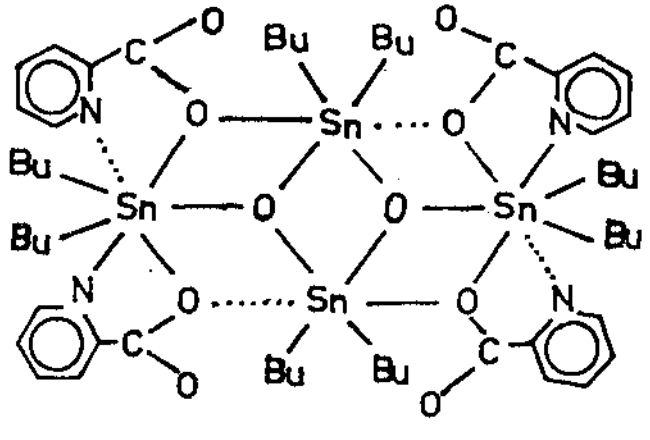
Crystal structure determination of $[Bu_2SnOCOC_5H_4N)_2O]_2$ [130] reveals that the 2-pyridine carboxylate ligand introduces a major change in the dicarboxylato tetraorgano stannoxane structure as a result of the formation of Sn—N bond [XVIII]. The centrosymmetric dimer features two unique carboxylate groups, one of which bridges two tin centres via one oxygen atom (the pendant oxygen atom is not coordinated but the N atom is weakly associated to tin).
The other carboxylate functions essentially in the monodentate mode (the carboxylate oxygen atom is involved in weak bridging interaction) and a chelate ring is formed through the formation of Sn—N bond. One tin atom is six coordinate and the other is seven coordinate by virtue of weak but significant intramolecular

interactions.



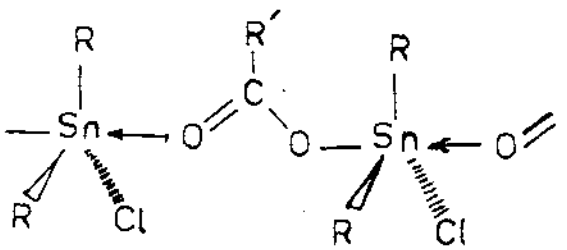
XVII

The dialkyl halotin carboxylates $R_2Sn(OCOCR')X$ are believed

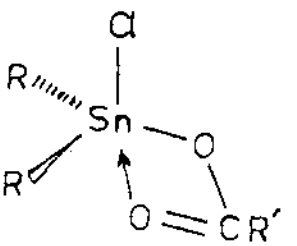


XVIII

to possess intermolecularly bridging and intramolecularly chelated structures XIX and XX, in solid state and solution respectively, with the tin atoms occupying a trigonal bipyramidal cis-R_2SnX_3 geometry[38]. These structures are quite similar to the structures I and III of the triorganotin carboxylates, the halogen atom of the former occupying the position of a R group of the latter.

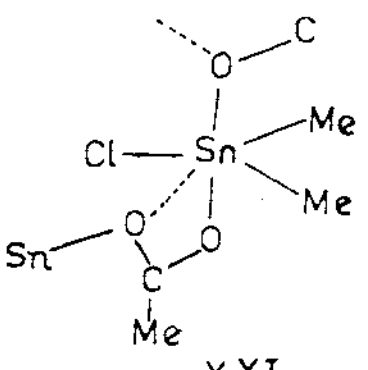


XIX



XX

X-ray studies of polymeric dimethyl chlorotin acetate[191], however, reveals that the tin atom is in a distorted trigonal bipyramidal environment, the distortion being attributed to a weak but

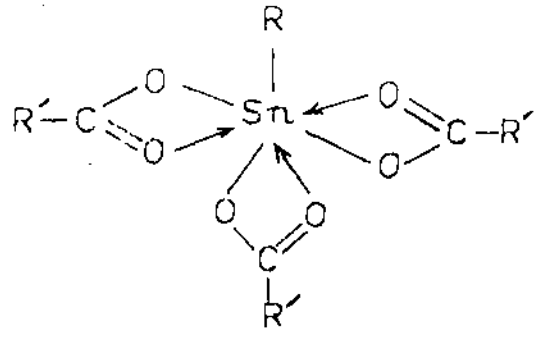


XXI

significant carbonyl O---Sn interaction resulting in the tin atom becoming six coordinate [XXI], resembling the structure of triphenyltin acetate [IV].

II.5.C. Monoorganotin Tricarboxylates [$RSn(OCOR')_3$] :

The structure of this type of organotin carboxylates have not been adequately elucidated. No X-ray studies are yet available on any monoorganotin tricarboxylate. The IR spectra of a number of monoorganotin esters in CCl_4 solution show coordinated carbonyl stretching bands, and additionally, $BuSn(OCOMe)_3$ and $BuSn(OCOEt)_3$ were found to be monomeric in camphor solution[42]. This is indicative of seven coordinated tin atom geometry for these compounds in solution [XXII].



XXII

II.6. *Organotin Keto carboxylates :*

Although triorganotin(IV) carboxylates are mostly five coordinate carboxylate-bridged polymers whose repeat units are

propagated in a zig-zag or helical manner in the crystal lattice[192], a bonding mode alternative to carboxyl bridging may become possible if the carboxylate group contains a substituent carrying a donor atom. The involvement of the additional donor atom in bonding may result in either a intramolecularly chelated ring structure or intermolecularly bridging polymeric structure. This latter option is adopted in trimethyltin glycinate [VI], where bridging occurs axially at tin along the chain through the amino nitrogen atom[112]. This seems unusual, since the affinity of tin for oxygen coordination is believed to be greater, and has generated tremendous interest in the solid state structure of organotin carboxylates containing an additional potential donor atom in the carboxylate moiety. Among many such compounds organotin esters of substituted benzoic acids and some amino acid derivatives have received much attention in recent years.

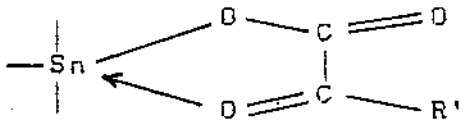
Keto carboxylic acids, though potentially polydentate, and apparently capable of forming a chelate ring, have not received adequate attention. KumarDas et.al. have investigated the tri- and diorganotin esters of some γ-keto carboxylic acids, viz, hippuric acid, succinanilic acid, levulinic acid[193] and 3-benzoyl propionic acid[98]. On the basis of IR and ^{119}Sn Mossbauer spectra the diorganotin compounds have been shown to adopt in the solid state, trans-R_2SnX_4 octahedral geometries and the triorganotin compounds, trans-R_3SnX_2 trigonal bipyramidal geometries, in which the carboxyl oxygen, rather than the ketonic oxygen, participates

in intermolecular coordination to tin. X-ray studies on the triphenyltin ester of 3-benzoyl propionic acid[93] has confirmed a carboxylate bridged rigid polymeric structure. The ketonic oxygen is not involved in coordination. The tri- and diorganotin esters of 2-benzoyl benzoic acid, which also has two carbon atoms separating the carboxyl and ketonic carbons, are also reported to have identical carboxylate bridged trans-R_3SnX_2 and six coordinate trans-R_2SnX_4 structures respectively[121]. The triorganotin acetylacetates (β-keto carboxylates) might be expected to be more rigid than the levulinates but their reported IR spectra[134] are rather similar to those of the levulinates. However, the organotin derivatives of β-keto carboxylic acids are yet to be investigated thoroughly.

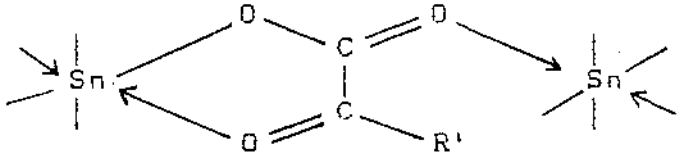
Although metal complexes, especially mixed ligand complexes of pyruvic acid, the first member of the α-keto carboxylic acid series are well known[135-140], reports on the organotin esters of α-keto acids are scanty. Only sketchy reports on the preparation[6] and IR spectra[106] of Bu_3Sn-derivatives and Mossbauer spectra of Ph_3Sn-derivative[141] of pyruvic acid have appeared so far. The ease with which the α- and β-keto carboxylic acids, as well as their metal derivatives undergo polymerisation, decarboxylation and decarbonylation may be one of the main reasons for the apparent lack of interest in organotin derivatives of keto carboxylic acids.

In comparison to the γ-keto acids studied so far[93,133] the

keto group in the α-keto acids is more suitably placed for being involved in a chelate ring in their organotin derivatives as shown below:

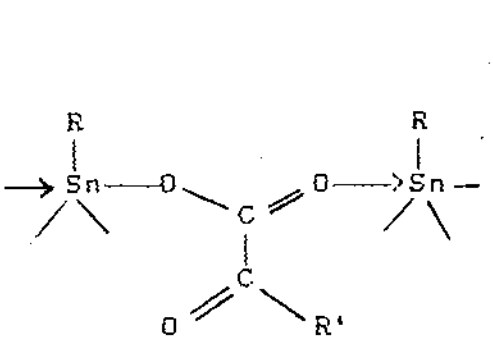


However, formation of such a chelate ring does not, in any way, preclude polymerisation, as the carboxyl C=O may be involved in bridging interaction as shown below :

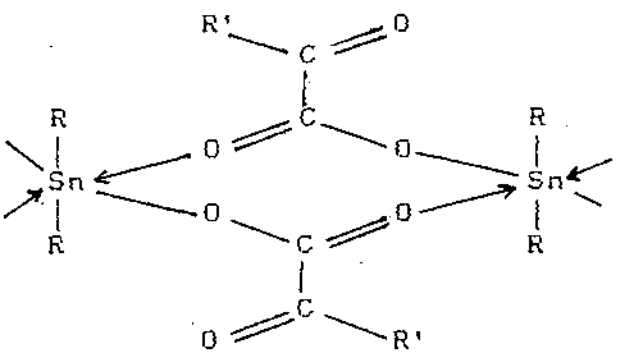


The high electronegativity of the $R'COCOO^-$ moiety is likely to increase the Lewis acidity of the tin atom, thereby helping the nucleophilic attack on it by the carboxyl C=O of another ring, leading to polymeric structure.

Besides, irrespective of the role of the keto group, polymerisation is likely to proceed through the involvement of carboxyl group in intermolecular bridging mode, which is a general feature of all compounds incorporating strongly electronegative acid ligands[63], resulting into one dimensional rigid polymeric structures, such as,



;



etc.

The ultimate demonstration of whether or not a ketonic group in the organotin esters of keto carboxylic acids is involved in coordination must await further investigation.

BIBLIOGRAPHY.

1. Poller R.C., *The Chemistry of Organotin Compounds.*, Logos Press, London, 1970, Ch-10.
2. Neuman W.P., *The Organic Chemistry of Tin.*, Wiley, London 1970, Ch-17.
3. Okawara R. and Wada M., *Advances in Organometallic Chemistry.* Academic Press, N.Y., 1967, Vol-V, P-137.
4. Okawara R. and Ohara M., *Organotin Compounds.*, Ed. A.K. Sawyer, Marcel Dekker, N.Y., 1971, Vol-II, P-253.
5. Davies A.G. and Smith P.J., *Comprehensive Organometallic Chemistry.*, Ed. G.Wilkinson., Pergamon Press, 1982, Ch-11, P-564.
6. Dunn P. and Norris T., *Austral. Comm. Dept. Suppl. Def. Std. Lab. Rept.*, 1964, No.269, P-21.
7. Vilarem M. and Maire J.C., *Compt. Rend. Ser.*, 1966, 262 C, 460.
8. Japanese Patent., *Chem. Abstr.*, 1966, 65, 2298g.
9. ,, ,, ,, ,, 12240c.
10. ,, ,, 1968, 69, 87186.
11. U.S. Patent., ,, 1966, 65, 12240b.
12. Polish Patent., ,, 1968, 68, 49776.
13. Ford B.F.E. and Sams J.R., *J. Organomet. Chem.*, 1971, 31, 47.
14. Poller R.C., Ruddick J.N.R., Taylor B. and Toley D.L.B., *J. Organomet. Chem.*, 1970, 24, 341.
15. French Patent., *Chem. Abstr.*, 1965, 62, 16296a.
16. Deacon G.B. and Farquharson G.J., *J. Organomet. Chem.*, 1977, 135, 73.

17. Frankel M., Gertner D., Wagner D. and Zilkha A., *J. Organomet. Chem.*, 1967, 9, 83.

18. Ford B.F.E., Liengme B.V. and Sams J.R., *J. Organomet. Chem.*, 1969, 19, 53.

19. Srivastava T.N. and Tandon S.K., *J. Prakt. Chem.*, 1969, 311(5), 878.

20. Clark H.C., O'Brien R.J. and Fickard A.L., *J. Organomet. Chem.*, 1965, 4, 43.

21. Peruzzo V., Plazzogna G. and Tagliavini G., *J. Organomet. Chem.*, 1972, 40, 121.

22. Anderson H.H. *Inorg. Chem.*, 1962, 1, 647.

23. Henderson A. and Holliday A.K., *J. Organomet. Chem.*, 1965, 4, 377.

24. Wiberg E. and Behringer H., *Z. Anorg. Allgen. Chem.*, 1964, 290, 329.

25. Ingham R.K., Rosenberg S.D. and Gilman M., *Chem. Rev.*, 1960, 60, 459.

26. Peruzzo V., Plazzogna G. and Tagliavini G., *J. Organomet. Chem.*, 1969, 16, 500.

27. Sawyer A.K. and Kuivila H.G., *J. Org. Chem.*, 1962, 27, 610.

28. Weber S. and Becker E.I., *J. Org. Chem.*, 1962, 27, 1258.

29. Kuivila H.G., *Adv. Organomet. Chem.*, 1964, 1, 82.

30. Hester R.E., *J. Organomet. Chem.*, 1970, 23, 123.

31. Sawyer A.K. and Kuivila H.G., *J. Org. Chem.*, 1962, 27, 837.

32. Adams S., Drager M. and Mathiasch B., *J. Organomet. Chem.*, 1987, 326(2), 173.

33. Alleston D.L. and Davies A.G., *J. Chem. Soc.*, 1962, 2050.

34. Sawyer A.K. and Kuivila H.G., *Chem. Ind.*, 1961, 260.

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

36. Okawara R. and Rochow E.G., *J. Am. Chem. Soc.*, 1960, 82, 3285.

37. Wang C.S.C. and Shreeve J.M., *J. Organomet. Chem.*, 1972, 38, 287.

38. Honnick W.D. and Zuckerman J.J., *J. Organomet. Chem.*, 1979, 178, 133.

39. Rzaev Z.M., Kochkin D.A. and Zubov P.I., *Dokl. Akad. Nauk. SSSR.*, (Eng. trans), Consultants Bureau, 1967, Vol.-172(No-103), 364.

40. Anderson H.H., *J. Org. Chem.*, 1954, 19, 1766.

41. Biswas G., Ph.D. Thesis, North Bengal Univ., India (1977).

42. Anderson H.H., *Inorg. Chem.*, 1964, 3, 912.

43. Ingham R.K., Rosenberg S.D. and Gilman H., *Chem. Rev.*, 1960, 60, 490.

44. Alleston D.L., Davies A.G., Hancock M. and White R.F.M., *J. Chem. Soc.*, 1963, 5469.

45. Davies A.G., Smith L. and Smith P.J., *J. Organomet. Chem.*, 1972, 39, 279.

46. Deacon G.B., *Organomet. Chem. Rev.*, (A), 1970, 5, 355.

47. Okawara R. and Ohara M., *J. Organomet. Chem.*, 1965, 3, 484.

48. Luijten J.G.A. and Van der Kerk G.J.M., *Recl. Trav. Chim. Pays-Bas.* 1964, 83, 295.

49. Luijten J.G.A. and Van der Kerk G.J.M., *J. Appl. Chem.*, 1956, 6, 93.

50. Seyferth D., Armbrecht(Jr.) F.M., Prokai B. and Cross R.J., *J. Organomet. Chem.*, 1966, 6, 573.

51. Anderson H.H., *J. Org. Chem.*, 1956, 21, 869.

52. Thies C. and Kissinger J.B., *Inorg. Chem.*, 1964, 3 ,551.

53. Cohen H.J., *J. Organomet. Chem.*, 1967, 177.

54. Crowe A.J., Hill R., Smith P.J., Brooks J.S. and Formstone R., *J. Organomet. Chem.*, 1981, 204 ,47.

55. Cohen A.D. and Dillard C.R., *J. Organomet. Chem.*, 1970, 25 ,421.

56. Bloodworth A.J., Davies A.G. and Graham I.F., *J. Organomet. Chem.*, 1968, 13 ,351.

57. Zhivukhim S.M., Dudikova E.D. and Ter-Sarkisjan E.M., *J. Gen. Chem. USSR.*, 1962, 32 ,3010.

58. Zemlyanskii N.N., Panov E.N., Samagina O.P. and Kocheskov K.A., *J. Gen. Chem. USSR.*, 1965, 35 ,1034.

59. Zemlyanskii N.N., Panov E.N., Slovokhotova N.A., Samagina O.P. and Kocheskov K.A., *Proc. Acad. Sci. USSR.*, 1963, 149 ,205.

60. Henry M.C. and Davidsohn W. '*Organotin Compounds.*',Ed. A.K.Sawyer, Marcel Dekker, N.Y., 1972, Vol-III, P-975.

61. Subramanian R.V. and Garg B.K., *Polym-Plast. Technol.,Eng.*, 1978, 11 ,81.

62. Graddon D.P. and Rana B.A., *J. Organomet. Chem.*, 1977, 136 ,19.

63. Molloy K.C., Blunden S.J. and Hill R., *J.Chem.Soc. Dalton.Trans.*, 1988(5),1259.

64. Huber F., Enders M. and Kaiser R., *Z. Naturforsch.*, 1966, 21B, 83.

65. Garner C.D., Hughes B. and King T.J., *J.Chem.Soc. Dalton. Trans.*, 1975, 572.

66. Ford B.F.E. and Sams J.R., *Inorg. Chim. Acta.*, 1978, 28 ,L173.

67. Harrison P.G. and Phillips R.C., *J.Organomet.Chem.*, 1979,162 ,37.

68. Siddiqui K.S., Zaidi F.R., Khan T.A. and Zaidi S.A.A., *Bull. Soc. Chim. Fr.*, 1983, 5-6 Pt-1, 140.

69. Srivastava T.N. and Sing J.D., *Ind. J. Chem.*, 1983, 22A(2), 128 ; 1983, 22A(8), 674 ; 1986, 24A(6), 489.

70. Siddiqui K.S., Kureshi R.I., Khan P. and Zaidi S.A.A., *Ind. J. Chem.*, 1983,22A(7), 616.

71. Narula S.P., Sharma R.K., Lata S., Kapur N. and Seth R., *Ind. J. Chem.*, 1983, 22A(3), 248.

72. Midha A.and Verma R.D., *J. Ind. Chem. Soc.*, 1985, 62(6), 421.

73. Srivastava T.N., Siddiqui M.A., Sing J.D. and Srivastava S., *Ind. J. Chem.*, 1987, 26A(2), 158.

74. Beattie I.R. and Gilson T., *J. Chem. Soc.*, 1961, 2585.

75. Freeman J.P., *J. Am. Chem. Soc.*, 1958, 80 ,5954.

76. Okawara R., Webster D.E. and Rochow E.G., *J. Am. Chem. Soc.*, 1960, 82 ,3287.

77. Itoch K. and Bernstein H.J., *Can. J. Chem.*, 1956, 34 ,170.

78. Chih H. and Penford B.R., *J. Cryst. Mol. Struct.*, 1973, 3 ,285.

79. Alcock N.W. and Timms R.E., *J. Chem. Soc. (A).*, 1968, 1873.

80. Calogero S., Clemente D.A.,Peruzzo V. and Tagliavini G., *J. Chem. Soc. Dalton. Trans.*, 1979, 1172.

81. Sandhu G.K., Verma S.P. and Tiekink E.R.T., *J. Organomet. Chem.*, 1990, 393 ,195.

82. Simons P.B. and Graham W.A.G., *J. Organomet. Chem.*, 1967, 6 ,479.

83. Reichle W.T., *Inorg. Chem.*, 1966, 5 ,67.

84. Zimmer H., Homberg O.A. and Jayawant M., *J.Org.Chem.*,1966,31,3857.

85. Alcock N.W. and Timms R.E., *J. Chem. Soc. (A).*, 1968, 1876.

86. Barbieri R., Pellerito L., Bertazzi N. and Stocco G.C., *Inorg. Chim. Acta.*, 1974, 11 ,173.

87. Burke J.J. and Lauterbur P.C., *J. Am. Chem. Soc.*, 1961, 83 ,326.

88. Molloy K.C., Purcell T.G., Han E., Schumann H. and Zuckerman J.J., *Organometallics.*, 1985, 5 ,85.

89. Schubert U., *J. Organomet. Chem.*, 1978, 155 ,285.

90. Sharma C.P., Kumar N., Chandra S. and Bhide V.G., *J. Inorg. Nucl. Chem.*, 1981, 43 ,2659.

91. Holmes R.R., Day R.O., Chandrashekhar V., Vollano J.F. and Holmes J.M., *Inorg. Chem.*, 1986, 25 ,2490.

92. Holmes R.R., Day R.O., Chandrashekhar V., Holmes J.M. and Smith P.J., *Inorg. Chem.*, 1986, 25 ,2495.

93. Ng S.W., KumarDas V.G. and Syed A., *J. Organomet. Chem.*, 1989, 364(3), 353.

94. Ng S.W., Amini M.M., Fidelis K., Heeg M.J., Muchmore C.R. and Zuckerman J.J., *J. Organomet. Chem.*, 1989, 365 ,103.

95. Ng S.W., Chin K.L., Chen W., KumarDas V.G. and Butcher R.J., *J. Organomet. Chem.*, 1989, 376 ,277.

96. Swisher R.G., Vollano J.F.,Chandrashekhar V., Day R.O. and Holmes R.R., *Inorg. Chem.*, 1984, 23 ,3147.

97. Vollano J.F., Day R.O., Rau D.N., Chandrashekhar V. and Holmes R.R., *Inorg. Chem.*, 1984, 23 ,3153.

98. Ng S.W., KumarDas V.G., vanMeurs F., Schagen J.D. and Shavers L.H. *Acta. Crystallogr. C.*, 1989, 45 ,568.

99. Molloy K.C., Purcell T.G., Quill K. and Nowell I.W., *J. Organomet. Chem.*, 1984, 267 ,237.

100. Debye N.W.G., Fenton D.E., Ulrich S.E. and Zuckerman J.J., *J. Organomet. Chem.*, 1971, 28 ,339.

101. Harisson P.G., King T.J. and Molloy K.C., *J. Organomet. Chem.*, 1980, 185 ,199.

102. Sandhu G.K., Verma S.P., Moore L.S. and Parish R.V., *J. Organomet. Chem.*, 1987, 321 ,15.

103. Sandhu G.K. and Kaur G., *J. Organomet. Chem.*, 1990, 388 ,63.

104. Poller R.C., *J. Inorg. Nucl. Chem.*, 1962, 24 ,593.

105. Egorochkin A.N., Domarchev G.A., Vyazankim N.S., Khorshev S.Ya., Djachkovskaya O.S. and Bychkov V.I., *Izvest. Akad. Nauk. SSSR., Ser. Khim.*, 1971, B ,164.

106. Cummins R.A. and Dunn F., *Austral. Comm. Dept. Suppl. Def. Std. Lab. Rept.*, 1963 No-266, P-106.

107. Molloy K.C., Quill K., Blunden S.J. and Hill R., *Polyhedron.*, 1986, 5 ,959.

108. Harrison P.G., Lambert K., King T.J. and Majee B., *J. Chem. Soc., Dalton. Trans.*, 1983, 363.

109. Majee B. and Banerjee S., *J. Organomet. Chem.*, (a) 1977, 139 ,39. (b) 1977, 140 ,151.

110. Majee B., Chattopadhyay T.K. and Sengupta A., *Ind. J. Chem.*, 1982, 21A ,1090.

111. Majee B., Chattopadhyay T.K. and BasuBaul T.S., *Polyhedron.*, 1983, 2 ,635.

112. Ho B.Y.K., Molloy K.C., Zuckerman J.J., Reidinger F. and Zubieta J.A., *J. Organomet. Chem.*, 1980, 187 ,213.

113. Smith P.J., *Organomet. Chem. Rev.(A).*, 1970, 5 ,373.

114. Ruddick J.N.R., *Rev. Silicon, Germanium, Tin, Lead Compds.*, 1976, 2 ,115.

115. Maeda Y. and Okawara R., *J. Organomet. Chem.*, 1967, 10 ,247.

116. Chandrashekhar V., Day R.O., Holmes J.M. and Holmes R.R., *Inorg. Chem.*, 1988, 27(5), 958.

117. Sandhu G.K., Sharma N. and Tiekink E.R.T., *J. Organomet. Chem.*, 1989, 371(1), C-1.

118. Ng S.W., KumarDas V.G., Skelton B.W. and White A.H., *J. Organomet. Chem.*, 1989, 377 ,221.

119. Parulekar C.S., Jain V.K., Kesavadas T. and Tiekink E.R.T., *J. Organomet. Chem.*, 1990, 387(2), 163.

120. Ng S.W., KumarDas V.G., Yip W.-H., Wang R.-J. and Mak T.C.W., *J. Organomet. Chem.*, 1990, 393 ,201.

121. Ng S.W. and Zuckerman J.J., *J. Organomet. Chem.*, 1983, 249 ,81.

122. Sandhu G.K., Sandhu S.S., Gupta R. and Parish R.V., *Polyhedron.*, 1985, 4(1), 81.

123. Sandhu G.K., Sandhu S.S., Gupta R., Parish R.V. and Moore L.S., *J. Organomet. Chem.*, 1986, 311 ,281.

124. Sandhu G.K., Sandhu S.S., Gupta R., Parish R.V. and Brown K., *J. Organomet. Chem.*, 1985, 279 ,373.

125. Graziani R., Bombieri G., Forsellini E., Furlan R., Peruzzo V. and Tagliavini G., *J. Organomet. Chem.*, 1977, 125 ,43.

126. Valle G., Peruzzo V., Tagliavini G. and Ganis P., *J. Organomet. Chem.*, 1984, 276 ,325.

127. Birchall T., Frampton C.S. and Jhonson J.P., *Acta.Crystallogr. C.*, 1987, 43 ,1492.

128. Narula S.P., Bharadwaj S.K., Sharma H.K., Mairesse G., Barbier P. and Nowogrocki G., *J. Chem. Soc., Dalton. Trans.*, 1988, 1719.

129. Peruzzo V. and Tagliavini G., *J. Organomet. Chem.*, 1974, 66 ,437.

130. Parulekar C.S., Jain V.K., Das T.K., Gupta A.R., Hopkins B.F. and Tiekink E.R.T., *J. Organomet. Chem.*, 1989, 372 ,193.

131. Allen D.W., Nowell I.W., Brooks J.S. and Clarkson R.W., *J. Organomet. Chem.*, 1981, 219 ,29.

132. Ng S.W., Chen W. and KumarDas V.G., *J.Organomet.Chem.*,1988,345,59.

133. Ng S.W., Chen W., Yap C.K., KumarDas V.G. and Mak T.C.W., *J. Organomet. Chem.*, 1986, 311 ,289.

134. Chan J.K. and Marcus E., *Chem. Ind.*, 1966, 1767.

135. Leusing D. L. and Shultz D.C., *J. Am. Chem. Soc.*, 1964, 86 ,4846.

136. Leusing D.L. and Tallman D.E., *J. Am. Chem. Soc.*, 1969, 91 ,6253; 6256 ; and references cited therein.

137. Harrowfield J.M. and Sargeson A.M., *J. Am. Chem. Soc.*, 1979, 101(6), 1514.

138. Palrecha M.M. and Gaur J.N., *Ind. J. Chem.*, 1969, 7(10), 1035.

139. Ghandour M.A., Mansour H., Abu-El-Wafa M.H.M. and Khodary M., *J. Ind. Chem. Soc.*, 1988, 65 ,713 ; 827 ; and references cited therein.

140. Gaifullin A.A., Kharlampidi Kh.E., Efanova E.A., Koshkina G.M. and Lebedeva W.M., *Neftekhimiya.*, 1988, 28(3), 388.

141. Ng S.W. and KumarDas V.G., Unpublished work, cited in Ref.93.

142. Lockhart T.P. and Davidson F., *Organometallics.*, 1987, 6 ,2471.

143. Ng S.W., KumarDas V.G. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 403(1-2), 111.

144. BasuBaul T.S. and Rivarola E., *Ind. J. Chem.*, 1993, 32A(10), 905.

145. Ng S W., Chin K.L., Wei C., KumarDas V.G. and Mak T.C.W., *J. Organomet. Chem.*, 1989, 365 ,207.

146. Preut H., Mundus B., Huber F. and Barbieri R., *Acta. Crystallogr. Sect.C. Cryst. Struct. Commun.*, 1989, C45(5), 728.

147. Vatsa C., Jain V.K., Kesavadas T. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 410(2), 135.

148. Sandhu G.K., Sharma N. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 403(1-2), 119.

149. Sandhu G.K. and Poparov N.S., *J. Organomet. Chem.*, 1991, 411 ,89.

150. Sandhu G.K., Hundal R. and Tiekink E.R.T., *J. Organomet. Chem.*, 1991, 412(1-2), 31.

151. Hager C.D., Huber F., Silvestri A., Barbieri A. and Barbieri R., *Gazzetta Chimica Italiana.*, 1993, 123(10), 583.

152. Lockhart T.P., *Organometallics.*, 1988, 7(6), 1438.

153. Vatsa C., Jain V.K., Das T.K. and Tiekink E.R.T., *J. Organomet. Chem.*, 1990, 396(1), 9.

CHAPTER-III

ORGANOTIN DERIVATIVES OF α-KETO CARBOXYLIC ACIDS.

ORGANOTIN DERIVATIVES OF α-KETO CARBOXYLIC ACIDS :

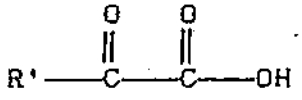
(Preparation, Properties and Spectroscopic Studies).

III.1. *Introduction :*

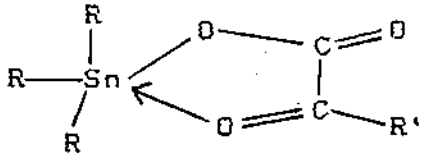
A survey of literature shows that although tremendous amount of work has already been done on the synthesis and structure of organotin carboxylates with almost all conceivable type of substituents on both the tin atom and the carboxyl moiety, the organotin esters of α-keto acids [I] are yet to be adequately investigated. Only a few reports on the preparation[1] and spectral studies[2] on the triphenyl and tributyltin esters of pyruvic acid have appeared so far. Organotin derivatives of α-keto carboxylic acids would be of interest in two respects :

(i) Organotin carboxylates, unlike organotin halides, are somewhat reluctant to form addition complexes with Lewis bases, although a number of their adducts with N, O and S containing ligands have, recently, been reported[3-10]. Apart from the hydrate adducts of di and tri organotin carboxylates[16-18] and the anionic acetate adduct of $Me_2Sn(OAc)_2$[19], the organotin carboxylate moiety, in majority of these complexes reported so far, is a derivative of a trihalocarboxylic acid such as CF_3COOH or CCl_3COOH[6,7,10,12-15]. Most obviously, the electronegativity of the $RCOO^-$ moiety in these carboxylates profoundly influences the Lewis acidity of the tin atom[15], thereby making it susceptible to nucleophilic attack. The

α-keto acids, possessing a suitably placed keto group and high acid strength (electronegativity) appear to be suitable for the realisation of organotin carboxylates of the type II, in which the carboxylato group is part of a chelated ring structure, formed as a result of intra molecular nucleophilic attack. It is therefore, of great interest to know whether, such coordination would occur in organotin derivatives of α-keto carboxylic acids, or not.



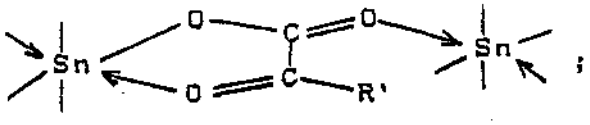
I



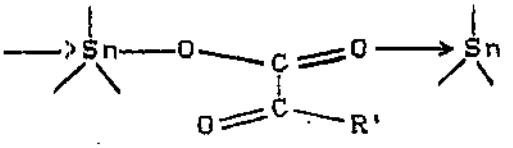
II

It should be pointed out here, that the formation of such a chelate ring does not necessarily exclude the possibility of intermolecular coordination in these organotin derivatives of the α-keto acids. The enhanced Lewis acidity of the tin atom due to high electronegativity of the $R'COCOO^-$ moiety makes it equally susceptible to intra molecular as well as intermolecular nucleophilic attack. Thus, favourable electronic and steric factors are likely to introduce intermolecular coordination leading to either of the following structures III or IV, without regard to the role of the keto group in the complex.

(ii) Pyruvic acid, the first member of the α-keto acid series, is very important biologically since it is an intermediate product



III



IV

in the metabolism of carbohydrates and proteins. Recently, Pt-complexes of pyruvic acid have been found to possess remarkable anti-tumour activity[21-24]. Therefore, synthesis and study of the tin complexes of pyruvic acid and its homologues are important from the biological point of view as well.

Moreover, it is also interesting to know the various factors which influence the course of the reaction between the keto acids and organostannoxanes.

These considerations led us to investigate the organotin derivatives of α-keto carboxylic acids. The keto acids used in the present investigation have been named and abbreviated as shown below.

Sl.no.	Structure	Name	Abbreviation
1.	$CH_3-C(=O)-C(=O)-OH$	Pyruvic acid (2-Oxo-Propanoic acid)	PvH
2.	$PhCH_2-C(=O)-C(=O)-OH$	Phenyl Pyruvic acid (2-Oxo-3-Phenyl Propanoic acid)	PPvH
3.	$Ph-C(=O)-C(=O)-OH$	Benzoyl Formic acid (2-Oxo-2-Phenyl Acetic acid)	BFH

III.2. *Experimental :*

The organotin compounds used were purchased from Fluka (Switzerland) and Aldrich (USA) and were used without further purification except Ph_3SnCl, which was purified by repeated recrystallisation from petroleum ether (Bp. 60-80°c) until the product attained the mp. 106°c. Ph_3SnCl was also prepared from Ph_4Sn by standard method[25] and purified in the same manner. $(PhCH_2)_3SnCl$ was prepared by the method described by Sisido et.al.[26] and recrystallised from ethyl acetate.

All solvents were purified by standard methods[27] as and when necessary. Unless otherwise stated, petroleum ether used refers to the fraction boiling at 60-80°c. All melting points were observed by open capillary method and are uncorrected.

III.2A. Preparation Of The Ligands :

(i) Pyruvic acid (PvH) :

Pyruvic acid was prepared according to the method described by Gilman and Blatt[28a], and purified by fractional distillation. The fraction boiling at 75-80°C/25 mm was collected.

(ii) Phenyl Pyruvic acid (PPvH) :

Phenyl pyruvic acid was prepared according to the method described by Gilman and Blatt[28b], and dried in a vacuum desiccator over $CaCl_2$ and KOH. Mp. 156-158°C.

(iii) Benzoyl Formic acid (BFH) :

Benzoyl formic acid was purchased from Fluka (Switzerland) and used without further purification. Mp. 62-64°C.

III.2B. Preparation of the Organotin Derivatives :

1. Reaction of NaPv with Ph_3SnCl :

0.77 g (0.002 mole) of Ph_3SnCl was stirred with large excess of NaPv (0.5 g,0.005 mole) in dry ether containing some methanol at room temperature for 8 hours. The solvent was completely removed at room temperature under vacuum and the resultant mass extracted with hot pet.ether. The pet.ether extract was allowed to stand and the first fraction of product was repeatedly recrystallised from pet.ether.

Yield :0.085 g (ca.10%). Mp. 114-6°C.

Analysis :	%Sn	%C	%H
Found :	26.1	58.8	4.6
Calculated for Ph_3SnPv :	27.06	57.7	4.13

2. Reaction of PvH with $(Ph_3Sn)_2O$:

(i) 1.79 g (0.0025 mole) of $(Ph_3Sn)_2O$ was dissolved in 40 ml dry dry ether, 0.44 g (0.005 mole) of PvH was added and refluxed using Dean and Stark water separator for about 1 hour and filtered. The filtrate was evaporated to dryness at room temperature and the

resulting mass extracted with pet.ether. The pet.ether extract on evaporation and recrystallisation from the same solvent gave 0.065 g (3%) white solid melting at 114-6°C.

Analysis :	%Sn	%C	%H
Found :	25.8	59.1	4.8
Calculated for Ph_3SnPv :	27.06	57.7	4.13

The residue obtained after reflux and after extraction with pet.ether were repeatedly washed with benzene and ether and dried. Both were found to be identical on the basis of IR and analytical data. The combined mass of the residue was 1.75 g (80%) and it did not melt.

Analysis :	% Sn	% C	% H
Found :	30.1	48.1	3.8
Calculated for $Ph_2Sn(Pv)OH$:	31.38	47.87	3.72

(ii) The same amount of $(Ph_3Sn)_2O$ and PvH as above were taken in benzene-free solvent ether and refluxed under the same condition and the solvent ether was carefully distilled out completely. The UV spectrum of the distillate was recorded in the 280-230 nm region using a Shimadzu UV240 spectrophotometre. The UV spectrum showed the presence of benzene in the distillate indicating that one of the reaction products is benzene.

(iii) The same amount of $(Ph_3Sn)_2O$ and PvH as above were taken in 40 ml dry benzene and refluxed using water separator for 12 hours. Filtered and the residue washed with ether. On

recrystallisation from methanol 0.8 g of yellow solid, which decomposed above 280°C without melting, was obtained.

Analysis :	% Sn	% C	% H
Found :	38.5	34.8	2.8
Calculated for $[PhSn(Pv)O]_n$:	39.6	36.2	2.7

The filtrate was evaporated to dryness and extracted with hot benzene-pet.ether mixture (80:20). The solution was concentrated and allowed to crystallise. On repeated recrystallisation from the same solvent 0.19 g of crystalline solid, melting at 227-8°c, were obtained. This was found to be Ph_4Sn from analytical data and mixed melting point determination with an authentic sample of Ph_4Sn.

The residue after extraction with benzene-pet.ether mixture was washed with ether and dried. The yellow solid weighed 0.5 g and did not melt.

Analysis :	% Sn	% C	% H
Found :	30.9	49.3	3.4
Calculated for $Ph_2Sn(Pv)OH$:	31.38	47.87	3.72

3. Reaction of NaPv with Bu_3SnCl :

0.32 g (0.001 mole) of Bu_3SnCl was added to a suspension of excess NaPv (0.2 g, ~ 0.002 mole) in 20 ml ether and stirred for 8 hours using magnetic stirrer. The solvent was then removed at room temperature and the residue was extracted with pet.ether.

The pet.ether solution was evaporated and the resulting mass recrystallised from the same solvent.

Yield : 0.04 g (ca. 11%). Mp. 80-82°C.

Analysis :	% Sn	% C	% H
Found :	31.02	49.0	8.5
Calculated for Bu_3SnPv :	31.38	47.9	7.98

4. Reaction of PvH with $(Bu_3Sn)_2O$:

1.49 g of $(Bu_3Sn)_2O$ (0.0025 mole) was dissolved in 40 ml dry benzene and refluxed with 0.46 g (>0.005 mole) of PvH for 16 hours using water separator. The yellow solution was filtered and shaken vigorously with $NaHCO_3$. Filtered and the filtrate was evaporated to very small volume (3-4 ml), diluted with 5 ml pet.ether and stored at 5°C. A viscous dark yellow liquid settled at the bottom. The clear supernatant liquid was decanted and further diluted with little pet.ether and kept at 5°C. The same process was repeated till no more viscous liquid separated. The supernatant liquid on evaporation at room temperature gave yellowish crystals which were recrystallised from pet.ether and dried under vacuum over $CaCl_2$.

Yield : 0.36 g (ca. 20%). Mp. 80-82°C.

Analysis :	% Sn	% C	% H
Found :	31.1	48.8	8.4
Calculated for Bu_3SnPv :	31.38	47.9	7.98

5.(i) Reaction of NaPv with $(PhCH_2)_3SnCl$:

0.426 g (0.001 mole) of $(PhCH_2)_3SnCl$ was stirred with excess NaPv (0.27 g, ~ 0.003 mole) in dry ether containing some methanol at room temperature for 6 hours. The solvent was completely removed at room temperature and the residue extracted with cold ether and allowed to stand. The first crop of product was rejected and the second crop recrystallised from ether.

Yield :0.04 g (ca. 8%). Mp. 104-108^{o}C.

Analysis :	% Sn	% C	% H
Found :	-	61.3	4.8
Calculated for $(PhCH_2)_3SnPv$:	24.69	60.25	5.02

(ii) Reaction of PvH with $[(PhCH_2)_3Sn]_2O$:

1.0 g (0.00125 mole) oxide was dissolved in 40 ml dry benzene and refluxed with 0.22 g (<0.0025 mole) PvH for 10 hours. The light yellow solid deposited was filtered out, washed with ether and recrystallised from methanol. The product weighed 0.55 g and did not melt.

Analysis :	% Sn	% C	% H
Found :	36.26	39.2	3.5
Calculated for $[BzSn(Pv)O]_n$:	37.82	38.46	3.2

6. Reaction of PvH with Oct_2SnO :

(i) 0.45 g (0.00125 mole) of Oct_2SnO was suspended in about 15 ml dry benzene, warmed and 0.22 g (0.0025 mole) of PvH added

drop wise with shaking. The oxide went into solution. Allowed to stand for 1-2 minutes and the solution was carefully decanted leaving behind unreacted substances. Precipitation was completed by addition of pet.ether and allowed to settle. The supernatant liquid decanted off and the residue washed with benzene. It was then dissolved in ether and reprecipitated with pet.ether. The light yellow precipitate was filtered and washed with ether-pet.ether mixture. It was dried first in air and then in vacuum over $CaCl_2$.

Yield : 0.47 g (ca. 80%). Did not melt (decomposed above 150°C).

Analysis :	% Sn	% C	% H
Found :	25.2	51.6	7.5
Calculated for $Oct_2Sn(Pv)OH$:	26.34	50.89	8.48

(ii) 0.45 g of Oct_2SnO and 0.22 g of PvH were taken in 40 ml dry benzene and refluxed for 10 hours using water separator. The yellow solution was filtered and the filtrate shaken vigourously with $NaHCO_3$. Filtered and the filtrate evaporated to a small volume, diluted with equal volume of pet.ether and stored at 5°C. The first fraction of precipitate (a small amount of yellow solid) was discarded and the clear solution on cooling for several days gave a white product. It was recrystallised from benzene-pet.ether mixture.

Yield : 0.25 g (ca. 40%). Mp. 112-114°C.

Analysis :	% Sn	% C	% H
Found :	23.72	51.7	8.02
Calculated for $Oct_2Sn(Pv)_2$:	22.78	50.96	7.72

7. Reaction of PvH with Bu_2SnO :

(i) 0.62 g (0.0025 mole) of Bu_2SnO was suspended in 15 ml benzene-ether mixture (80:20), warmed and shaken with 0.44 g (0.005 mole) of PvH added drop wise. Shaking continued for 2-3 minutes, when the oxide went into solution. Allowed to stand for 1-2 minutes and the solution carefully decanted leaving behind traces of unreacted substances. Pet.ether was then added to the solution and the precipitate formed allowed to settle. The supernatant liquid was decanted off and the residue washed repeatedly with ether. The yellowish white residue was dried first in air and then under vacuum over $CaCl_2$.

Yield : 0.82 g (ca. 84%). Decomposed above 234°C.

Analysis :	% Sn	% C	% H
Found :	34.64	40.45	6.1
Calculated for $Bu_2Sn(Pv)OH$:	35.1	39.3	6.54

(ii) 0.62 g of Bu_2SnO and 0.44 g of PvH were taken in 40 ml dry benzene and refluxed for 20 hours using water separator. The yellow solution was filtered and shaken vigourously with $NaHCO_3$. Filtered and the filtrate evaporated to a small volume and diluted with equal volume of pet.ether and stored at 5°C, when a viscous dark yellow liquid settled at the bottom. The clear upper layer

was decanted and again kept at 5°C. The same process was repeated till no more viscous liquid separated. The supernatant liquid on dilution with more pet.ether and cooling gave a white product. This was recrystallised from benzene-pet.ether mixture.

Yield : 0.22 g (ca. 23%). Mp. 157°C

Analysis :	% Sn	% C	% H
Found :	30.82	42.1	6.5
Calculated for $Bu_2Sn(Pv)_2$:	29.06	41.4	5.9

8. Reaction of PvH with Me_2SnO :

(i) 0.41 g (0.0025 mole) of Me_2SnO was suspended in 15 ml hot benzene-ether mixture (80:20) and reacted with 0.44 g (0.005 mole) of PvH, following the same procedure used for the reaction 7(i) above. The product was collected and dried in the same manner.

Yield : 0.63 g (ca. 80%). Did not melt.

Analysis :	% Sn	% C	% H
Found :	46.16	23.3	4.4
Calculated for $Me_2Sn(Pv)OH$:	46.82	23.81	3.97

(ii) 0.41 g of Me_2SnO and 0.44 g of PvH were refluxed in 40 ml dry benzene for 16 hours using water separator. The benzene solution was filtered and shaken vigourously with $NaHCO_3$. Filtered, the filtrate concentrated and allowed to stand overnight. The yellowish white solid deposited was filtered and washed with benzene and ether, then dried.

Yield : 0.15 g (ca. 18%). Did not melt.

Analysis :	% Sn	% C	% H
Found :	34.9	29.28	3.8
Calculated for $Me_2Sn(Pv)_2$:	36.64	29.8	3.7

9. Reaction of PvH with Ph_2SnO :

(i) 0.72 g (0.0025 mole) of Ph_2SnO was reacted with 0.44 g of PvH following the same procedure as for the reaction 7(i) above and 0.8 g (ca. 78%) of a yellowish white product, which did not melt, was obtained.

Analysis :	% Sn	% C	% H
Found :	30.47	49.85	3.9
Calculated for $Ph_2Sn(Pv)OH$:	31.38	47.87	3.72

(ii) 0.72 g Ph_2SnO and 0.44 g PvH were refluxed in 40 ml dry benzene for 8 hours using water separator. The yellow solid deposited was filtered, washed with ether and recrystallised from methanol and dried. 0.62 g of yellow solid which decomposed above 280^{o}C were obtained.

Analysis :	% Sn	% C	% H
Found :	38.1	35.7	2.9
Calculated for $[PhSn(Pv)O]_n$:	39.6	36.2	2.7

10. Reaction of NaPPv with Ph_3SnCl :

0.38 g (~ 0.001 mole) of Ph_3SnCl and 0.28 g (> 0.001 mole) of NaPPv were taken in dry ether containing small amount of

methanol and stirred at room temperature for 6 hours. Evaporated to dryness at r.t. and extracted with cold ether and allowed to stand overnight at 5°C. First crop of products rejected and the second crop was recrystallised from ether.

Yield : 0.35 g (68%). Mp. 139-140°C.

Analysis :	% Sn	% C	% H
Found :	22.9	63.8	3.7
Calculated for Ph_3SnPPv :	23.0	63.15	4.28

11. Reaction of PPvH with $(Ph_3Sn)_2O$:

(i) 0.35 g (~ 0.0005 mole) of $(Ph_3Sn)_2O$ was dissolved in 5 ml dry benzene(or ether) and shaken with 0.16 g (0.001 mole) of PPvH for 2-3 minutes. The faint yellow solution obtained was diluted with 2-3 ml pet.ether and allowed to stand at 5°C. The first crop of product was rejected and the second crop washed with cold ether and dried, first in air and then under vacuum over $CaCl_2$.

Yield :0.375 g (70%). Mp. 139-140°C.

Analysis :	% Sn	% C	% H
Found :	22.9	63.79	3.65
Calculated for Ph_3SnPPv :	23.0	63.15	4.28

(ii) 1.4 g (~ 0.002 mole) of $(Ph_3Sn)_2O$ was dissolved in 20 ml dry benzene and 0.65 g (~ 0.004 mole) PPvH added. the light yellow solution was then refluxed using water separator for 12 hours. The yellow solid separated was filtered and washed with

ether. The solid weighed 0.98 g on drying and did not melt.

Analysis :	% Sn	% C	% H
Found :	32.6	47.3	3.7
Calculated for $[PhSn(PPv)O]_n$:	31.55	48.12	3.2

The filtrate was evaporated at room temperature, washed with cold ether and extracted with hot benzene-pet.ether mixture (80:20). The solution was concentrated and allowed to crystallise. On repeated recrystallisation from benzene-pet.ether mixture 0.17 g of crystalline solid melting at 227-8^{o}C were obtained. This was found to be Ph_4Sn from analytical data and mixed melting point determination.

The residue after extraction with benzene-pet.ether mixture weighed 0.43 g on drying and did not melt.

Analysis :	% Sn	% C	% H
Found :	27.56	57.4	3.7
Calculated for $Ph_2Sn(PPv)OH$:	26.1	55.75	3.98

When the reaction 11.(ii) was carried out in solvent ether and the solvent was carefully distilled out, benzene could be spectroscopically detected in the distillate, indicating that benzene was one of the products of the reaction.

12. Reaction of NaPPv with Bu_3SnCl :

0.32 g (0.001 mole) of Bu_3SnCl and 0.27 g (>0.001 Mole) of NaPPv were taken in dry ether containing little methanol and stirred at room temperature for 8 hours.Filtered, evaporated at

r.t. and extracted with cold pet.ether. The pet.ether extract on evaporation gave a colorless liquid product weighing 0.44 g (98%) containing no halogen.

Analysis :	% Sn	% C	% H
Found :	26.84	56.65	5.8
Calculated for Bu_3SnPPv :	26.1	55.75	7.52

13. Reaction of PPvH with $(Bu_3Sn)_2O$:

0.6 g (~ 0.001 mole) of $(Bu_3Sn)_2O$ and 0.4 g (>0.002 mole) of PPvH were taken in 20 ml dry benzene and refluxed for 10 hours using Dean and Stark water separator. The yellow solution obtained was shaken with $NaHCO_3$ and filtered. The filtrate was concentrated, diluted with pet.ether and kept at 5^oC overnight. Pasty yellow mass settled down and the clear upper layer decanted. The decant was allowed to evaporate at room temperature to a semisolid mass and then extracted with cold pet.ether. The pet.ether extract on evaporation gave a colorless viscous liquid weighing 0.49 g (55%).

Analysis :	% Sn	% C	% H
Found :	26.65	56.6	5.7
Calculated for Bu_3SnPPv :	26.1	55.75	7.52

14. Reaction of NaPPv with $(PhCH_2)_3SnCl$:

0.42 g (~ 0.001 mole) of $(PhCH_2)_3SnCl$ and 0.27 g (>0.001

mole) of NaPPv were taken in dry ether containing little methanol and stirred at room temperature for 7 hours and filtered. The filtrate was evaporated to dryness at r.t. and extracted with cold ether. The ether solution was stored at 5°C. The first crop of products was rejected and the second crop, recrystallised from ether, weighed 0.24 g (44%) on drying and melts at 134°C.

Analysis :	% Sn	% C	% H
Found :	21.86	64.25	5.6
Calculated for Bz_3SnPPv :	21.3	64.98	5.05

15. Reaction of PPvH with $[(PhCH_2)_3Sn]_2O$:

0.4 g (0.0005 mole) of the oxide was dissolved in 10 ml benzene-ether mixture (50:50) and 0.17 g (~ 0.001 mole) acid added. Warmed and shaken for 2-3 minutes. The clear solution obtained was diluted with pet.ether and kept overnight at 5°C. The solid deposited was recrystallised from cold ether and dried.

Yield : 0.42 g (78%). Mp. 134°C.

Analysis :	% Sn	% C	% H
Found :	22.1	64.56	5.4
Calculated for Bz_3SnPPv :	21.3	64.98	5.05

16. Reaction of PPvH with Bu_2SnO :

(i) 0.25 g (0.001 mole) of Bu_2SnO and 0.33 g (0.002 mole) of PPvH were shaken in 10 ml warm benzene-ether mixture (50:50) for 10 minutes and filtered. The filtrate was diluted with pet.ether

and allowed to stand at 5°C. The solid deposited was recrystallised from benzene-pet.ether mixture and the product obtained was washed with cold ether and dried.

Yield : 0.4 g (ca. 72%). Decomposed above 170°C.

Analysis :	% Sn	% C	% H
Found :	22.49	54.8	5.6
Calculated for $Bu_2Sn(PPv)_2$:	21.15	55.91	5.73

(ii) 0.25 g Bu_2SnO and 0.33 g PPvH were refluxed in 20 ml benzene-ether mixture (50:50) for 8 hours. The residue was filtered and recrystallised from acetone and dried under vacuum.

Yield : 0.14 g (ca. 25%). Mp. 191°C.

Analysis :	% Sn	% C	% H
Found :	30.15	48.8	5.4
Calculated for $Bu_2Sn(PPv)OH$:	28.64	49.51	6.3

The filtrate was shaken with $NaHCO_3$, filtered, concentrated and diluted with pet.ether and allowed to stand at 5°C. The first crop of products was rejected and the second crop recrystallised from benzene-pet.ether mixture.

Yield : 0.38 g (ca. 68%). Decomposed above 170°C.

Analytical data identical with that of $Bu_2Sn(PPv)_2$.

17. Reaction of PPvH with Oct_2SnO :

(i) 0.18 g (0.0005 mole) of Oct_2SnO was suspended in 10 ml hot ether and shaken with 0.16 g (0.001 mole) of PPvH for 5 minutes. The solution was filtered, diluted with 5 ml pet.ether and stored

at 5°C. The white product obtained was recrystallised from ether-pet.ether mixture and dried under vacuum over $CaCl_2$.

Yield : 0.2 g (ca. 60%). Mp. 74-6°C.

Analysis :	% Sn	% C	% H
Found :	18.65	59.02	6.85
Calculated for $Oct_2Sn(PPv)_2$:	17.61	60.89	7.13

(ii) 0.36 g (0.001 mole) of Oct_2SnO and 0.35 g (>0.002 mole) of PPvH were taken in 20 ml benzene-ether mixture (50:50) and refluxed for 9 hours. Filtered and the residue recrystallised from acetone. The solid on drying weighed 0.37 g (ca. 55%). Mp. 124°C.

Analysis :	% Sn	% C	% H
Found :	23.76	58.74	7.5
Calculated for $Oct_2Sn(PPv)OH$:	22.52	57.25	8.01

The filtrate was shaken with $NaHCO_3$, concentrated, diluted with pet.ether and kept at 5°C. The first crop was discarded and the second crop was recrystallised from ether-pet.ether mixture. The product was found to be identical with $Oct_2Sn(PPv)_2$ on the basis of melting point, analytical data and IR spectra.

Yield : 0.1 g (ca. 15 %).

18. Reaction of PPvH with Me_2SnO :

(i) 0.16 g (~ 0.001 mole) of Me_2SnO was suspended in hot benzene-ether mixture (50:50) and shaken with 0.32 g (0.002 mole) of PPvH for 2-3 minutes. The clear supernatant solution was

decanted and allowed to stand. The solid precipitated from the solution was washed with ether and dried.

Yield : 0.225 g (ca. 46 %). Decomposes above 200°C.

Analysis :	% Sn	% C	% H
Found :	26.2	49.85	4.1
Calculated for $Me_2Sn(PPv)_2$:	24.89	50.63	4.22

(ii) 0.16 g of Me_2SnO and 0.32 g PPvH were refluxed in bez-ether mixture for 8 hours and filtered. The filtrate was shaken with $NaHCO_3$, filtered, concentrated, diluted with pet.ether and stored at 5°C. The yellowish white precipitate obtained was washed with ether and dried. Yield : 0.05 g (ca. 16%). Mp. 172°C.

Analysis :	% Sn	% C	% H
Found :	-	41.07	3.8
Calculated for $Me_2Sn(PPv)OH$:	35.97	40.24	4.26

19. Reaction of PPvH with Ph_2SnO :

0.28 g (~ 0.001 mole) of Ph_2SnO and 0.32 g (~ 0.002 mole) of PPvH were refluxed in benzene-ether mixture (50:50) for 1 hour and filtered. The filtrate was shaken with $NaHCO_3$, concentrated and allowed to stand. The precipitate obtained was washed with ether and dried.

Yield : 0.055 g (ca. 12%). Does not melt.

Analysis :	% Sn	% C	% H
Found :	-	57.16	4.3
Calculated for $Ph_2Sn(PPv)OH$:	26.1	55.75	3.98

20. Reaction of NaBF with Ph_3SnCl :

0.19 g (~ 0.0005 mole) of Ph_3SnCl and 0.095 g (>0.0005 mole) of NaBF were stirred at room temperature for 6 hours in dry ether containing little methanol. The resultant suspension was evaporated at room temperature, extracted with cold bez-pet.ether mixture (50:50) and stored at 5^oC. The first crop of products was rejected and the second crop was recrystallised from benzene-pet.ether.

Yield : 0.1 g (ca. 42 %). Mp. 149-50^oC.

Analysis :	% Sn	% C	% H
Found :	23.1	61.8	4.5
Calculated for Ph_3SnBF :	23.69	62.65	4.02

21. Reaction of BFH with $(Ph_3Sn)_2O$:

0.35 g (~ 0.0005 mole) $(Ph_3Sn)_2O$ was dissolved in 10 ml benzene-ether mixture (50:50) by warming and the solution shaken with 0.15 g (~ 0.001 mole) BFH for 5 minutes.The clear solution was diluted with pet.ether and stored at 5^oC. The white product obtained was recrystallised from cold benzene-pet.ether mixture and dried under vacuum over $CaCl_2$. The product was identified with Ph_3SnBF on the basis of melting point, analytical data and IR spectra.

Yield : 0.45 g (ca. 90%).

22. Reaction of NaBF with Bu_3SnCl :

0.32 g (~ 0.001 mole) of Bu_3SnCl was added to a suspension of excess NaBF (0.3 g, ~ 0.002 mole) in 20 ml ether and stirred for 10 hours using a magnetic stirrer and filtered. The solvent was evaporated to a small volume (~ 5 ml), diluted with equal volume of pet.ether and stored at $5^{o}C$ for several days. No precipitation occurred and the solvent was removed at room temperature. The colorless viscous liquid obtained, after drying under vacuum, weighed 0.43 g (ca. 100 %).

Analysis :	% Sn	% C	% H
Found :	26.5	55.3	7.6
Calculated for Bu_3SnBF :	26.94	54.79	7.3

23. Reaction of BFH with $(Bu_3Sn)_2O$:

0.3 g (~ 0.0005 mole) of $(Bu_3Sn)_2O$ and 0.2 g (>0.001 mole) of BFH were refluxed in 20 ml dry benzene for 4 hours using water separator. The solution was shaken vigourously with $NaHCO_3$, filtered, concentrated to about 5 ml, diluted with pet.ether and stored at $5^{o}C$ for a week. The slight turbidity formed was removed by filtration and evaporated at room temperature. The colorless viscous liquid was dried under vacuum. Yield : 0.38 g (ca. 96 %).

Analysis :	% Sn	% C	% H
Found :	26.6	55.1	7.7
Calculated for Bu_3SnBF :	26.94	54.79	7.3

24. Reaction of NaBF with Bz_3SnCl :

0.42 g (~ 0.001 mole) of Bz_3SnCl was added to a suspension of excess NaBF (0.3 g ~ 0.002 mole) in 20 ml ether and stirred magnetically for 6 hours. The solvent was removed at room temperature and the residue extracted with bez-pet.ether mixture. The extract was concentrated and stored at 5^oC. The first crop of solids on recrystallisation from benzene-pet.ether mixture and drying gave 0.24 g (ca. 45%) of product melting at 152-4^oC.

Analysis :	% Sn	% C	% H
Found :	20.96	64.68	5.0
Calculated for Bz_3SnBF :	21.85	64.4	4.8

25. Reaction of BFH with $(Bz_3Sn)_2O$:

0.4 g (~ 0.0005 mole) of $(Bz_3Sn)_2O$ and 0.15 g (~ 0.001 mole)of BFH were refluxed in benzene for 15-20 minutes. The faint yellow solution was shaken with $NaHCO_3$, filtered and allowed to stand when slight turbidity appeared.Turbidity was removed by filtration, diluted with pet.ether and stored at 5^oC overnight. The first crop of product was recrystallised from bez-pet.ether mixture and was identified as Bz_3SnBF on the basis of mixed melting point, IR and analytical data. Yield : 0.3 g (ca. 55 %).

26. Reaction of BFH with Bu_2SnO :

0.26 g (>0.001 mole) of Bu_2SnO and 0.3 g (0.002 mole) of BFH

were shaken for 5 minutes in 10 ml warm benzene-ether mixture (50:50) and filtered. The filtrate was diluted with pet.ether and allowed to stand at 5°C. The white precipitate obtained was recrystallised from benzene-pet.ether mixture and dried.

Yield : 0.44 g (ca. 82 %). Mp. 65-68°C.

Analysis :	% Sn	% C	% H
Found :	20.86	54.9	5.4
Calculated for $Bu_2Sn(BF)_2$:	22.26	54.34	5.28

27. Reaction of BFH with Oct_2SnO :

0.18 g (0.0005 mole) of Oct_2SnO and 0.15 g (0.001 mole) of BFH were shaken for 5 minutes in 10 ml warm benzene-ether mixture (50:50). The clear solution was diluted with pet.ether and stored at 5°C. The white solid obtained was recrystallised from benzene-pet.ether mixture and dried.

Yield : 0.25 g (ca. 80 %). Mp. 73-49°C.

Analysis :	% Sn	% C	% H
Found :	18.72	59.2	5.9
Calculated for $Oct_2Sn(BF)_2$:	18.38	59.81	6.85

28. Reaction of BFH with Me_2SnO :

0.08 g (~ 0.0005 mole) of Me_2SnO and 0.15 g (~ 0.001 mole) of BFH were taken in 5ml benzene-ether mixture (50:50) and shaken for 5 minutes. Filtered and the filtrate allowed to stand at 5°C.

The white solid separated was recrystallised from ether and dried.

Yield : 0.155 g (ca. 70 %). Mp. 182^{o}C.

Analysis :	% Sn	% C	% H
Found :	-	48.75	3.5
Calculated for $Me_2Sn(BF)_2$:	26.46	48.43	3.59

29. Reaction of BFH with Ph_2SnO :

0.15 g (~ 0.0005 mole) of Ph_2SnO and 0.15 g (0.001 mole) of BFH were reacted following the same method as for reaction 28 above and the product collected in the same way.

Yield : 0.18 g (ca. 64%). Mp. 117^{o}C.

Analysis :	% Sn	% C	% H
Found :	-	59.4	4.15
Calculated for $Ph_2Sn(BF)_2$:	20.7	58.95	3.5

III.2.C. Physical measurements :

All analytical work were carried out at C.D.R.I.,Lucknow, India. The IR spectra were recorded in KBr discs using PERKIN ELMER 983 and 783 spectrophotometers at R.S.I.C., NEHU and I.A.C.S. Jadavpur, India, respectively. IR spectra in Nujol mull were recorded using a PYE UNICAM SP3-300S spectrophotometer at North Bengal University, Dist. Darjeeling ,India.

All UV spectra were recorded with a SHIMADZU UV240 spectrophotometer using 1 cm quartz cells at North Bengal University.

^{1}H NMR spectra were recorded with VARIAN XL-200 and EM-390 spectrometers at I.A.C.S., Jadavpur and R.S.I.C., NEHU and JEOL GSX 400 NB at I.I.T., Madras, India.

III.3. *Results and discussion :*

In order to prepare the organotin α-keto carboxylates the following two methods were used :

(i) Reaction of the Na -salt of the α-keto acid with the triorganotin halides in ether or methanol,

$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}COONa + R_3SnCl \longrightarrow 2\ R_3SnOCO\overset{O}{\overset{\|}{C}}\text{-}R' + H_2O \quad \text{------[1]}$$

and (ii) reaction of the α-keto acid (HL) with the appropriate organostannoxane in dry benzene/solvent ether,

$$2\ R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}COOH + (R_3Sn)_2O \longrightarrow 2\ R_3SnOCO\overset{O}{\overset{\|}{C}}\text{-}R' + H_2O \quad \text{-----[2]}$$

$$2\ R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}COOH + R_2SnO \longrightarrow R_2Sn(OCO\overset{O}{\overset{\|}{C}}\text{-}R')_2 + H_2O \quad \text{-----[3]}$$

While the reaction between triorganotin halides and the Na-salts of the acids proceeded as expected giving triorganotin carboxylates, the reaction between the acids and organotin oxides yielded a variety of apparently unexpected products in addition to the carboxylates, depending on the reactants and reaction conditions used. In fact, the yield of the triorganotin

carboxylates were almost negligible (<10 %) in some of the latter case indicating a profound influence of the α-keto group on the reaction. In order to understand the rather surprising results of these reactions, it is necessary to first discuss the different products obtained.

The most interesting feature of these reactions is the formation of addition complexes of the type $R_3SnOH.HL$. The reactions of $CH_3COCOOH$ (PvH) and $PhCH_2COCOOH$ (PPvH) with some hexaorgano distannoxanes under very mild conditions, leading to the addition products, deserve special attention. For example, when a solution of $(Ph_3Sn)_2O$ in benzene/ether is stirred with PvH in 1:2 proportion for 2-3 minutes a white solid is precipitated immediately. This product has an empirical formula of $Ph_3SnOH.PvH$ on the basis of elemental analysis and possesses very interesting

P.T.O.

chemical and spectroscopic properties. Because of the uniqueness of these compounds their preparation and characterisation will be discussed separately.

These acids also produce other interesting compounds of the type $R_2Sn(L)OH$, which are hydrolysates of the diorganotin dicarboxylates. Incidentally, $Ph_2Sn(L)OH$ type of compounds have also been formed during the reaction of $(Ph_3Sn)_2O$ with the acids, presumably, through the cleavage of Ph—Sn bonds.

Interestingly, the reaction of PhCOCOOH (BFH) with the stannoxanes has produced only the carboxylate derivatives of the type $R_nSn(OCOCOR')_{4-n}$ (n = 2,3).

In the present chapter, characterisation of the tri- and diorganotin keto carboxylates and the hydrolysates of the diorganotin derivatives are being presented. A summary of the reaction conditions used for the preparation of the keto carboxylates, their yields and melting points are given in table-III.1. Analytical data and the solubilities of the compounds are recorded in table-III.2.

III.3.1. Characterisation Of The Products :

A reference to the table-III.3. would reveal that the reaction of triorganotin halides with the Na-salts of benzoyl formic acid (BFH) and phenyl pyruvic acid (PPvH) gives moderately

Table:-III.1.

Summary of reaction conditions and products.

Sl. no.	Reactants and mole ratio	Reaction conditons	Time	Product	% yield, Mp.
1.	Ph_3SnCl + NaPv (1:1)	Stirred in ether containing little methanol and excess NaPv. Evaporated to dryness and extracted with pet.ether. Solid obtained from the extract recrystallised from same solvent.	8 hrs.	Ph_3SnPv	10, 114-6°C
2. (i)	$(Ph_3Sn)_2O$ + PvH (1:2)	Refluxed in ether. Filtered, and filtrate evaporated at r.t. The resultant mass extracted with pet.ether. Pet. ether extract on evaporation and recrystallisation from the same solvent gave (a)	1 hr.	(a) Ph_3SnPv	3, 114-6°C
		The residue after reflux and that from the pet.ether extract on washing with bez. and ether gave identical products (b)		(b) $Ph_2Sn(Pv)OH$	-
		When the ether was distilled out completely after the reaction, the distillate was found to contain benzene in ether (c).		(c) C_6H_6	

Table-III.1(contd.).

2. (ii)	$(Ph_3Sn)_2O$ + PvH (1:2)	Refluxed in bez. Filtered, residue washed with bez. and ether gave (a) Filtrate evaporated at r.t. and washed with cold ether. The remaining solid was extracted with hot bez., concentrated and allowed to crystallise. Product recrystallised with bez-pet.ether (b). The residue from the bez.-extract on washing with ether and recrystallisation from methanol gave (c).	12 hrs.	(a) $[PhSn(Pv)O]_n$	-
				(b) Ph_4Sn	227°C
				(c) $Ph_2Sn(Pv)OH$	-
3.	Bu_3SnCl + NaPv (1:1)	Stirred in ether with excess NaPv. Evaporated to dryness at r.t. and extracted with pet.ether. Solid separated from the extract was recrystallised.	8 hrs.	Bu_3SnPv	11, 80-2°C
4.	$(Bu_3Sn)_2O$ + PvH (1:2)	Refluxed in dry bez. Solution shaken with $NaHCO_3$ and filtered. Filtrate concentrated to a small volume, diluted with pet.ether and stored at 5°C. Thick yellow liquid separated. Upper pet.ether-bez layer crystallised.	16 hrs.	Bu_3SnPv	20, 80-2°C

Table-III.1(contd.).

5. (i)	Bz_3SnCl + NaPv (1:1)	Stirred in ether containing little methanol with excess NaPv. Evaporated to dryness at r.t. and extracted with cold ether and allowed to crystallise. The second crop recrystallised from cold ether.	6 hrs.	Bz_3SnPv	8, 104-8°C
5. (ii)	$(Bz_3Sn)_2O$ + PvH (1:2)	Refluxed in bez. and filtered. Residue washed with ether and recrystallised from methanol.	10 hrs.	$[BzSn(Pv)O]_n$	-
6. (i)	Oct_2SnO + PvH (1:2)	Oxide and acid shaken in bez. Decanted and precipitated with pet.ether. Solid dissolved in ether and reprecipitated with pet.ether.	5 min.	$Oct_2Sn(Pv)OH$	80, Decomp. >150°C
6. (ii)	,,	Refluxed in bez. Solution shaken with $NaHCO_3$, concentrated, diluted with pet.ether. Product recrystallised from bez.-pet.ether.	10 hrs.	$Oct_2Sn(Pv)_2$	32, 112-4°C
7. (i)	Bu_2SnO + PvH (1:2)	Organotin and acid shaken in warm bez-ether (1:1) mixture. Solution decanted and precipitated with pet.ether. Solid washed with ether.	2-3 min.	$Bu_2Sn(Pv)OH$	84, Decomp. >234°C

Table-III.1(contd.).

7. (ii)	,,	Refluxed in dry bez. Solution shaken with $NaHCO_3$, concentrated, diluted with pet.ether and stored at 5°C. Thick yellow liquid separated. Upper pet.-bez layer crystallised.	14 hrs.	$Bu_2Sn(Pv)_2$	23, 157°C
8. (i)	Me_2SnO + PvH (1:2)	Organotin and acid shaken in warm bez-ether mixture. Solution decanted and precipitated with pet.ether. Solid washed with ether	2-3 min.	$Me_2Sn(Pv)OH$	80, -
8. (ii)	,,	Refluxed in bez. Solution shaken with $NaHCO_3$, and concentrated.	8 hrs.	$Me_2Sn(Pv)_2$	18, -
9. (i)	Ph_2SnO + PvH (1:2)	Organotin and acid shaken in warm bez-ether (1:1) mixture. Solution decanted, precipitated with pet.ether. Solid washed with ether.	2-3 min.	$Ph_2Sn(Pv)OH$	78, -
9. (ii)	,,	Refluxed in bez. Residue washed with ether and recrystallised from methanol.	8 hrs.	$[PhSn(Pv)O]_n$	-
10.	Ph_3SnCl + NaPPv (1:1)	Stirred in ether containing little methanol. Evaporated and extracted with cold ether. Recrystallised from bez-pet.ether.	6 hrs.	Ph_3SnPPv	68, 139-40°C

Table-III.1(contd.).

11. (i)	$(Ph_3Sn)_2O$ + PPvH (1:2)	Solution of stannoxane in bez/ ether shaken with acid, diluted with pet.ether, allowed to stand at 5°C for several hrs. Product washed with cold ether.	5 min.	Ph_3SnPPv	70, 139-40°C
11. (ii)	$(Ph_3Sn)_2O$ + PPvH (1:2)	Refluxed in bez. Filtered, residue washed with ether, gave (a). Filtrate evaporated at r.t. and washed with cold ether and residue extracted with hot bez. Bez. extract gave (b) on recrystallisation from bez. -pet.ether. Remaining residue (c) was recrystallised from methanol. When refluxed in ether, the above reaction [11.(ii)] gave C_6H_6 as one of the products, along with (a) and (c).	12 hrs.	(a) $[PhSn(PPv)O]_n$	-
				(b) Ph_4Sn	227°C
				(c) $Ph_2Sn(PPv)OH$	-
12.	Bu_3SnCl + NaPPv (1:1)	Stirred in ether containing little methanol with excess of NaPPv. Filtered, evaporated at r.t. and extracted with pet.ether and evaporated.	8 hrs.	Bu_3SnPPv	98, Liq.
13.	$(Bu_3Sn)_2O$ + PPvH (1:2)	Refluxed in bez. with excess acid. Solution shaken with $NaHCO_3$ and filtered. Evaporated at r.t. and extracted with cold pet.ether and the solvent allowed to evaporate.	10 hrs.	Bu_3SnPPv	55, Liq.

Table-III.1(contd.).

14.	Bz_3SnCl + NaPPv (1:1)	Stirred in ether containing MeOH. Filtered, Evaporated at r.t. and extracted with ether. The extract stored at 5^oC.	7 hrs.	Bz_3SnPPv	45, 134^oC
15.	$(Bz_3Sn)_2O$ + PPvH (1:2)	Shaken in Bez.-ether mixture. Solution kept at 5^oC. The solid product obtained was washed with cold ether.	5 min.	Bz_3SnPPv	78, 134^oC
16. (i)	Bu_2SnO + PPvH (1:2)	Shaken in warm bez.-ether mix. Filtered, diluted with ether and allowed to stand at 5^oC.	10 min.	$Bu_2Sn(PPv)_2$	72, Decomp $>170^oC$
16. (ii)	,,	Refluxed in bez.-ether mixture and filtered. Residue recrystallised from acetone, gave (a). Filtrate shaken with $NaHCO_3$, filtered, concentrated, diluted with pet.ether and stored at 5^oC. First crop of products rejected and the second crop recrystallised from bez.-pet.-ether (b).	8 hrs.	(a) $Bu_2Sn(PPv)OH$	25, 191^oC
				(b) $Bu_2Sn(PPv)_2$	68, Decomp $>170^oC$
17. (i)	Oct_2SnO + PPvH (1:2)	Shaken in hot ether, filtered, concentrated, diluted with pet -ether and kept in freeze. Product recrystallised from ether-pet.ether mix.	5 min.	$Oct_2Sn(PPv)_2$	60, $74-6^oC$
17. (ii)	,,	Refluxed in bez.-ether mixture and filtered. Residue rec-	9 hrs.	(a) $Oct_2Sn(PPv)OH$	55, 124^oC

Table-III.1(contd.).

		rystallised from acetone (a). Filtrate shaken with $NaHCO_3$, concentrated, diluted with pet. -ether and stored at 5°C. First crop recrystallised from acetone (a) and the second crop (b) recrystallised from ether-pet.ether mix.		(b) $Oct_2Sn(PPv)_2$	15, 74-6°C
18. (i)	Me_2SnO + PPvH (1:2)	Stannoxane and acid shaken in bez.-ether mix. Solution decanted and allowed to stand. Ppt. washed with ether.	2-3 min.	$Me_2Sn(PPv)_2$	46, Decomp >200°C
18. (ii)	,,	Refluxed in bez.-ether mix. filtered, shaken with $NaHCO_3$, concentrated, diluted with pet.ether and stored at 5°C.	8 hrs.	$Me_2Sn(PPv)OH$	16, 172°C
19.	Ph_2SnO + PPvH (1:2)	Refluxed in bez.-ether mix. Solution shaken with $NaHCO_3$, and allowed to stand. Ppt. washed with ether.	1 hr.	$Ph_2Sn(PPv)OH$	12, -
20.	Ph_3SnCl + NaBF (1:1)	Stirred in ether containing little MeOH, with excess Na-salt. Evaporated at r.t. and extracted with bez.-pet.ether mix., concentrated and allowed to crystallise. 2nd crop of products recrystallised from bez.-pet.ether.	6 hrs.	Ph_3SnBF	42, 149°C

Table-III.1(contd.).

21.	$(Ph_3Sn)_2O$ + BFH (1:2)	Solution of stannoxane in bez.-ether mix. shaken with acid. Diluted with pet.ether and kept at 5°C. product recrystallised from cold bez.-pet.ether.	5 min.	Ph_3SnBF	90, 149-50°C
22.	Bu_3SnCl + NaBF (1:1)	Stirred in ether with excess NaBF and filtered. Solvent evaporated at r.t. Redissolved in pet.ether, filtered and again evaporated at r.t.	10 hrs.	Bu_3SnBF	100, Liq.
23.	$(Bu_3Sn)_2O$ + BFH (1:2)	Refluxed in bez. with excess acid. Shaken with $NaHCO_3$, concentrated, diluted with pet. ether and stored at 5°C. Slight turbidity formed was removed by filtration. Solvent removed from the filtrate at r.t.	4 hrs.	Bu_3SnBF	96, Liq.
24.	Bz_3SnCl + NaBF (1:1)	Stirred in ether with excess NaBF and solvent removed at r.t. Extracted with bez.-pet. ether mixture, concentrated and allowed to crystallise. First crop recrystallised from bez.-pet.ether.	6 hrs.	Bz_3SnBF	45, 152-4°C
25.	$(Bz_3Sn)_2O$ + BFH (1:2)	Refluxed in bez.-ether mixture. Shaken with $NaHCO_3$, concentrated and allowed to stand. Sli-	20 min.	Bz_3SnBF	55, 152-4°C

Table-III.1(contd.).

		ght turbidity appeared, removed by filtration. Diluted with pet.ether and stored at 5°C. First crop of products recrysllised from bez.-pet.ether mix.			
26.	Bu_2SnO + BFH (1:2)	Shaken in hot bez.-ether mix., with small excess of oxide, filtered, diluted with pet.-ether and stored at 5°C. Product recrystallised from bez.-pet.ether mixture.	5 min.	$Bu_2Sn(BF)_2$	82, 65-8°C
27.	Oct_2SnO + BFH (1:2)	,,	5 min.	$Oct_2Sn(BF)_2$	80, 73-4°C
28.	Me_2SnO + BFH (1:2)	Shaken in hot bez.-ether mix., with small excess of oxide. Filtered and allowed to stand at 5°C. Product recrystallised from ether.	5 min.	$Me_2Sn(BF)_2$	70, 182°C
29.	Ph_2SnO + BFH (1:2)	,,	5 min.	$Ph_2Sn(BF)_2$	64, 117°C

Table:-III.2.

Analytical data and Solubilities of the Products.

Sl. No.	Compound	% Found / (Calculated) Sn	C	H	Solubilities
1.	Ph_3SnPv	26.1	58.8	4.6	Bez., P.eth., $CHCl_3$
		(27.06)	(57,8)	(4,13)	Et_2O, Ace.,Alc.
2.	Bu_3SnPv	31.02	49.0	8.5	,,
		(31.38)	(47.9)	(7.98)	
3.	Bz_3SnPv	-	61.3	4.8	,,
		(24.69)	(60.25)	(5.02)	
4.	$Bu_2Sn(Pv)_2$	30.82	42.1	6.5	,,
		(29.06)	(41.4)	(5.9)	
5.	$Me_2Sn(Pv)_2$	34.9	29.28	3.8	Alc.; slightly soluble
		(36.64)	(29.8)	(3.7)	in Et_2O, Bez., Ace.
6.	$Oct_2Sn(Pv)_2$	23.72	51.7	8.02	Bez., P.eth., $CHCl_3$,
		(22.78)	(50.96)	(7.72)	Et_2O, Ace., Alc.
7.	$Bu_2Sn(Pv)OH$	34.64	40.45	6.1	Alc.
		(35.1)	(39.3)	(6.54)	
8.	$Me_2Sn(Pv)OH$	46.16	23.3	4.4	,,
		(46.82)	(23.81)	(3.97)	
9.	$Oct_2Sn(Pv)OH$	25.2	51.6	7.5	Alc., Et_2O., Ace.
		(26.34)	(50.89)	(8.48)	
10.	$Ph_2Sn(Pv)OH$	30.1	48.1	3.8	Alc.
		(31.38)	(47.87)	(3.72)	
11.	$[PhSn(Pv)O]_n$	38.5	34.8	2.8	,,
		(39.6)	(36.2)	(2.7)	
12.	$[BzSn(Pv)O]_n$	36.26	39.2	3.48	,,
		(37.82)	(38.46)	(3.2)	
13.	Ph_3SnPPv	22.9	63.8	3.7	Alc., Ace., Et_2O, Bez.,
		(23.0)	(63.15)	(4.28)	Sl.sol.in $CHCl_3$(h).
14.	Bu_3SnPPv	26.84	56.65	5.8	Bez., P.eth, $CHCl_3$,
		(26.1)	(55.75)	(7.52)	Et_2O, Ace.,Alc.

Table-III.2(contd.).

15. Bz_3SnPPv	22.1 (21.3)	64.56 (64.98)	5.4 (5.05)	Alc., Ace., Et_2O. Bez., Sl.sol.in $CHCl_3$(h).
16. $Bu_2Sn(PPv)_2$	22.49 (21.15)	54.8 (55.91)	5.6 (5.73)	Alc., Ace., Et_2O, Bez., Sl.sol.in $CHCl_3$(h).
17. $Oct_2Sn(PPv)_2$	18.65 (17.61)	59.02 (60.89)	6.85 (7.13)	,,
18. $Me_2Sn(PPv)_2$	26.2 (24.89)	49.85 (50.63)	4.1 (4.22)	Alc., Sl.sol. in Ace., Et_2O, Bez.
19. $Bu_2Sn(PPv)OH$	30.15 (28.64)	48.8 (49.51)	5.4 (6.3)	Alc., Ace., Et_2O.
20. $Oct_2Sn(PPv)OH$	23.76 (22.52)	58.74 (57.25)	7.5 (8.01)	,,
21. $Me_2Sn(PPv)OH$	- (35.97)	41.07 (40.24)	3.8 (4.26)	Alc.
22. $Ph_2Sn(PPv)OH$	27.56 (26.1)	57.4 (55.75)	3.7 (3.98)	,,
23. $[PhSn(PPv)O]_n$	32.6 (31.55)	47.3 (48.12)	3.7 (3.2)	,,
24. Ph_3SnBF	23.1 (23.69)	61.8 (62.65)	4.5 (4.02)	Bez., $CHCl_3$, CCl_4(h), Et_2O, Ace., Alc.
25. Bu_3SnBF	26.6 (26.94)	55.1 (54.79)	7.7 (7.3)	,,
26. Bz_3SnBF	20.96 (21.85)	64.68 (64.4)	5.0 (4.8)	,,
27. $Bu_2Sn(BF)_2$	20.86 (22.26)	54.9 (54.34)	5.4 (5.28)	,,
28. $Me_2Sn(BF)_2$	- (26.46)	48.75 (48.43)	3.5 (3.59)	Bez.(h), $CHCl_3$, Et_2O,
29. $Oct_2Sn(BF)_2$	18.72 (18.38)	59.2 (59.81)	5.9 (6.85)	Bez., P.eth., CCl_4, $CHCl_3$, Et_2O, Ace., Alc.
30. $Ph_2Sn(BF)_2$	- (20.7)	59.4 (58.95)	4.15 (3.5)	Bez., $CHCl_3$, Et_2O, Ace., Alc.

good yields of the triorganotin keto carboxylates, but with the Na-salt of pyruvic acid (PvH) the yields are very poor. Although no explanation for this observation is readily forthcoming , one of the probable reasons may be the fact that the pyruvate ion is susceptible to extensive polymerisation, catalysed by base[29], traces of which are produced due to absorption of moisture, by the extremely hygroscopic Na-pyruvate, during handling.

This method of reacting organotin halides with the Na-salts, has however, not been found to be suitable for the preparation of

Table-III.3.

Reaction of R_3SnCl with R'COCOONa producing $R_3SnOCOCOR'$:

	% yield of products.		
R_3SnCl / R'COCOONa	R = n-Bu	R = Ph	R = $PhCH_2$
R' = CH_3	11	10	8
R' = $PhCH_2$	98	68	44
R' = Ph	100	42	45

diorganotin derivatives of the keto acids, due to the formation of highly polymeric insoluble products, which are difficult to characterise.

The reaction between appropriate organostannoxanes and the keto acids, carried out by heating them in dry benzene/solvent ether in 1:2 mole ratio, on the other hand, have produced both tri- and diorganotin ketocarboxylates. While the carboxylate derivatives of benzoyl formic acid (BFH) and phenyl pyruvic acid (PPvH) were obtained in good yields under mild conditions, those of pyruvic (PvH) were obtained under comparatively drastic conditions and the yields were also very poor (table-III.1.). The percentage yields of the triorganotin ketocarboxylates obtained from the reaction of triorgano stannoxanes with the keto acids are shown in table-III.4.

Table:-III.4.

Reaction of $(R_3Sn)_2O$ with R'COCOOH producing $R_3SnOCOCOR'$.

	% yield of products.		
R R' (Taft's constant)	n-Bu	Ph	$PhCH_2$
CH_3 (-0.05)	20	3	-
$PhCH_2$ (0.04)	55	70	78
Ph (0.1)	90	90	55

From the data in tables III.3 and III.4 it is seen that both the methods give very high yields of the triorganotin derivatives of PhCOCOOH (BFH) and very low yields for the derivatives of $CH_3COCOOH$ (PvH) . This clearly displays a distinct pattern and if we look at the values of the Taft's constant of the R' groups (table-III.4.), we find that the yield of the carboxylates increases with increasing Taft's constant. This would suggest that electronic and other factors are responsible for the exceptionally poor yields of the triorganotin pyruvates.

These observations coupled with the fact, that pyruvic acid reacts with some bis(triorganotin) oxides giving very high yield of the addition product, whereas, benzoyl formic acid forms no such compound, shows that these acids differ remarkably in their reactions with organostannoxanes. This difference in the role of the ligand in relation to the formation of the ketocarboxylates or the addition products will be discussed latter.

The characteristics of the tri- and diorganotin ketocarboxylates and the carboxylato diorganotin hydroxides are now discussed separately.

III.3.1A. Triorganotin Keto Carboxylates ($R_3SnOCOCOR'$) :

Reference to tables-III.1 and III.2 reveals that the triorganotin ketocarboxylates have low melting points and are

fairly soluble in nonpolar organic solvents like typical organotin carboxylates. Analytical and spectroscopic data (tables III.2 and III.6, III.8, III.9) have provided valuable information regarding their composition and structure.

Before undertaking to discuss the spectroscopic properties of the triorganotin ketocarboxylates, it will be relevant as well as instructive to have a close look at the IR spectra and the molecular geometry of the free acids.

(i) IR spectra of the free acids :

The IR spectra of the α-keto acids used in the present investigation are shown in figures III.1-III.3 and the spectral data given in table-III.6A.

In free pyruvic acid (PvH) and benzoyl formic acid (BFH) there are very broad bands in the region 3600-2900 cm^{-1} indicating the presence of hydrogen bonded dimers. In CCl_4 solution of PvH this band, however, becomes sharp and absorbs moderately at 3420 cm^{-1} like monomers. The ν_{asOCO} and $\nu_{C=O}$ frequencies, which overlap into a strong broad band in the region 1750-1720 cm^{-1} in neat PvH also get split into two strong sharp bands at 1790 and 1725 cm^{-1} in CCl_4 solution. The 1790 cm^{-1} band in CCl_4 solution may reasonably be attributed to the carboxyl C=O stretch of the monomeric form of the acid[90]. Therefore, it is apparent that PvH is monomeric in CCl_4 solution and occurs as a dimeric species in

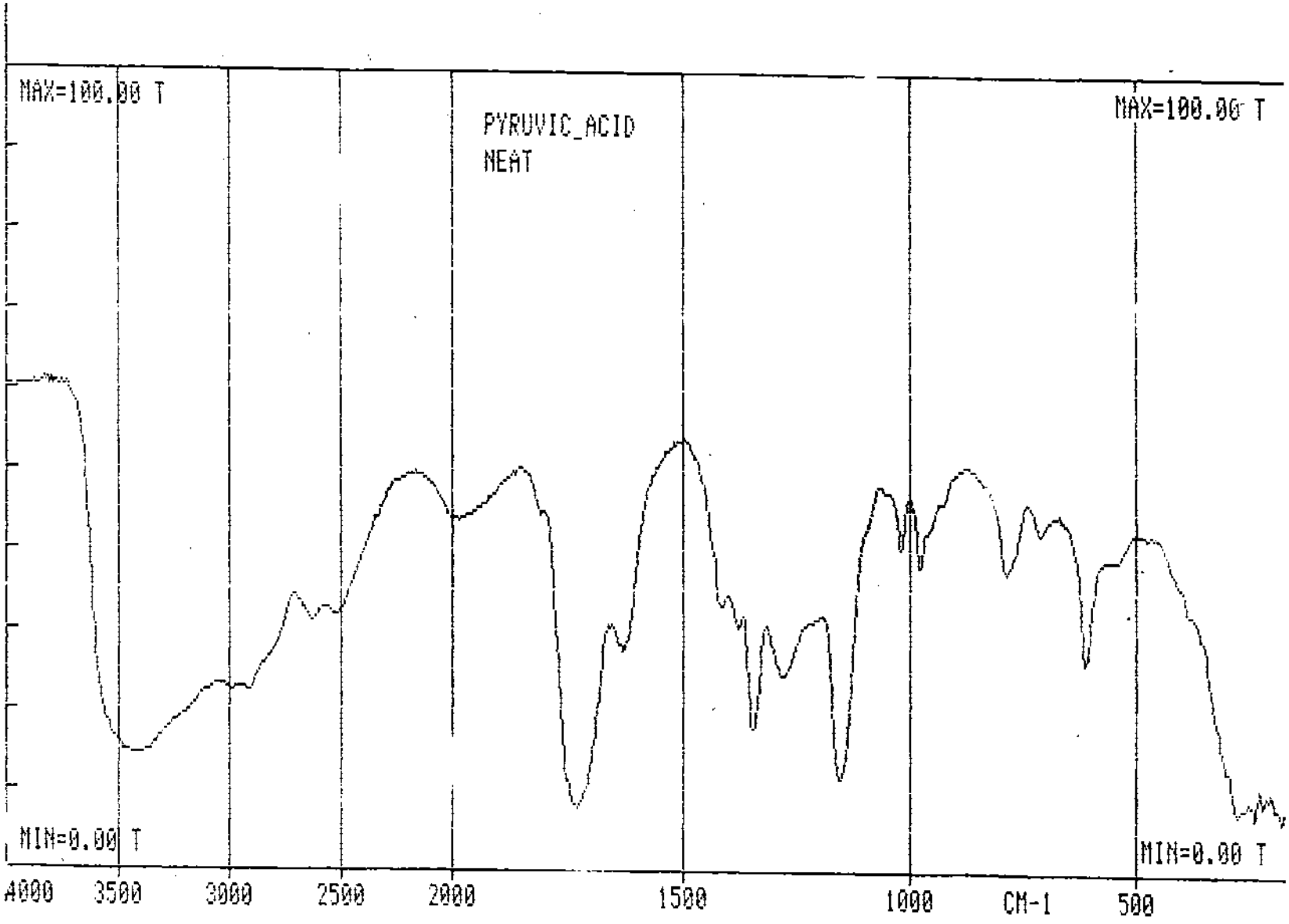


Fig.III.1. IR Spectrum of PvH (neat).

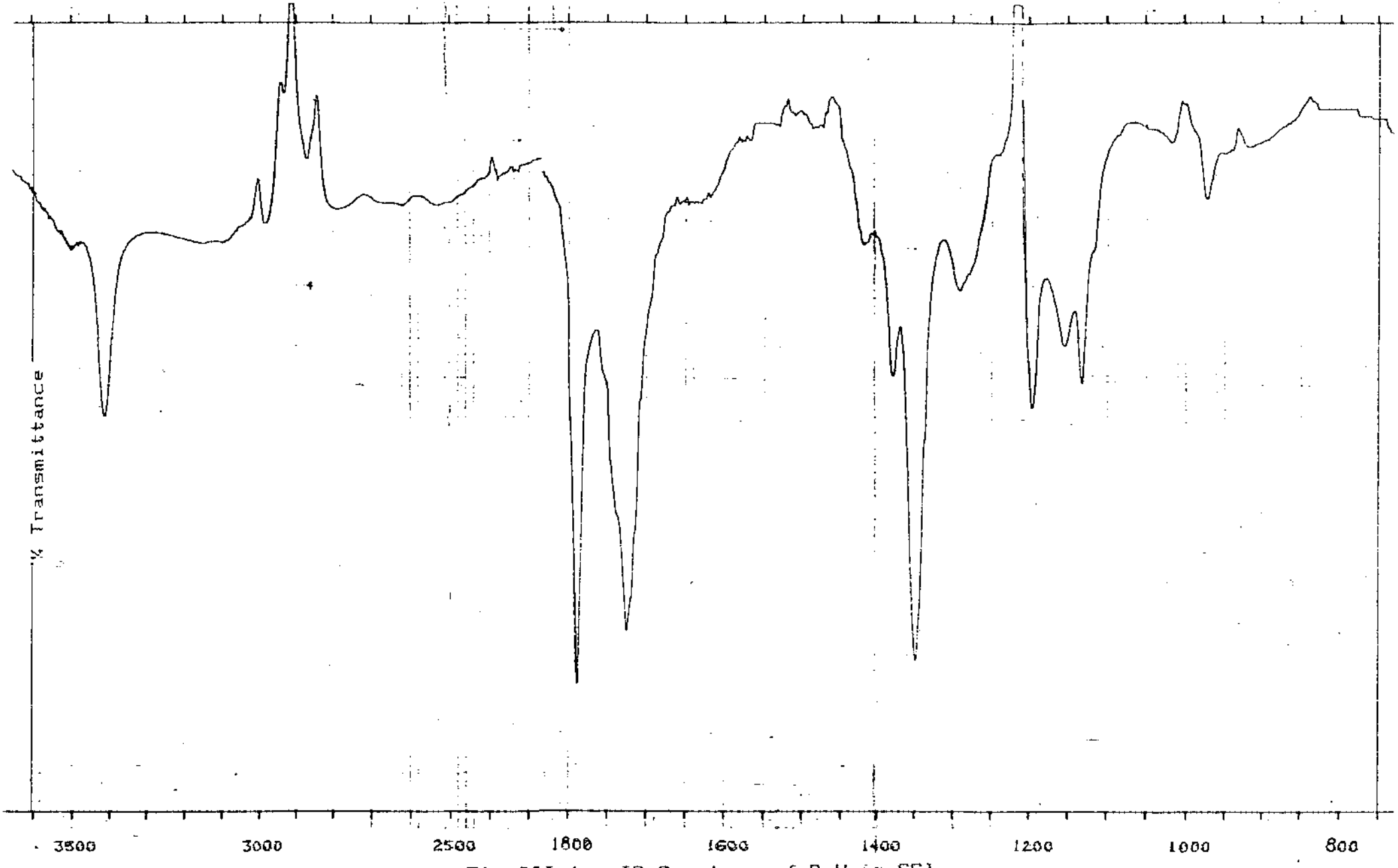


Fig.III.1a. IR Spectrum of PvH in CCl_4.

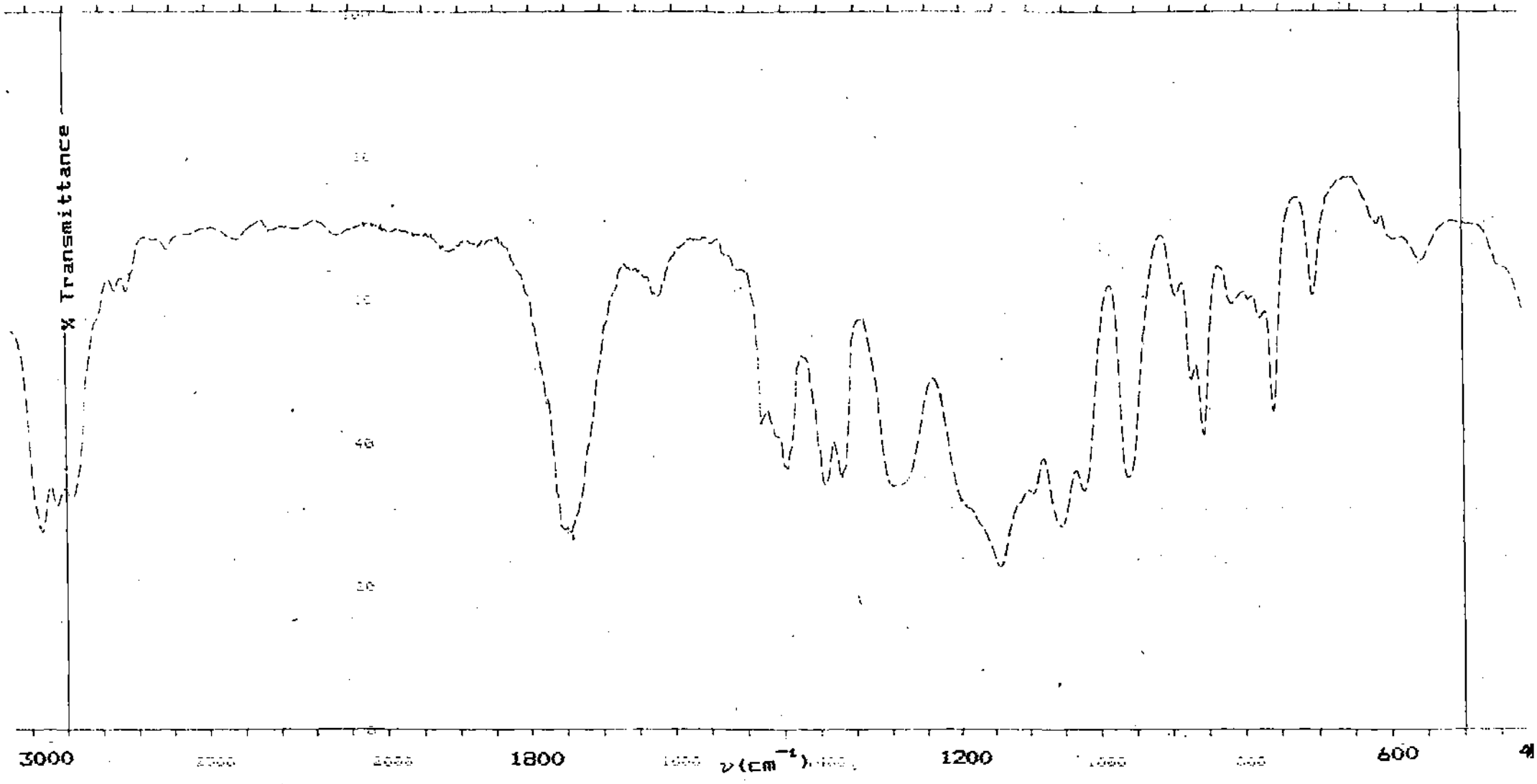


Fig.III.1b. IR Spectrum of PvEt (neat).

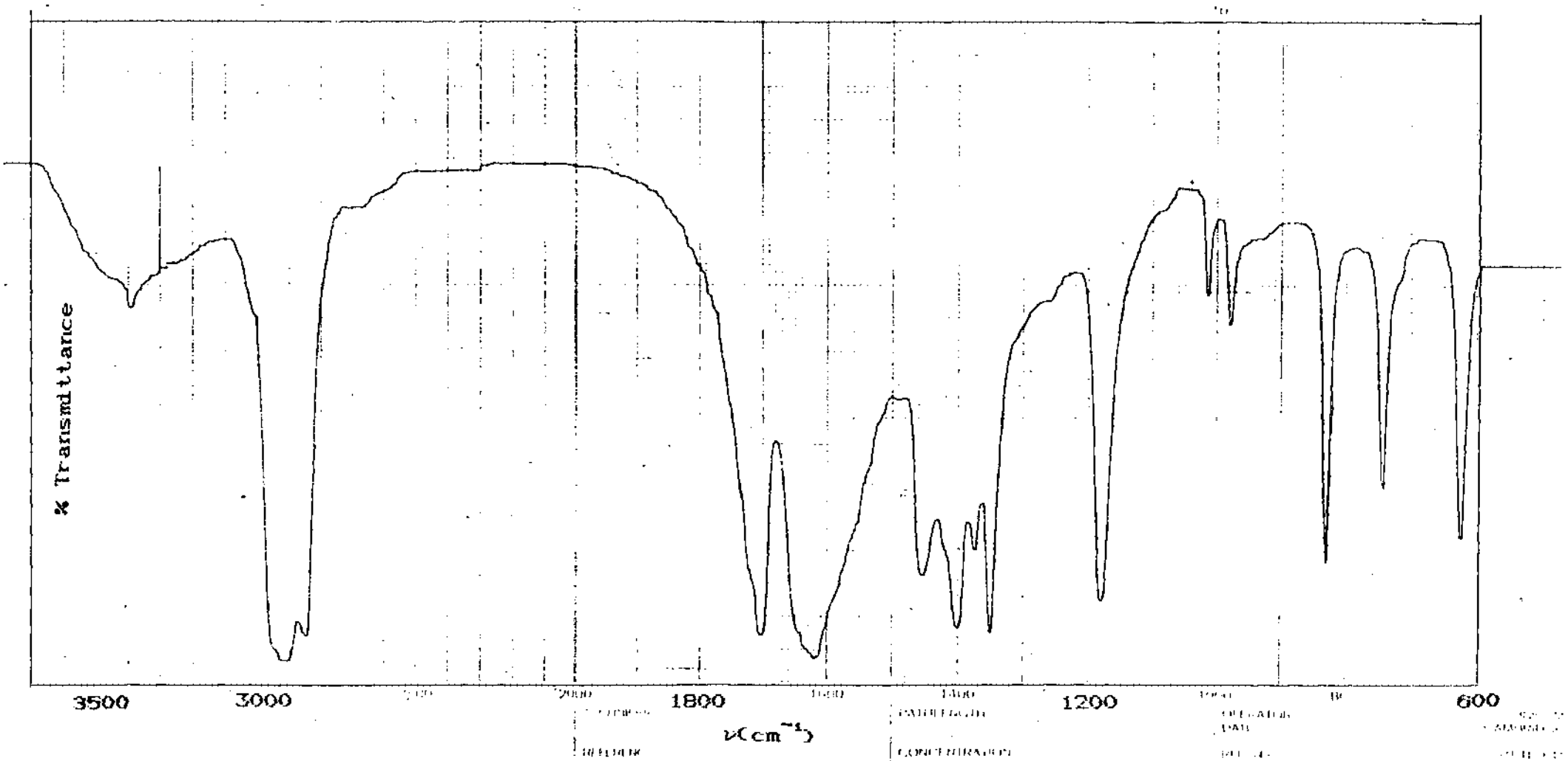


Fig.III.1c. IR Spectrum of NaPv in Nujol.

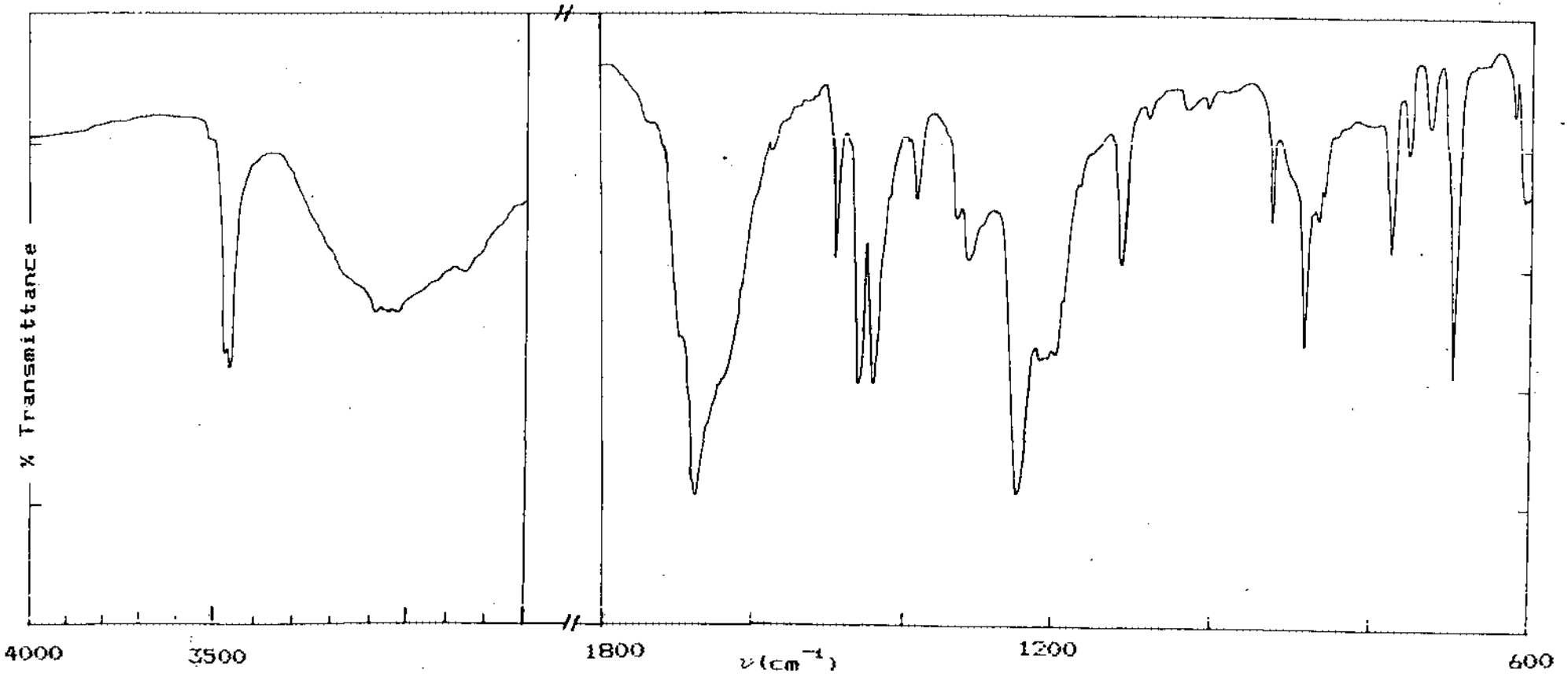


Fig.III.2. IR Spectrum of PPvH in KBr.

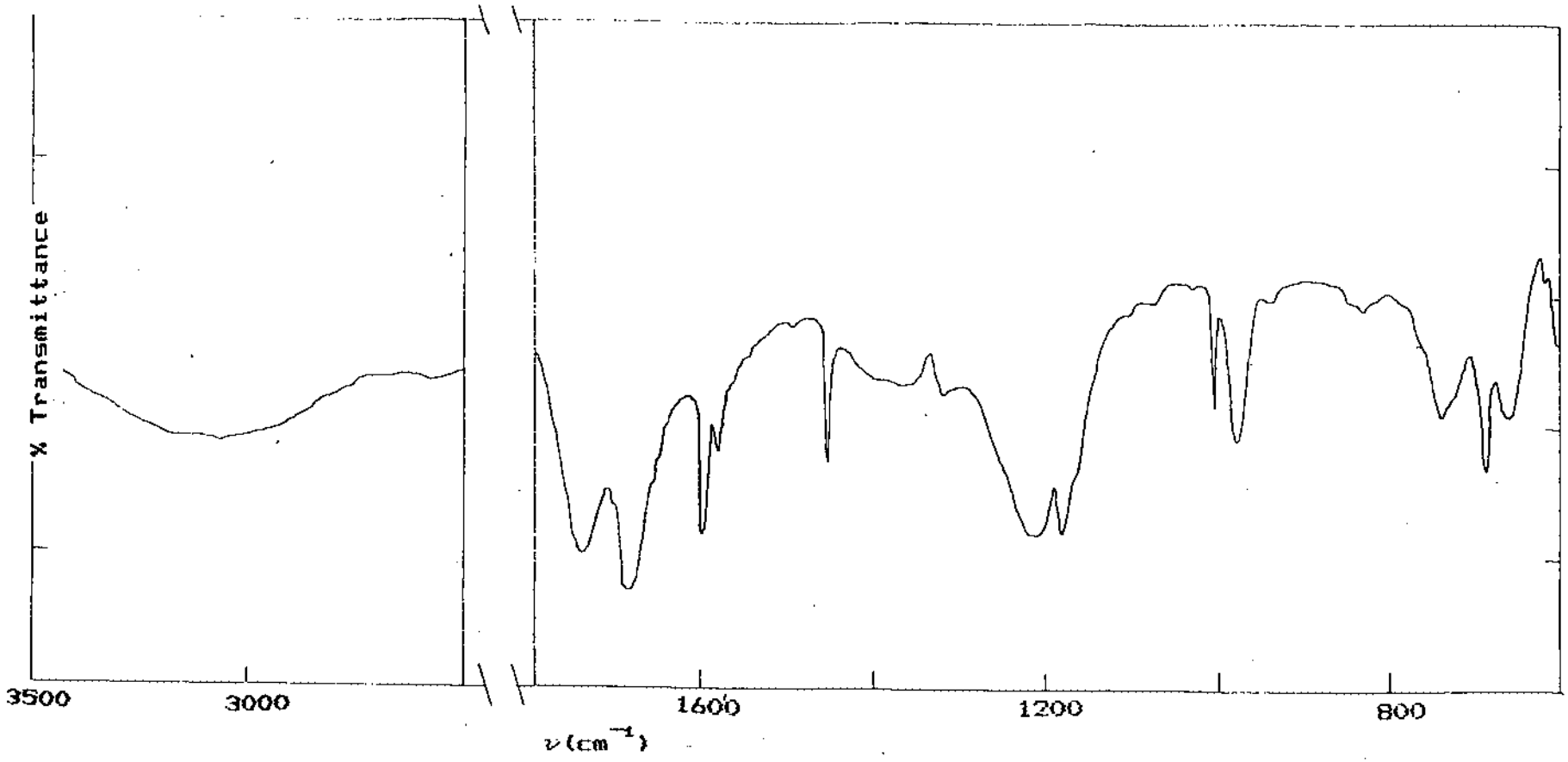


Fig.III.3. IR Spectrum of BFH in KBr.

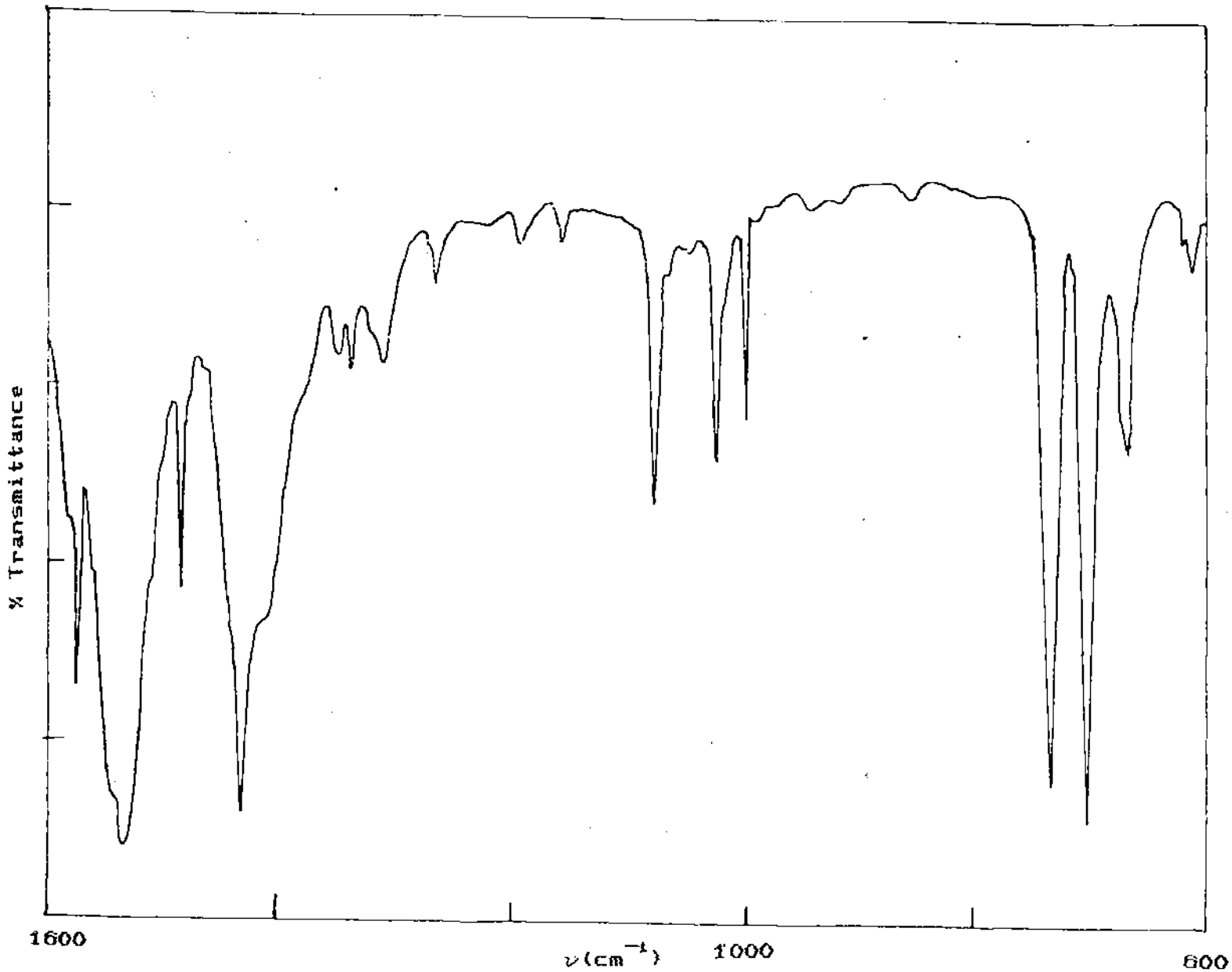


Fig.III.4. IR Spectrum of Ph_3SnPy in KBr.

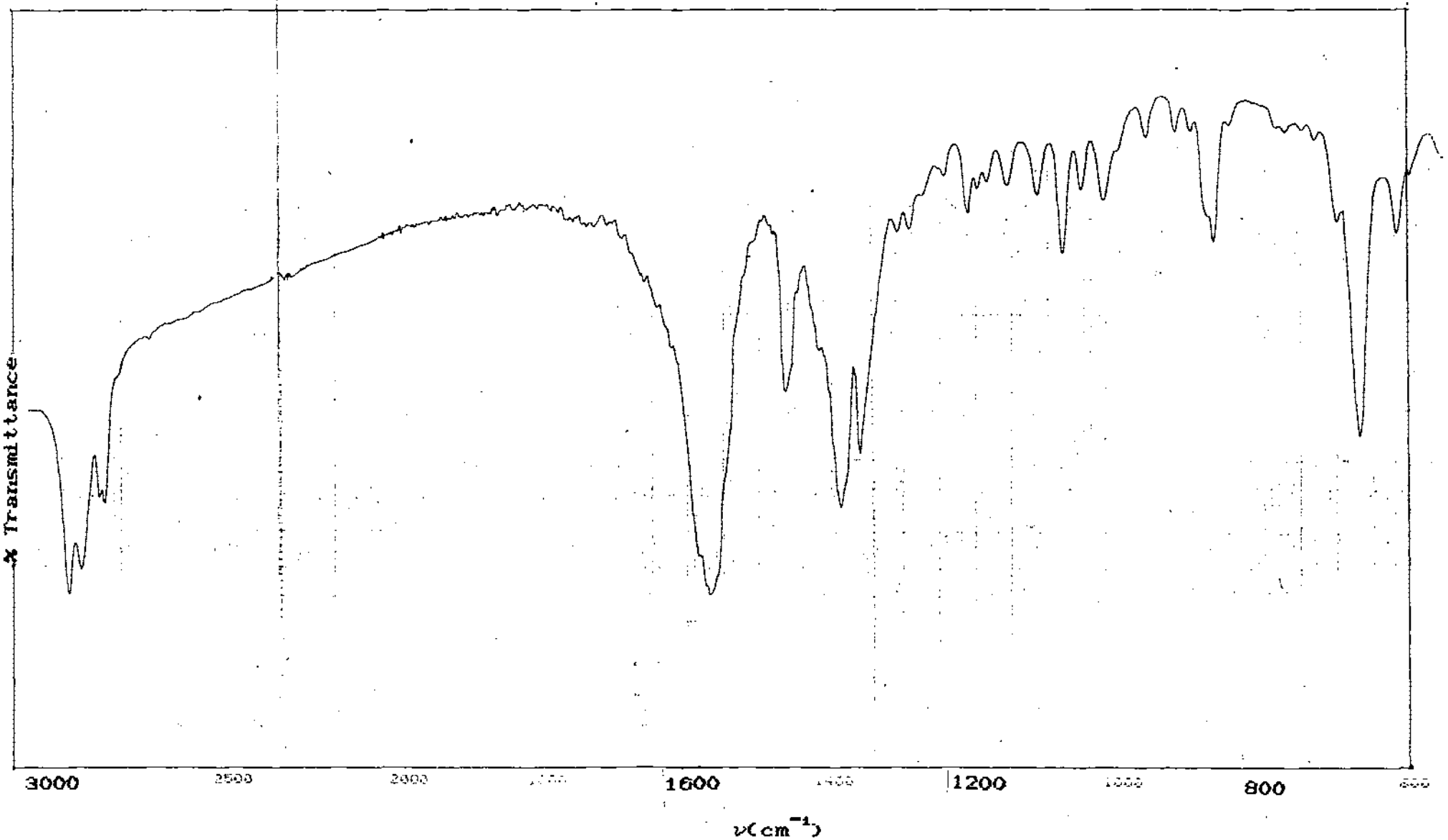


Fig.III.5. IR Spectrum of Bu_3SnPv in KBr.

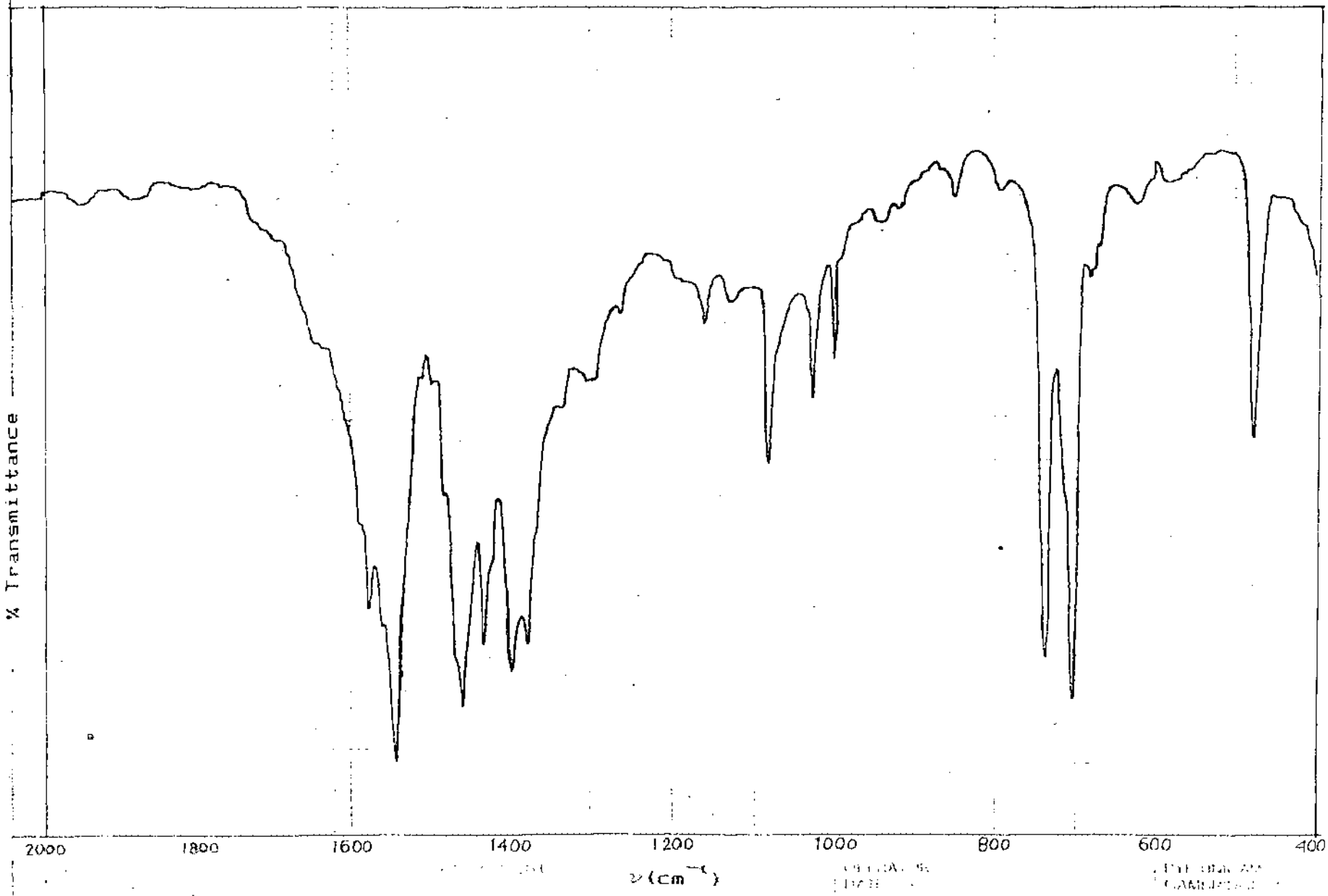


Fig.III.6. IR Spectrum of Ph_3SnPPv in Nujol.

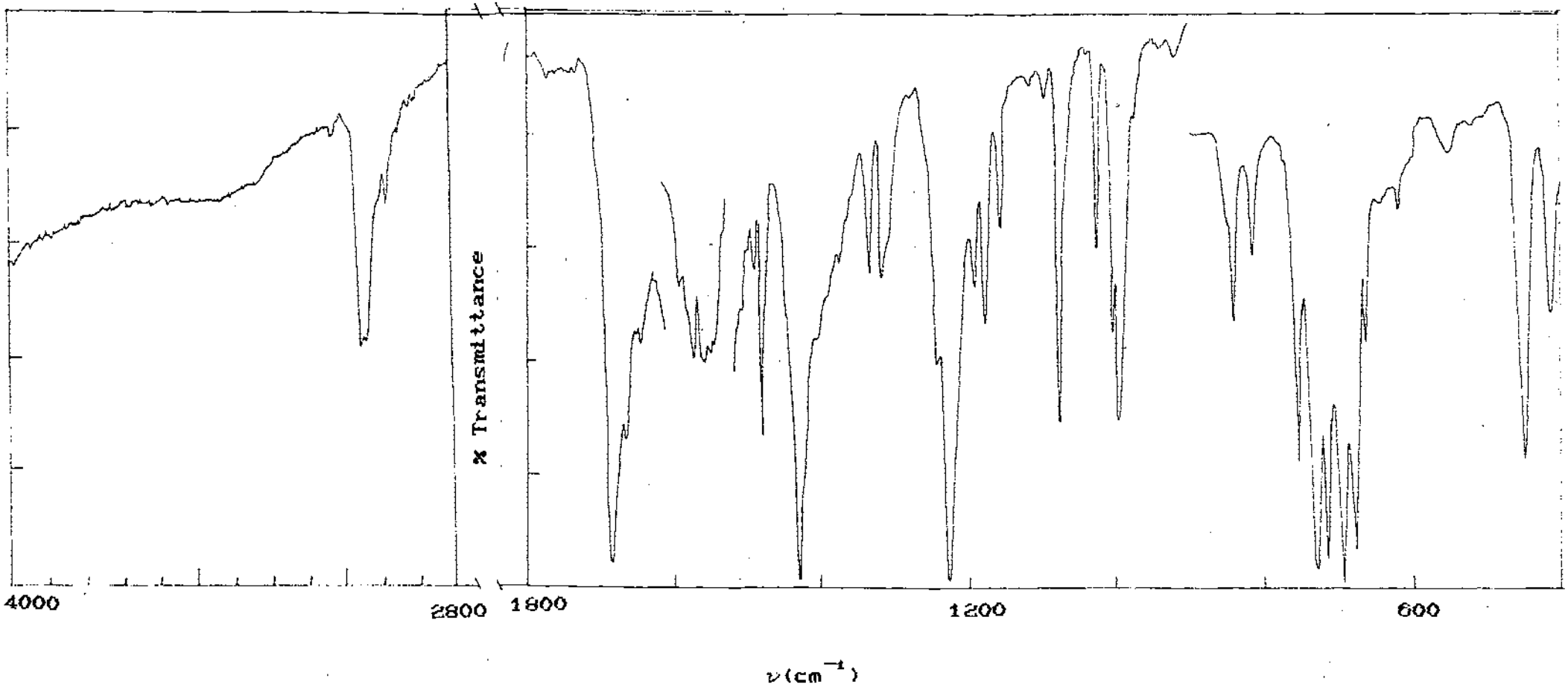


Fig.III.7. IR Spectrum of Ph_3SnBF in KBr.

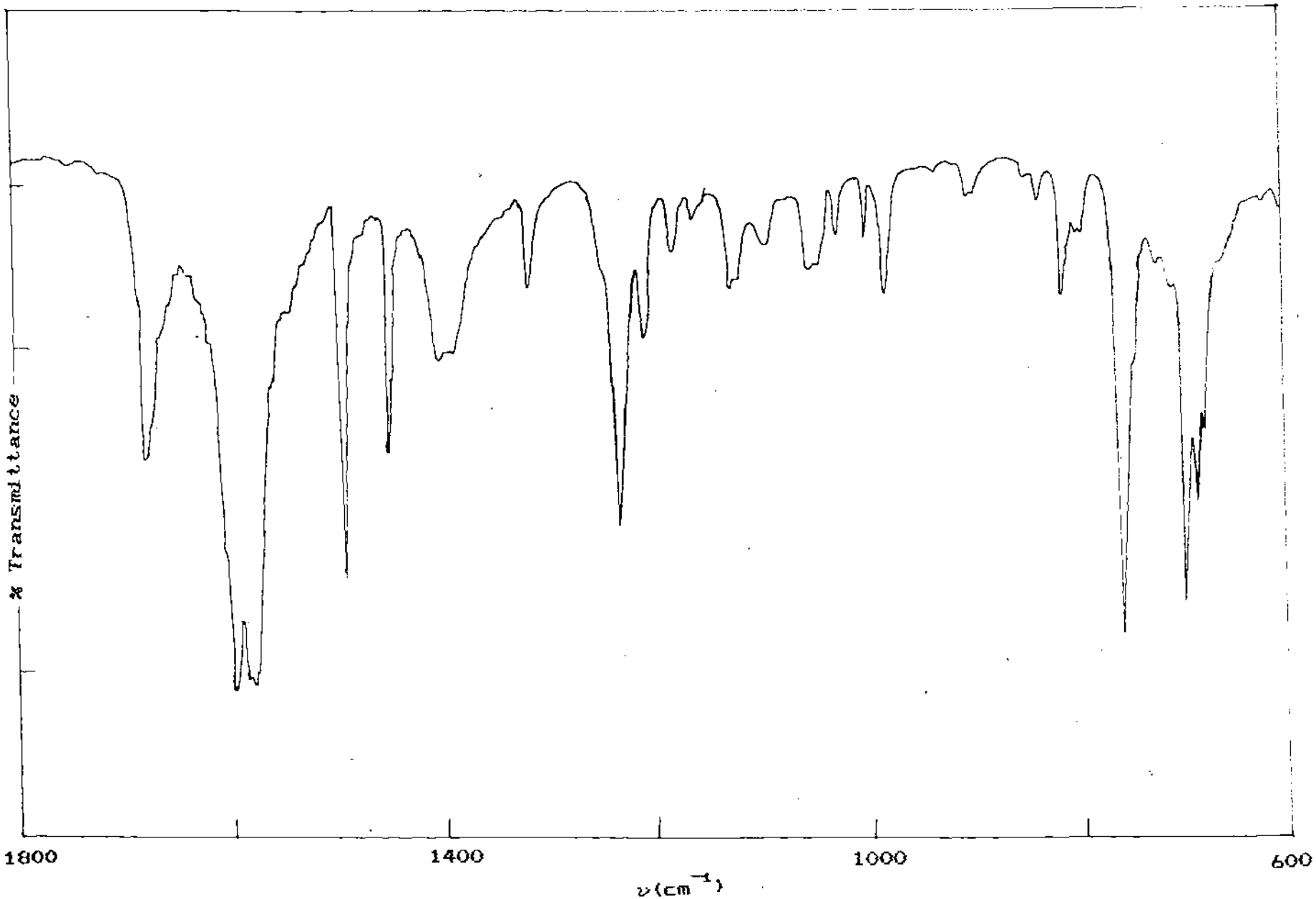


Fig.III.8. IR Spectrum of Bz_3SnBF in KBr.

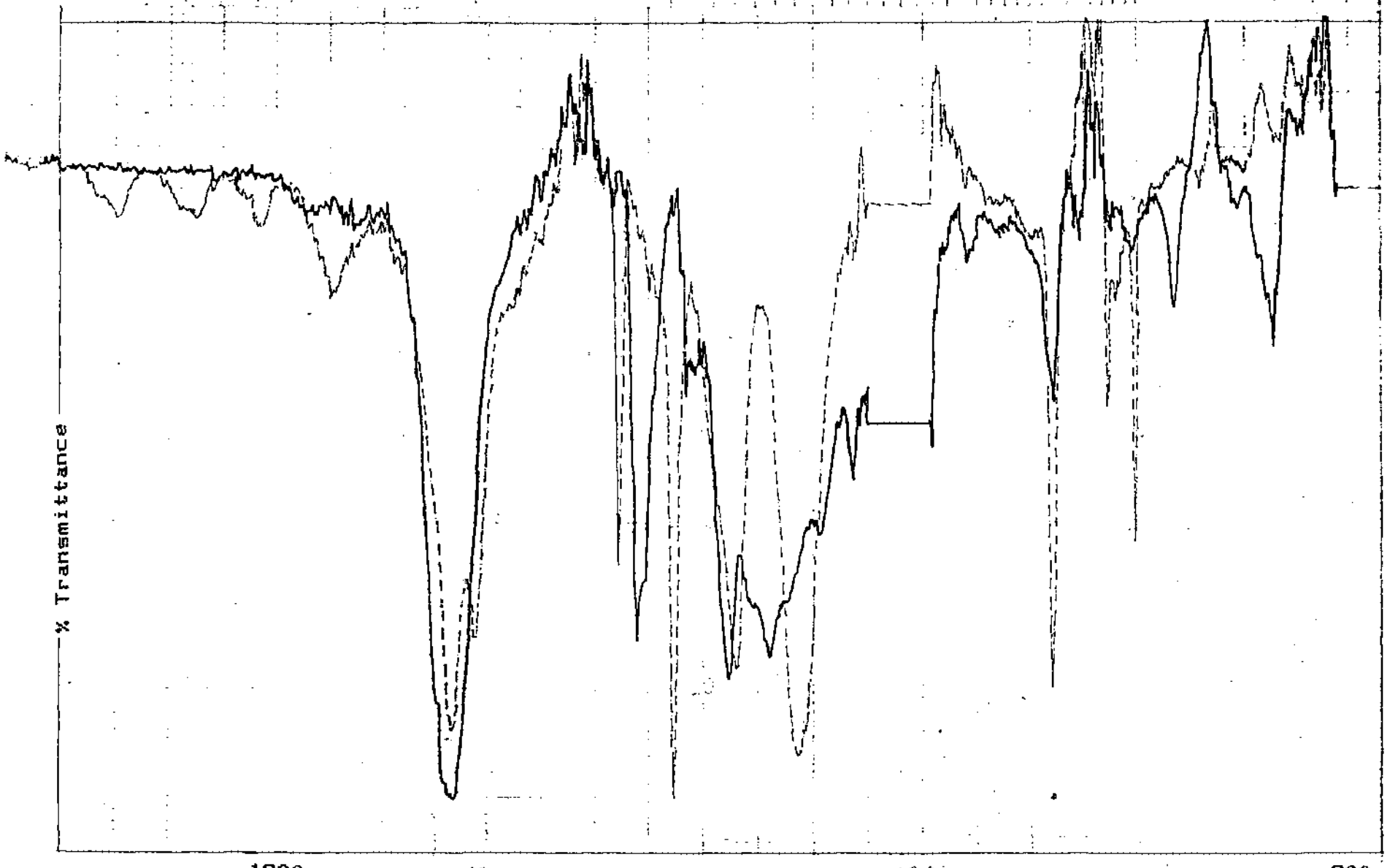


Fig.III.9. IR Spectra of Ph_3SnPv (------) and Bu_3SnPv (———) in $CHCl_3$.

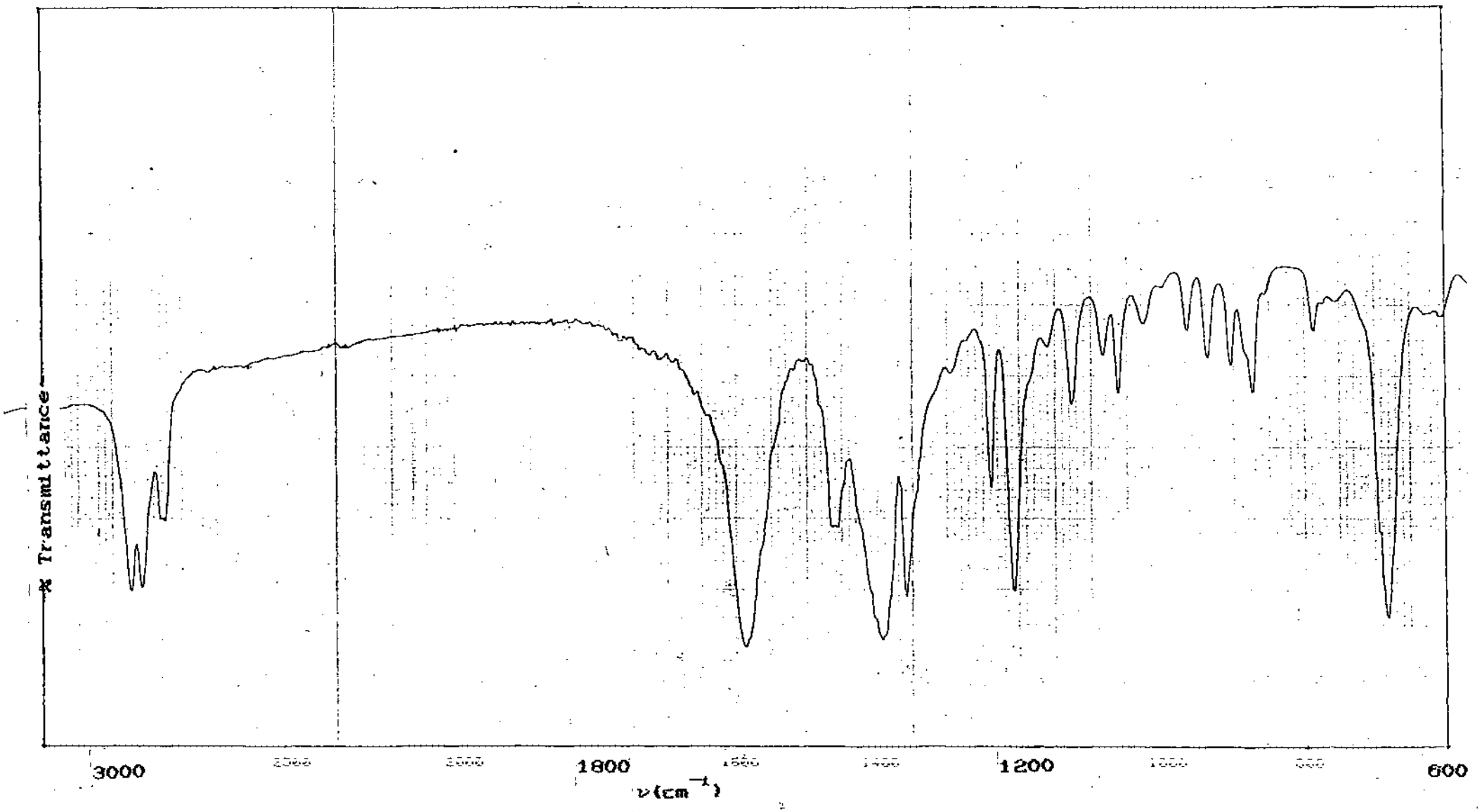


Fig.III.10. IR Spectrum of $Bu_2Sn(Pv)_2$ in KBr.

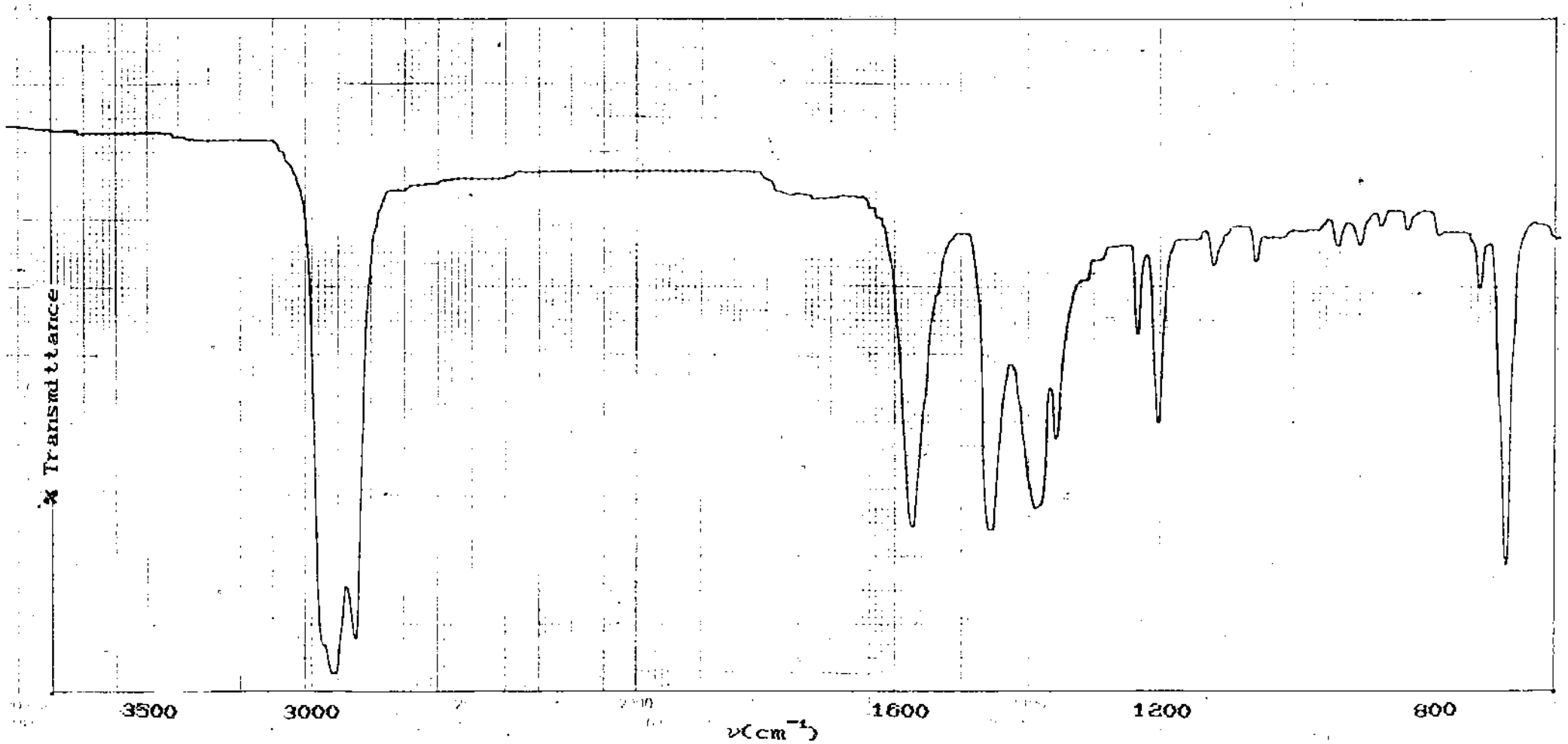


Fig.III.11. IR Spectrum of $Oct_2Sn(Pv)_2$ in Nujol.

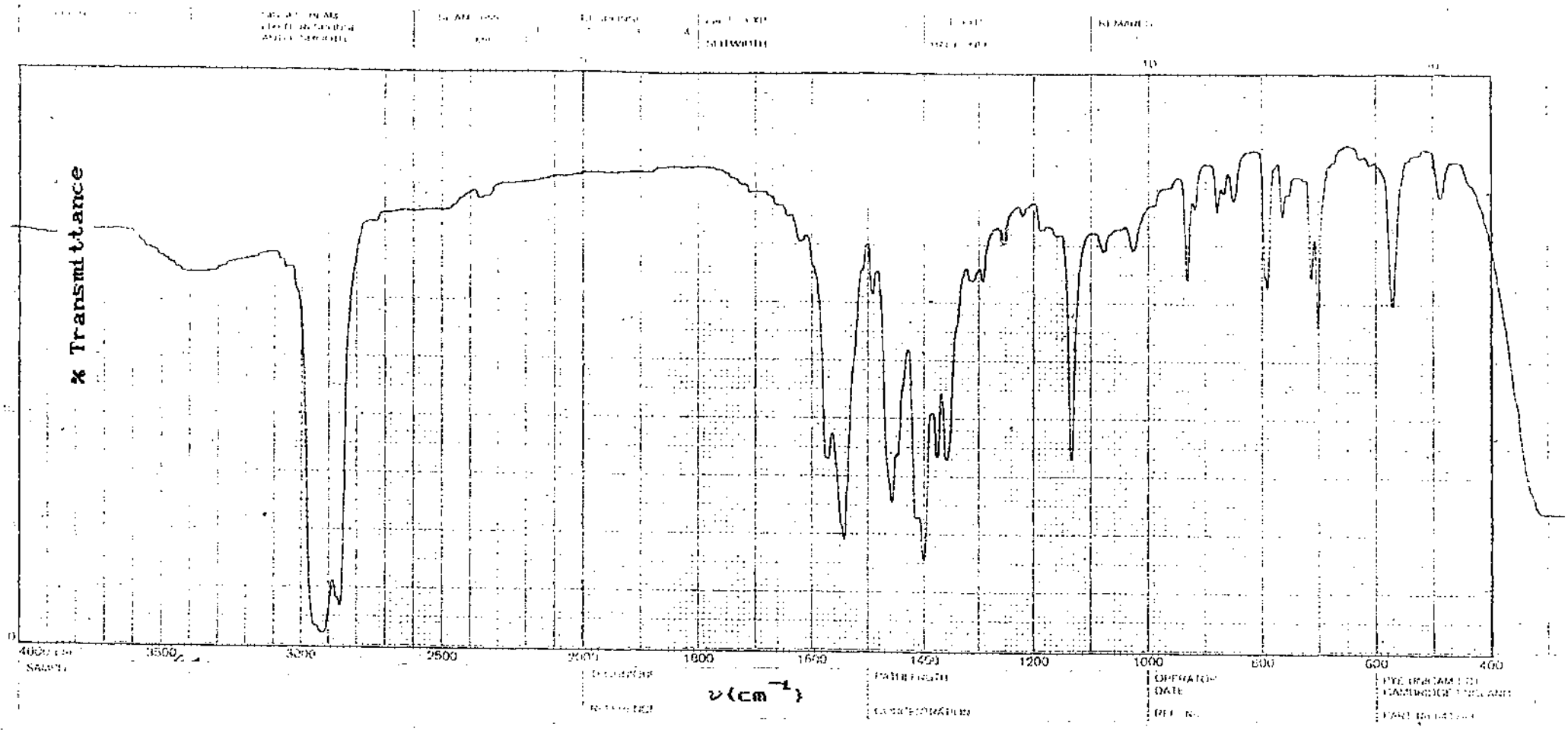


Fig.III.12. IR Spectrum of $Bu_2Sn(PPv)_2$ in Nujol.

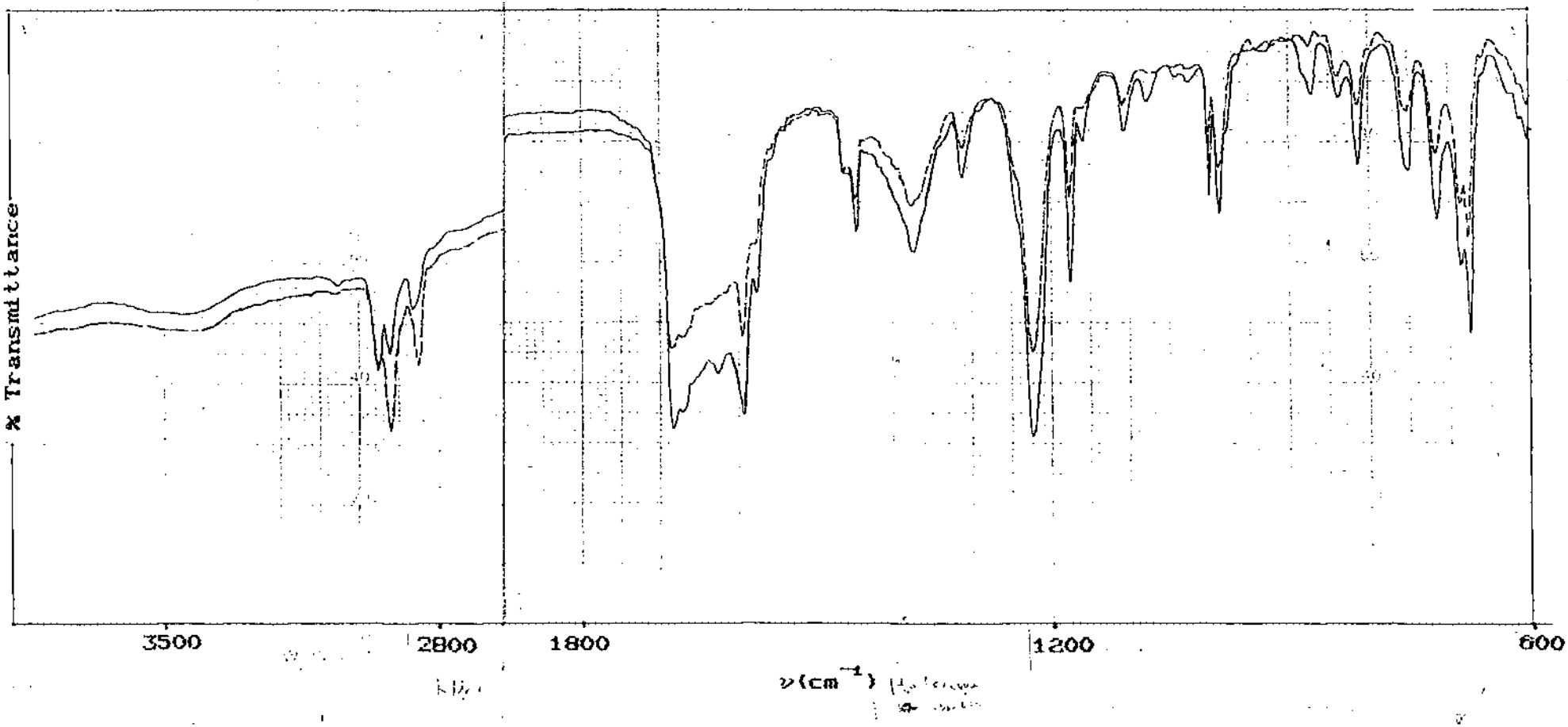


Fig.III.13. IR Spectra of $Oct_2Sn(BF)_2$ (------) and $Bu_2Sn(BF)_2$ (———) in KBr.

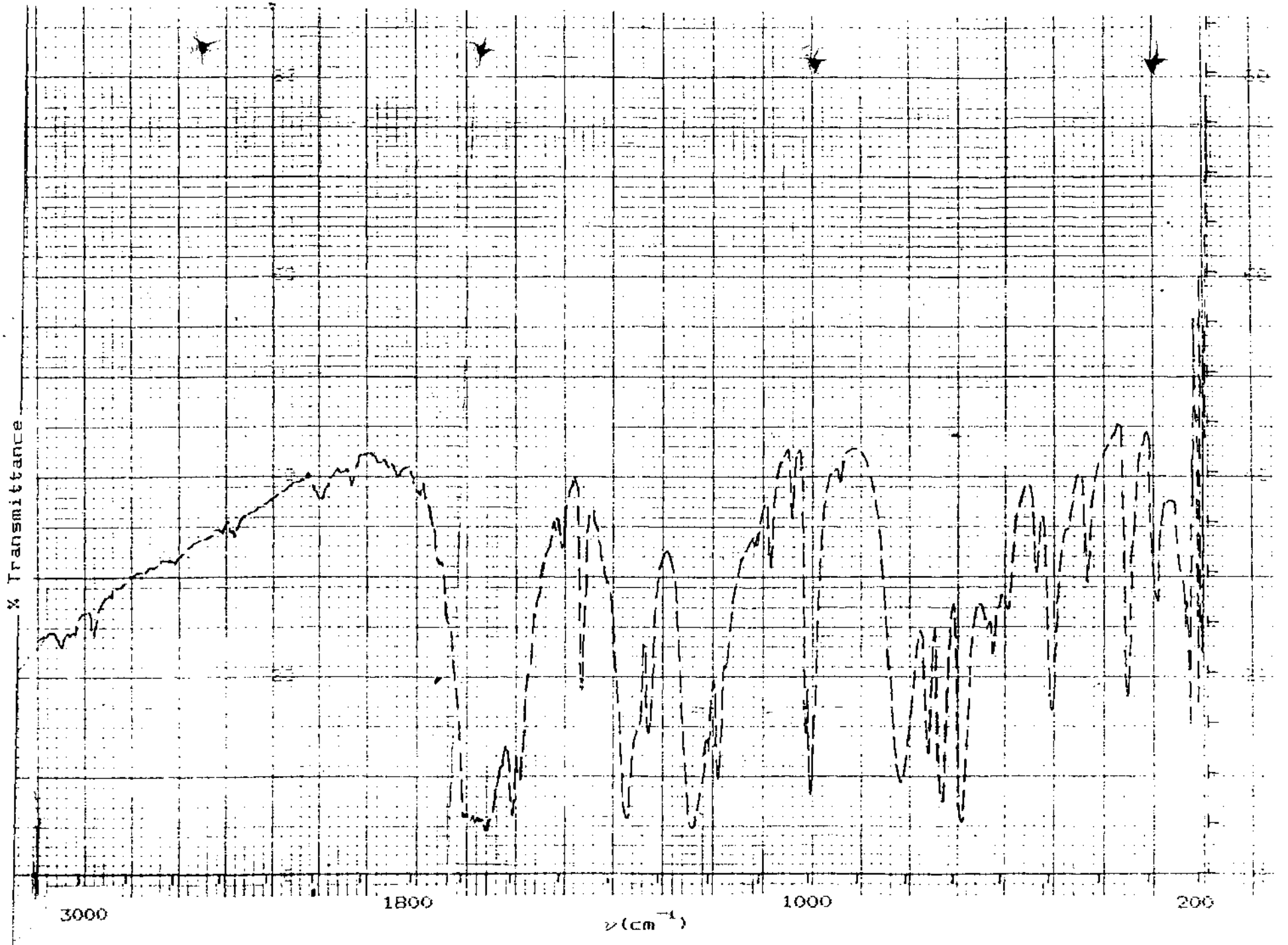


Fig.III.14. IR Spectrum of $Me_2Sn(BF)_2$ in KBr.

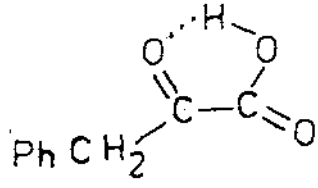
PERKIN ELMER
Printed in India

the neat liquid. The band occurring at 1725 cm^{-1} in CCl_4 solution may be assigned to ketonic C=O, from the comparison of the IR spectra of the acid and its ethyl ester.

In BFH the ν_{asOCO} and $\nu_{C=O}$ frequencies appear as broad bands at 1740 and 1685 cm^{-1} respectively, in the solid phase. The $\nu_{C=O}$ band occurs at a lower frequency compared to PvH due to conjugation with the phenyl ring. Because of the presence of a very broad OH stretching band centering near 3000 cm^{-1} and a medium intensity, slightly broad, out of plane OH deformation band at 975 cm^{-1}, it may be inferred that this acid exists primarily as carboxyl dimer in the solid state.

On the other hand, the presence of a medium intensity sharp band at 3460 cm^{-1}, in the case of phenyl pyruvic acid (PPvH), indicates the absence of dimeric form even in the solid state. However, the carboxyl stretch occurs as a broad band in the region 1690-1680 cm^{-1} showing a lowering of ν_{asOCO} This is, presumably, due to intramolecular hydrogen bonding as shown in structure-V. This is supported by the spectrum of the sodium salt where the $\nu_{C=O}$ (keto) is found at 1700 cm^{-1} and the ν_{asOCO} and ν_{sOCO} are found in the normal region for salts.

There are medium intensity bands in the 700-600 cm^{-1} which may be assigned to C=O wag in all these acids. In PvH and BFH this band occurs at 615 and 660 cm^{-1} respectively, whereas, in PPvH the



V

same band occurs at still higher frequency at 695 cm^{-1}. This also suggest the involvement of the ketonic C=O group in intramolecular H-bonding in PPvH.

The existence of the intramolecularly H-bonded monomeric structure [V] for PPvH requires the trans form of the acid to be more stable. Although, for PvH and BFH also, the more symmetrical trans form may be assumed to be more stable, no such inference can be drawn on the basis of IR spectra. A study of the computer generated molecular models of these acids and calculation of their energies, using Desk Top Molecular Modeller: Version 1.2[94], have shown that for all the free acids the trans-geometry offers the energetically more stable form (table-III.5). Thus, it is evident

Table-III.5.

Calculated molar energy content of the ligands.

Molecule	E in KJ/Mole. Cis-form	Trans-form
$CH_3COCOOH$	1.432	1.244
$PhCH_2COCOOH$	-4.511	-4.741
PhCOCOOH	10.769	7.784

that in these acids the potential donor O-atom of the keto group is suitably oriented for intramolecular coordination in their organotin derivatives.

(ii) IR spectra of triorganotin ketocarboxylates :

The IR spectral data of the organotin keto carboxylates are presented in table- III.6A, and some typical spectra are shown in figures III.4-III.9.

Although complete assignment of the absorption bands in the IR spectra of the triorganotin compounds is not possible due to the presence of strong ligand vibrations in all the relevant regions, important structural information may be obtained from a qualitative assignment of bands to ν_{OH}, ν_{asOCO}, $\nu_{C=O}$, ν_{sOCO} and ν_{Sn-O} vibrations. The main features of the IR spectra are noted below.

All the triorganotin derivatives are characterised by the presence of a number of strong intensity bands in the 1700-1500 cm^{-1} region, where the $\nu_{C=O}$ and ν_{asOCO} frequencies occur. These frequencies in these compounds have been identified by comparing their spectra with those of the free acids, their esters and Na-salts. However, in some cases these two frequencies overlap resulting into a broad band similar to that of the free acids, but at a lower frequency. In such cases the assignments are not precise.

Table:-III.6.A.

Characteristic IR freguencies(in Cm^{-1}) of α-keto acids & their organotin derivatives.

SL. no.	Compound.	Solid Phase(in Nujol/KBr)					Soln.Phase(in CCl_4/$CHCl_3$)			
		ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}	$\nu_{C=O}$ (wag)	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
1.	PvH	3600-2900[b]	1728	1740	1285 1160	615	4320	1725	1790	1280 1200
2.	PvEt	-	1745	1755	1370 1300	618		-		
3.	PvNa	-	1710	1625	1405	625		-		
4.	Ph_3SnPv	-	1572	1542 1535	1410	665		1612	1635	1370
5.	Bu_3SnPv	-	1584	1567[b]	1384	665		1635[a]	1635	1340
6.	Bz_3SnPv	-	1580	1567[b]	1403	665		-		
7.	$Bu_2Sn(Pv)_2$	-	1585[a]	1585[a]	1392	680		1608	1680	1370
8.	$Oct_2Sn(Pv)_2$	-	1580[a]	1580[a]	1395	680		1610	1678	1370
9.	$Me_2Sn(Pv)_2$	-	1628[sh] 1595	1560	1356	670		-		
10.	PPvH	3460	1686[a]	1686[a]	1248 1195	695		-		
11.	PPvNa	-	1702	1620	1395			-		
12.	Ph_3SnPPv	-	1583	1565 1547	1400			1610	1650	1370
13.	Bu_3SnPPv	-	1592[a]	1592[a]	1394			-		
14.	Bz_3SnPPv	-	1614[a]	1614[a] 1562	1386			1610	1650	1345
15.	$Bu_2Sn(PPv)_2$	-	1620[sh] 1580	1550	1406			-		

---

a - very broad band, probably due to overlap of ν_{asOCO} and $\nu_{sC=O}$.

b - broad ; sh - shoulder.

Table:-III.6.A(contd.).

SL. no.	Compound.	Solid Phase(in Nujol/KBr)					Soln.Phase(in CCl_4/$CHCl_3$)			
		ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}	$\nu_{C=O}$ (wag)	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
16.	$Oct_2Sn(PPv)_2$	-	1627[ah]					-		
			1577[a]	1577[a]	1394					
17.	$Me_2Sn(PPv)_2$	-	1628[ah]					-		
			1575[a]	1575[a]	1410					
18.	BFH	3400-2800[b]	1686	1742	1215[b] 1180	660		-		
19.	BFNa	-	1670	1570	1412			-		
20.	Ph_3SnBF	-	1686	1575 1550	1405	680		1690	1655	1360
21.	Bu_3SnBF	-	1648	1582 1550	1405	670		-		
22.	Bz_3SnBF	-	1678	1583	1405	680		1670	1610	1360
23.	$Bu_2Sn(BF)_2$	-	1686	1625[b]	1375[b]	680		1688	1645	1365
24.	$Oct_2Sn(BF)_2$	-	1686	1620[b]	1375[b]	675		1680	1640	1370
25.	$Me_2Sn(BF)_2$	-	1686	1647	1363	680		-		
26.	$Ph_2Sn(BF)_2$	-	1686	1635	1375[b]	678		-		

a - very broad band, probably due to overlap of ν_{asOCO} and $\nu_{sC=O}$.

b - broad ; sh - shoulder.

In most of the derivatives of PvH and PPvH both the $\nu_{C=O}$ and ν_{asOCO} frequencies appear below 1600 cm^{-1}, the lowest being for the triphenyltin derivatives, as expected. In the derivatives of BFH, however, the ketonic stretching frequency is either unchanged or shows only marginal -ve shift relative to the free acid and occurs as an unambiguously identifiable sharp band around 1680 cm^{-1}.

The symmetric carboxyl stretching vibrations in these compounds appear in the region 1410-1380 cm^{-1}, which are well above the corresponding frequencies in the free acids or their esters, but close to their Na-salts. However, identification of the ν_{sOCO} is not always unambiguous due to the presence of various other strong absorptions.

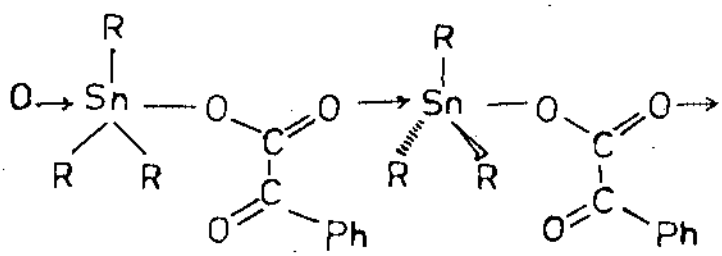
Thus, data from table-III.6A shows that both the asymmetric and symmetric carboxyl stretching vibrational bands of the parent acids, appearing in the region 1740-1688 cm^{-1} and 1280-1215 cm^{-1} respectively, get considerably shifted in the triorganotin ketocarboxylates, indicating organostannylation[32]. Like triorganotin acetates, formates etc.[33], the ν_{asOCO} and ν_{sOCO} bands of all the triorganotin ketocarboxylates appear in the 1590-1535 cm^{-1} and 1410-1380 cm^{-1} regions respectively, in the solid state. In $CHCl_3$ solution, the former band is raised to 1655-1610 cm^{-1} region and the latter is lowered to around 1370-1340 cm^{-1}. It can

also be seen from table-III.6A that the difference between ν_{asOCO} and ν_{sOCO} is always less than 200 cm^{-1} in the solid state and more than 250 cm^{-1} in solution.

These observations may be interpreted in terms of bidentate and almost symmetrical carboxyl group forming intermolecular bridges in the solid state giving rise to polymeric keto carboxylates[34], while in solution depolymerisation occurs resulting into ester like monomeric species.

All the triorganotin derivatives show weak to medium intensity bands in 600-400 cm^{-1} region. These bands may be assigned to ν_{Sn-O}, since comparison with ligand spectra showed no band attributable to ν_{Sn-C}, which is expected to occur further down the scale.

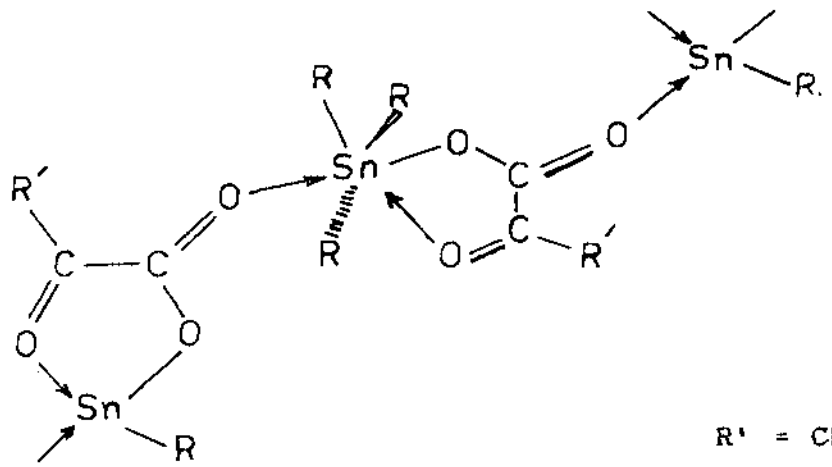
In the light of the above observations it is apparent that, the derivatives of BFH differ from the derivatives of the other acids in having the $\nu_{C=O}$ frequencies almost unaltered (at 1680 cm^{-1}), both in the solid and solution phase relative to the free acid, but having the carboxylic stretching frequencies in the same regions. Thus it may be inferred that, in the triorganotin benzoylformates, while the carboxyl group acts as intermolecular bridge giving rise to polymeric structure with trigonal bipyramidal geometry around tin in the solid state, the keto group remains free as shown in structure VI below :



VI

In the derivatives of PvH and PPvH, however, the ketonic stretching bands appear below 1600 cm^{-1} in the solid state, although the same bands in the free acids appear at 1728 cm^{-1} and 1688 cm^{-1} respectively. Such a large negative shift can only be explained by assuming the involvement of the keto group in intramolecular coordination, as the carboxyl group is less likely to act intramolecularly because of its small bite angle[35]. Thus, in the solid state the triorganotin esters of PvH and PPvH have polymeric structure, involving chelating C=O group and bridging carboxylic group, the tin atom geometry, presumably, being octahedral as shown in structure VII below.

This conclusion is supported by the fact that in $CHCl_3$ solution of these compounds, while the ν_{asOCO} frequency undergoes very large +ve shift due to depolymerisation, the $\nu_{C=O}$ is raised only slightly. In spite of the fact that in solution the ketonic C=O group remains intramolecularly coordinated, the small rise in $\nu_{C=O}$



VII

R' = CH_3, $PhCH_2$

R = n-Bu, Ph, $PhCH_2$

frequency may not be quite unlikely because of the change in the environment of the tin atom and its geometry from octahedral to trigonal bipyramidal.

Although in the +IV state tin is known to utilise its 5d orbital, hybridised with 5s and 5p orbitals, frequently in increasing its coordination number above four, the energy difference between the s or p orbital and the d orbital is such that the hybrid orbitals have relatively low d-character. In the trigonal bipyramidal geometry involving sp^3d hybrid orbitals, in complexes of the type $R_3SnX.L$ (L = ligand), the three orbitals in the equatorial plane around tin can be regarded as primarily sp^2 in character and are expected to form three strong covalent bonds with the R groups. The two apical orbitals may be regarded as

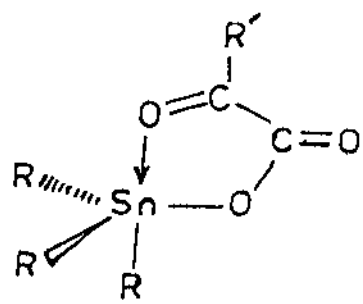
consisting of the p_z and the d orbitals, having predominant p-character and are most likely to overlap with the more electronegative X group[41,42] and the donor atom of the complexing agent. The bonds between tin and the axially placed electronegative atoms are, therefore, expected to be relatively weak. X-ray crystallographic studies by several authors on a number of $R_3SnX.L$ compounds[96-98], having trigonal bipyramidal geometry with cis-disposition of the R groups, support this contention. Tin-oxygen bond data for a few such complexes tabulated below [table-III.7] shows the weakness of the tin-axial oxygen bond.

Table:-III.7.

Tin-Oxygen bond data (A^o) in R_3Sn-Carboxylates.

Sl. no.	Compound.	Equatorial. Sn——O	Axial. Sn----O	Ref.
1.	$Ph_3Sn[O_2CC_6H_4(N_2R)-o]$ (R = 2-hdroxy 5-methyl phenyl)	2.070	2.463	36
2.	Ph_3Sn(ONPhCOPh)	2.091	2.308	,,
3.	Me_3Sn(ONPhCOPh) (mol-1)	2.064	2.392	,,
	(mol-2)	2.152	2.263	
4.	Ph_3Sn(OCPhCHPhO)	2.094	2.276	,,
5.	$Ph_3Sn[O_2CC_6H_4(XR)/(NR_2)]$			
	XR = OMe(-o)	2.054	2.781	37
	NR_2 = NH_2(-o)	2.043	2.823	38

On the basis of analogous line of reasoning, it may be inferred that in the monomeric forms of the triorganotin esters of PvH and PPvH in solution phase, the change in hybridisation from sp^3d^2 (octahedral) to sp^3d (trigonal bipyramidal) brings in a reorientation of the groups in such a way that the intramolecularly donating ketonic oxygen atom and a R group occupy axial positions. The resulting structure, with cis-disposition of R groups, in the solution phase, is shown below.



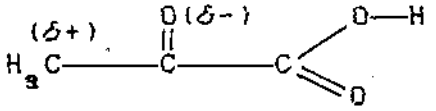
VIII

This change is expected to lower the strength of the Sn <—O (keto) bond, which is reflected in the rise of the $\nu_{C=O}$ frequency in going from solid phase (octahedral geometry) to solution (trigonal bipyramidal geometry).

From the foregoing discussion it is clear that the keto group in BFH is not involved in intramolecular coordination and thus behave differently from that of the other acids. This may,

probably, be due to steric as well as electronic reasons arising out of the presence, on the ketonic carbon atom in BFH, of a phenyl group. The delocalisation of the π electrons of C=O with the phenyl group is certain to diminish the electron density at the oxygen atom compared to that in the other cases, thereby, making intramolecular coordination unfavouable.

The values of the field effect (Taft's) constants for the three R' groups, [CH_3 (-0.05), $PhCH_2$ (0.04), and Ph (0.1)] of the carboxylic acids R'COCOOH used, clearly indicates that the basicity of the keto group is highest in $CH_3COCOOH$ (PvH) and lowest in PhCOCOOH (BFH). While the Ph group acts as an electron withdrawing group in PhCOCOOH, the electron releasing CH_3 group sufficiently enhances electron density at the ketonic oxygen atom in $CH_3COCOOH$ making it capable of coordinating to suitable electrophiles.



IX

This is in agreement with the observation that PvH can form not only intramolecularly coordinated carboxylates, but also, addition complexes. For PPvH the situation is expected to be intermediate between that of PvH and BFH. This is reflected in the fact that PPvH, in addition to forming intramolecularly coordinated

carboxylates, forms an addition complex with $(Bu_3Sn)_2O$, whose donor strength is the highest among the oxo-organotin compounds used.

(iii) Electronic Absorption Spectra :

The α-keto acids, being dicarbonyl systems, are expected to show $n-\pi^*$ transition at wavelengths well above 300 nm, in addition to the $\pi-\pi^*$ band which is expected to occur at much lower wavelength. As discussed earlier, the CO group in these acids plays an extremely important role in the formation of their organotin derivatives. Any involvement of the CO group must result in appreciable changes in either the position or intensity or both, of the $n-\pi^*$ band in these compounds. While in the simple carboxylate compounds like organotin formate or acetate etc., the $n-\pi^*$ transition occurs at a much lower wavelength, approximately at around 200 nm, and is, therefore, of little help in the elucidation of the structure of the organotin carboxylate, the present group of ligands offer a scope for studying the $n-\pi^*$ spectra of the free acids and their organotin derivatives vis-a-vis the role of the CO group in determining the structure of the carboxylates.

The electronic spectra of the keto acids in CCl_4 shows a weak band (ε ~ 10-90) at around 350-390 nm in addition to strong absorptions below 260 nm. The large hypsochromic shift of this

band in polar solvent, e.g., methanol, its low molar absorbance and the presence of vibrational structures in the spectra in non-polar solvents help to identify this band as due to $n-\pi^*$ transition. The position of the $n-\pi^*$ band in the different acids are shown in table-III.8. and some of the spectra are presented in figures III.15-III.26.

In the organotin esters of pyruvic acid (PvH) and phenyl pyruvic acid (PPvH) the $n-\pi^*$ transition bands suffer very large hypsochromic shift, indicating the stabilisation of the n-orbital on stannylation (cf. hypsochromic shift in MeOH). This, clearly indicates the participation of the carbonyl group in intramolecular coordination, which stabilises the lone pair thereby increasing the $n-\pi^*$ transition energy. The magnitude of the blue shift could be used as a measure of the strength of binding by the carbonyl group. Unfortunately, the $n-\pi^*$ bands in the organotin esters often get superimposed with the $\pi-\pi^*$ transition bands making it difficult to determine the position of the $n-\pi^*$ transition precisely in the organotin derivatives.

In the triorganotin esters of benzoyl formic acid (BFH), however, there is practically no change in the position, as well as, molar extinction of the $n-\pi^*$ transition band in comparison to the free acid. This shows the presence of non-interacting keto group in these compounds, corroborating the inference already

Table:-III.8.

Electronic spectral data of Triorganotin Keto Carboxylates:

Compounds.	$n-\pi^*$ peaks (nm) in CCl_4 Sol.	ϵ_{max}	$n-\pi^*$ peaks (nm) in MeOH Sol.	Remarks
$CH_3COCOOH$	370, 350, 335(sh)	9, 13	330	
$Ph_3SnOCOCOCH_3$	No peak above 300 nm. Inflection at 290nm.		290(sh), 275	Carbonyl gr. interacts.
$Bu_3SnOCOCOCH_3$	No peak above 300 nm.		<280	,,
$Bz_3SnOCOCOCH_3$	Inflection at 326 nm.		280	,,
$PhCH_2COCOOH$	385, 368 306	16.5, 23	345, 330, 300	
$Ph_3SnOCOCOCH_2Ph$	310, 296		320(sh), 304	,,
$Bu_3SnOCOCOCH_2Ph$	320(sh), 306, 294		320(sh), 302 288	,,
$Bz_3SnOCOCOCH_2Ph$	330, 310		280	,,
$PhCOCOOH$	393, 375	86, 93	346, 336, 292(sh)	
$Ph_3SnOCOCOPh$	395, 375, 360	58, 71 75	345, 335 ? 280	No CO interaction
$Bu_3SnOCOCOPh$	395, 375		345, 335? 280, 270	,,
$Bz_3SnOCOCOPh$	395, 375		345, 335	,,

sh-shoulder.

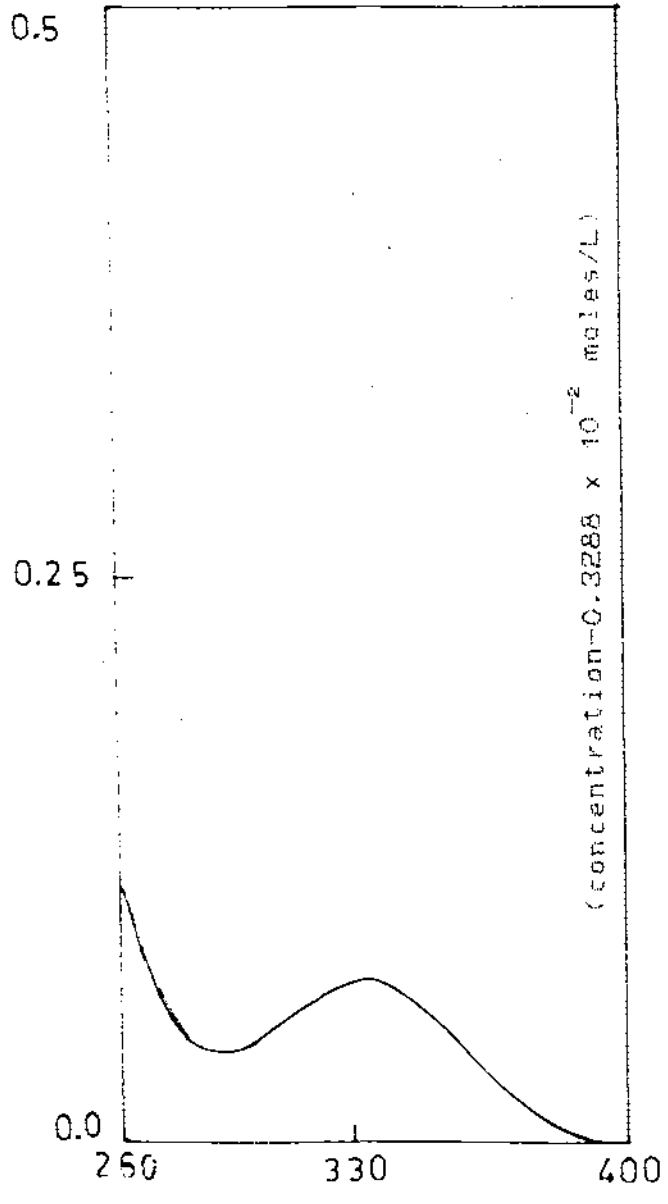


Fig.III.16. Electronic spectrum of PVH in MeOH.

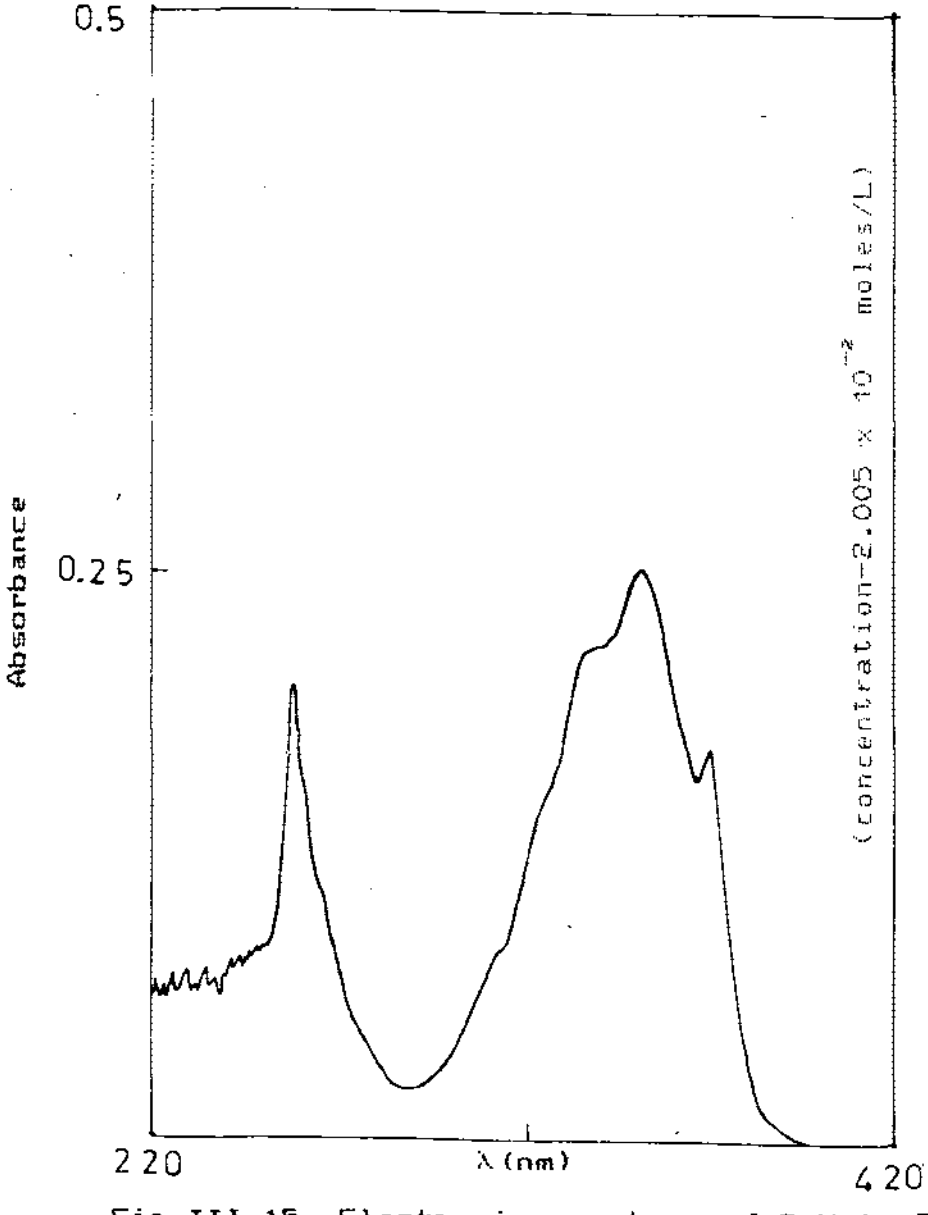


Fig.III.15. Electronic spectrum of PVH in CCl_4.

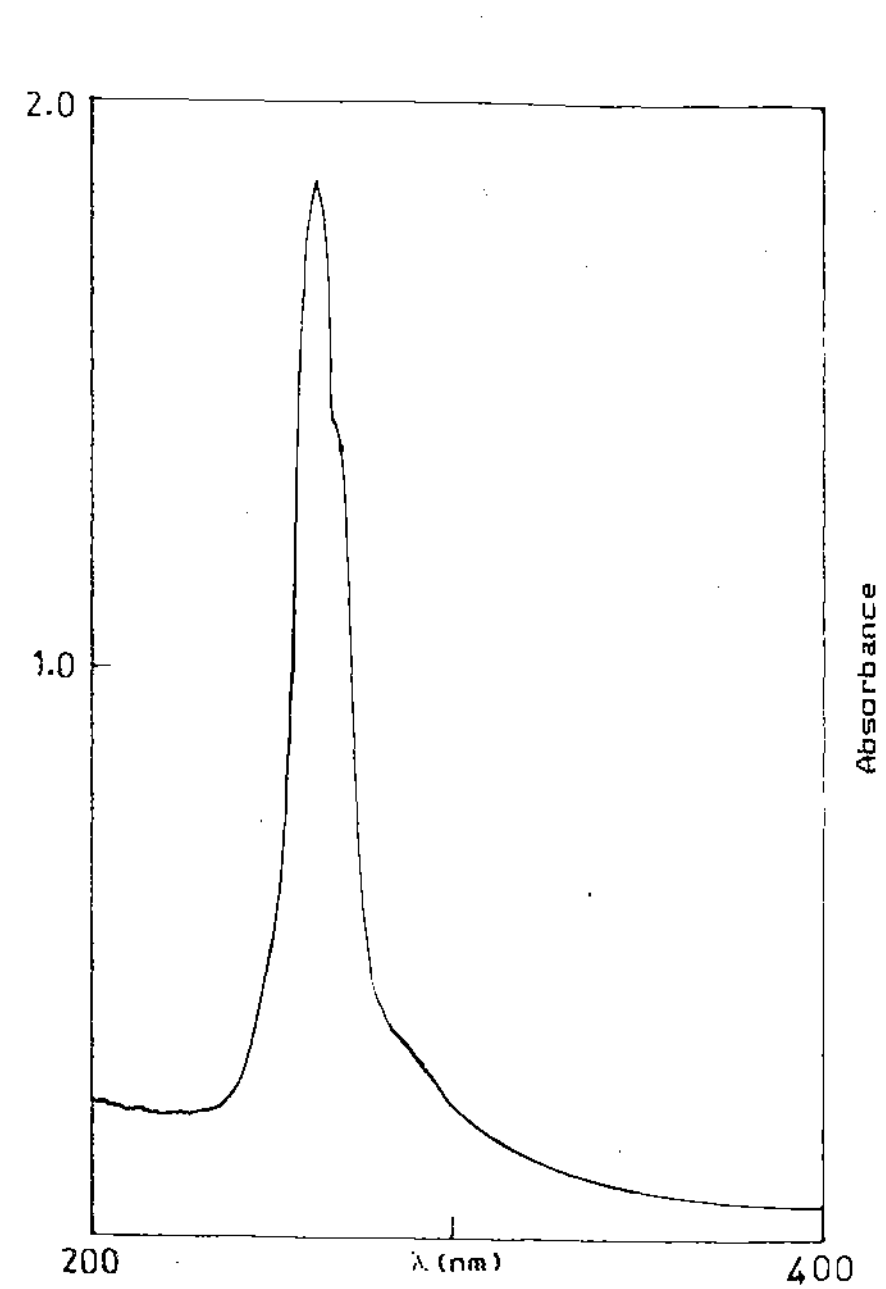


Fig.III.17. Electronic spectrum of Ph_3SnPv in CCl_4.

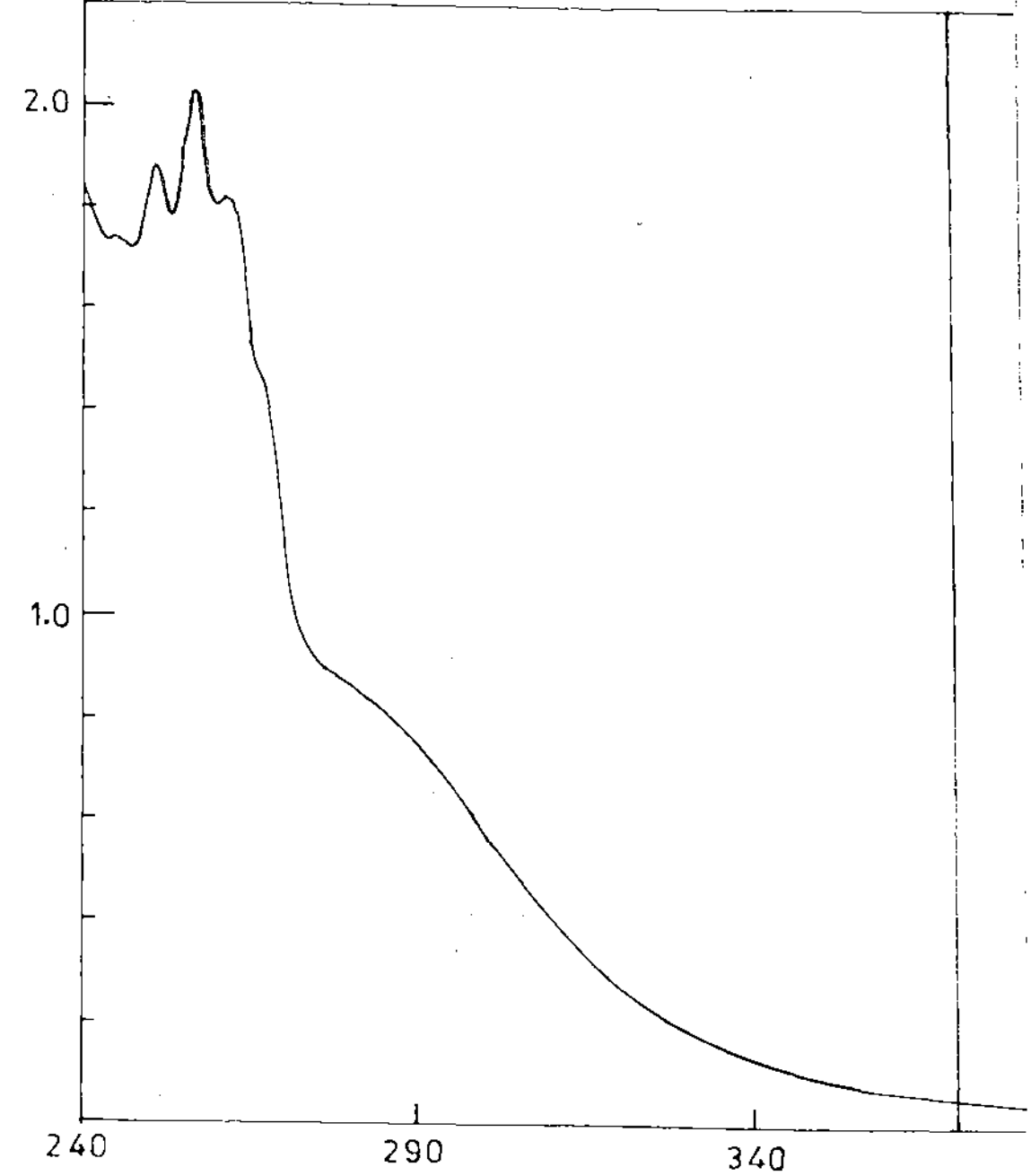
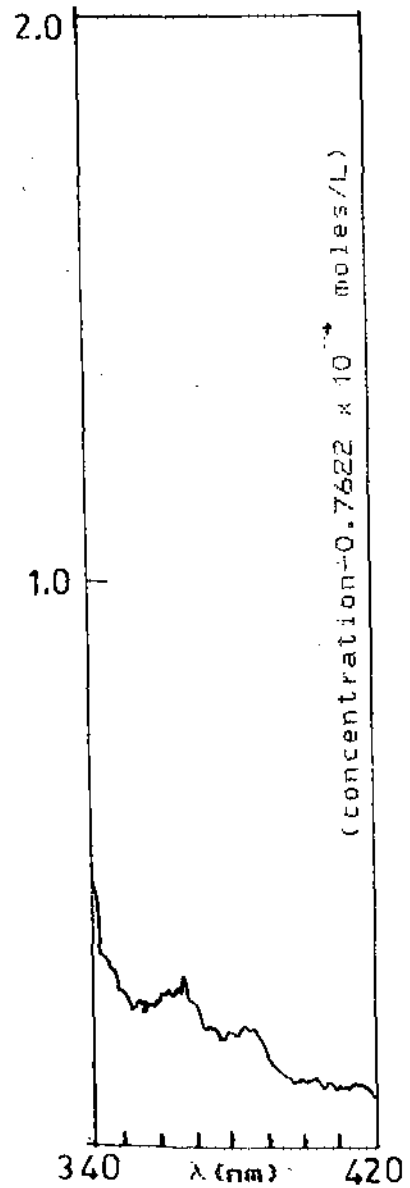


Fig.III.18. Electronic spectrum of Ph_3SnPv in MeOH.



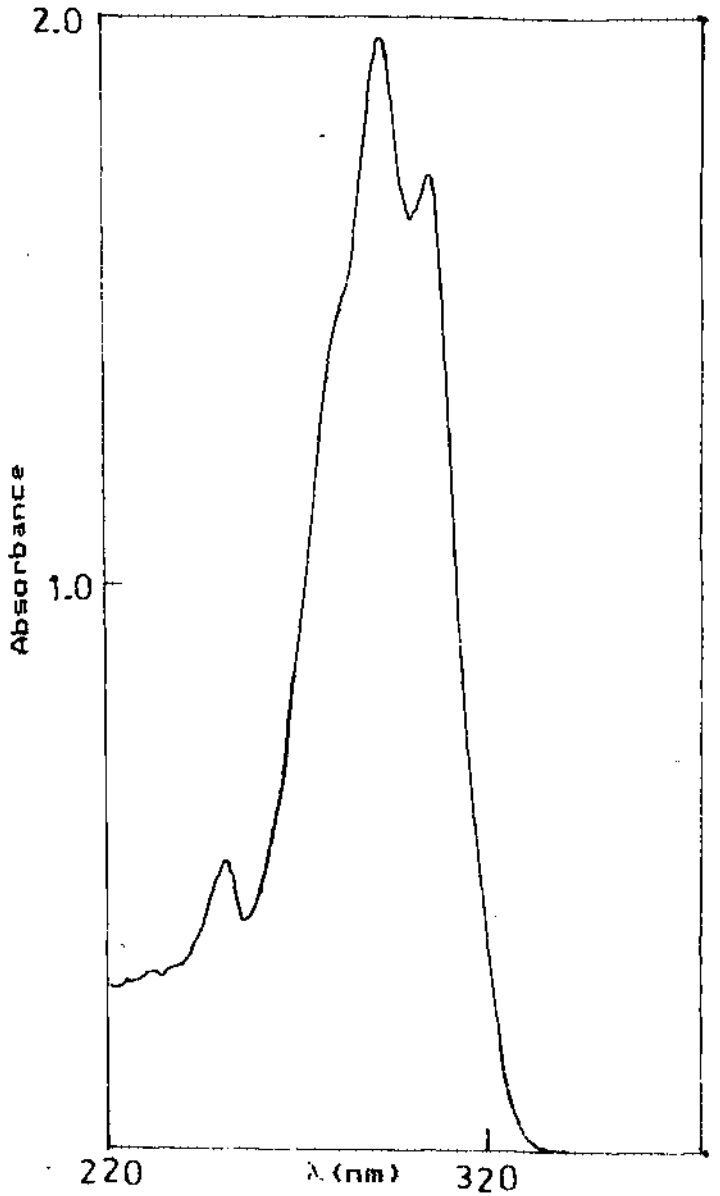


Fig.III.19. Electronic spectrum of PPvH in CCl_4.

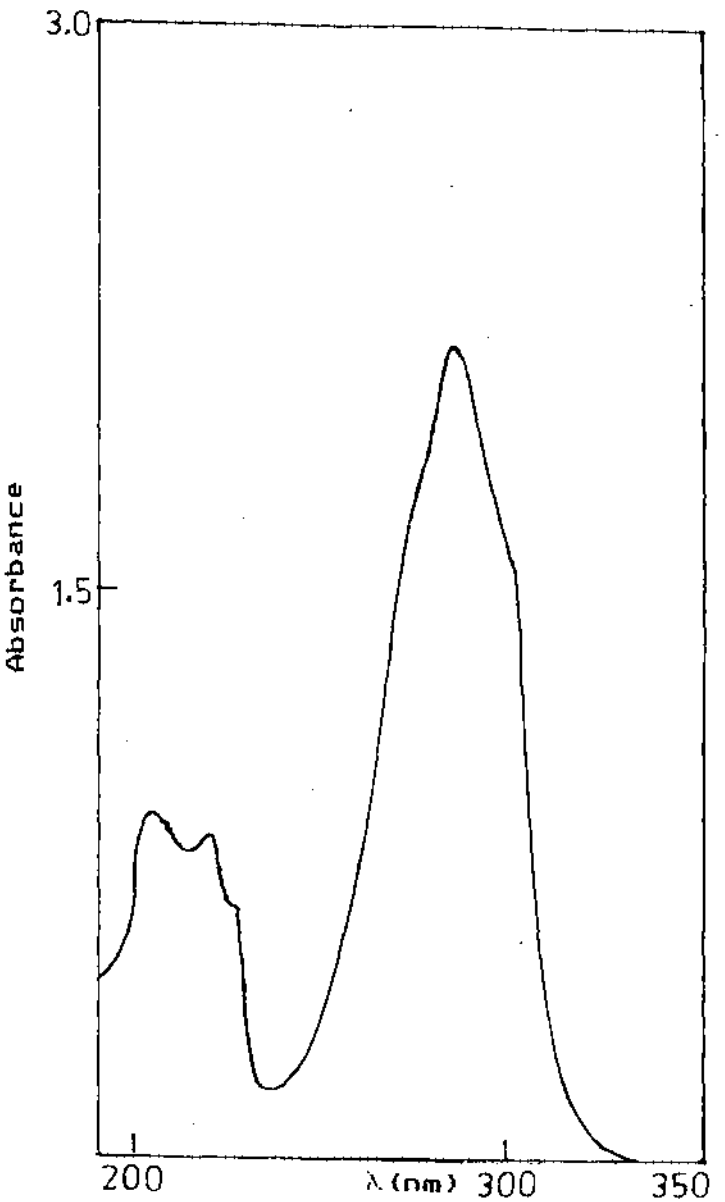


Fig.III.20. Electronic spectrum of PPvH in MeOH.

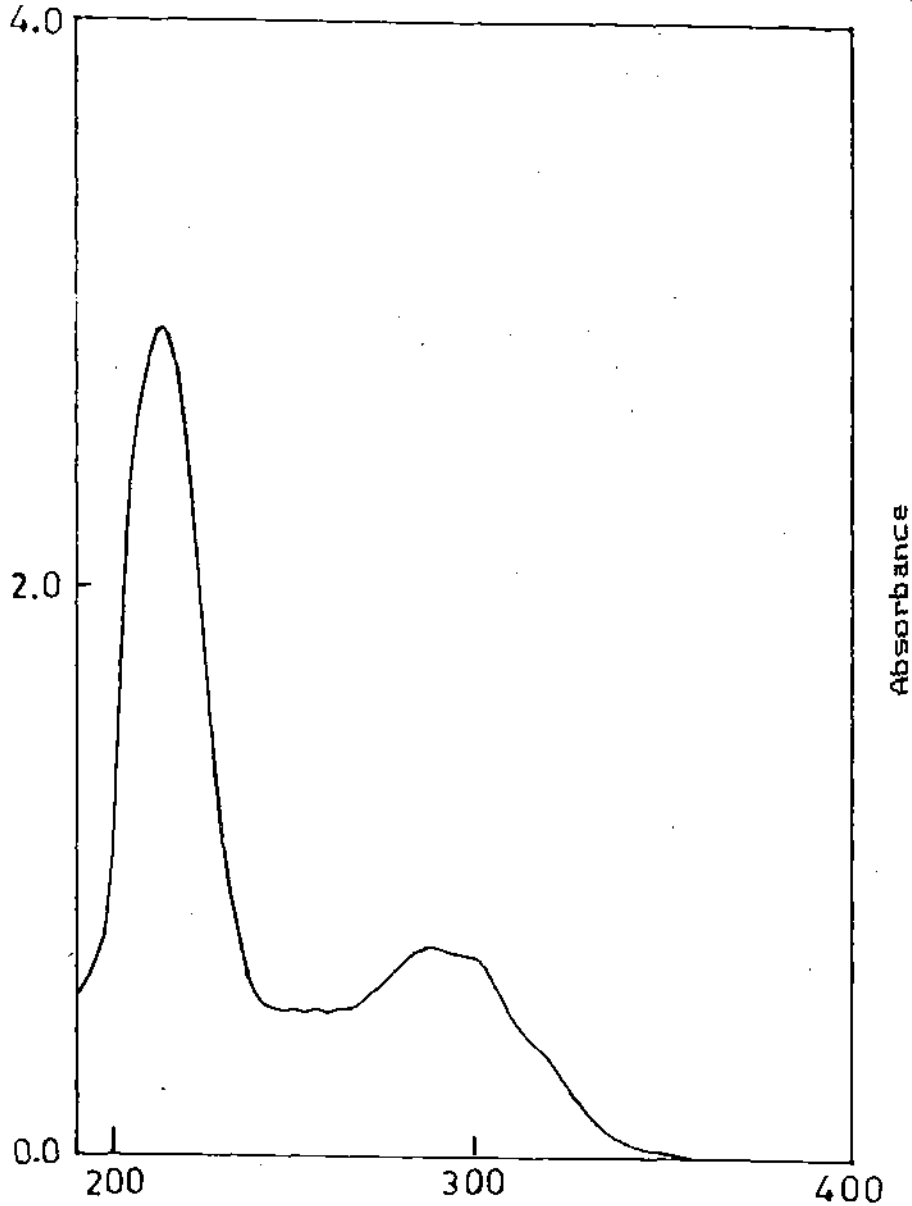


Fig.III.22. Electronic spectrum of Bu_3SnPPv in MeOH.

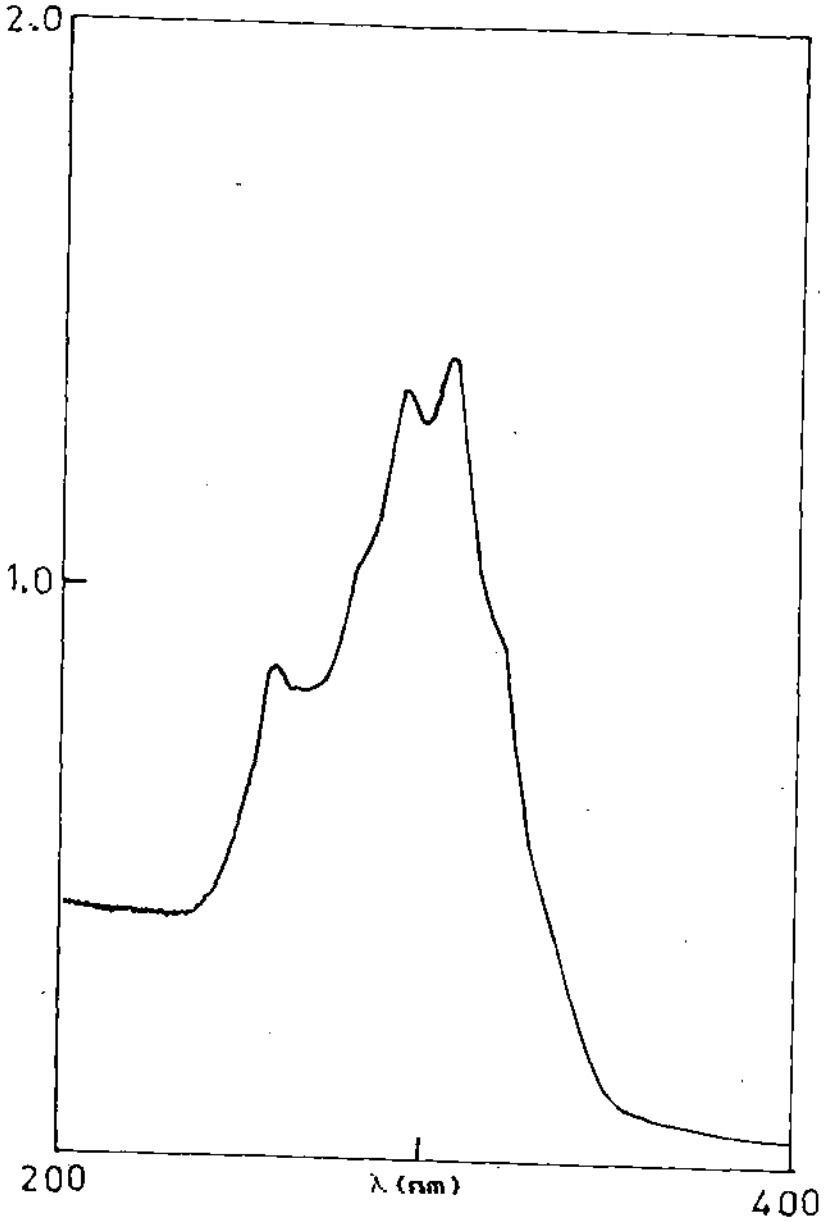


Fig.III.21. Electronic spectrum of Bu_3SnPPv in CCl_4.

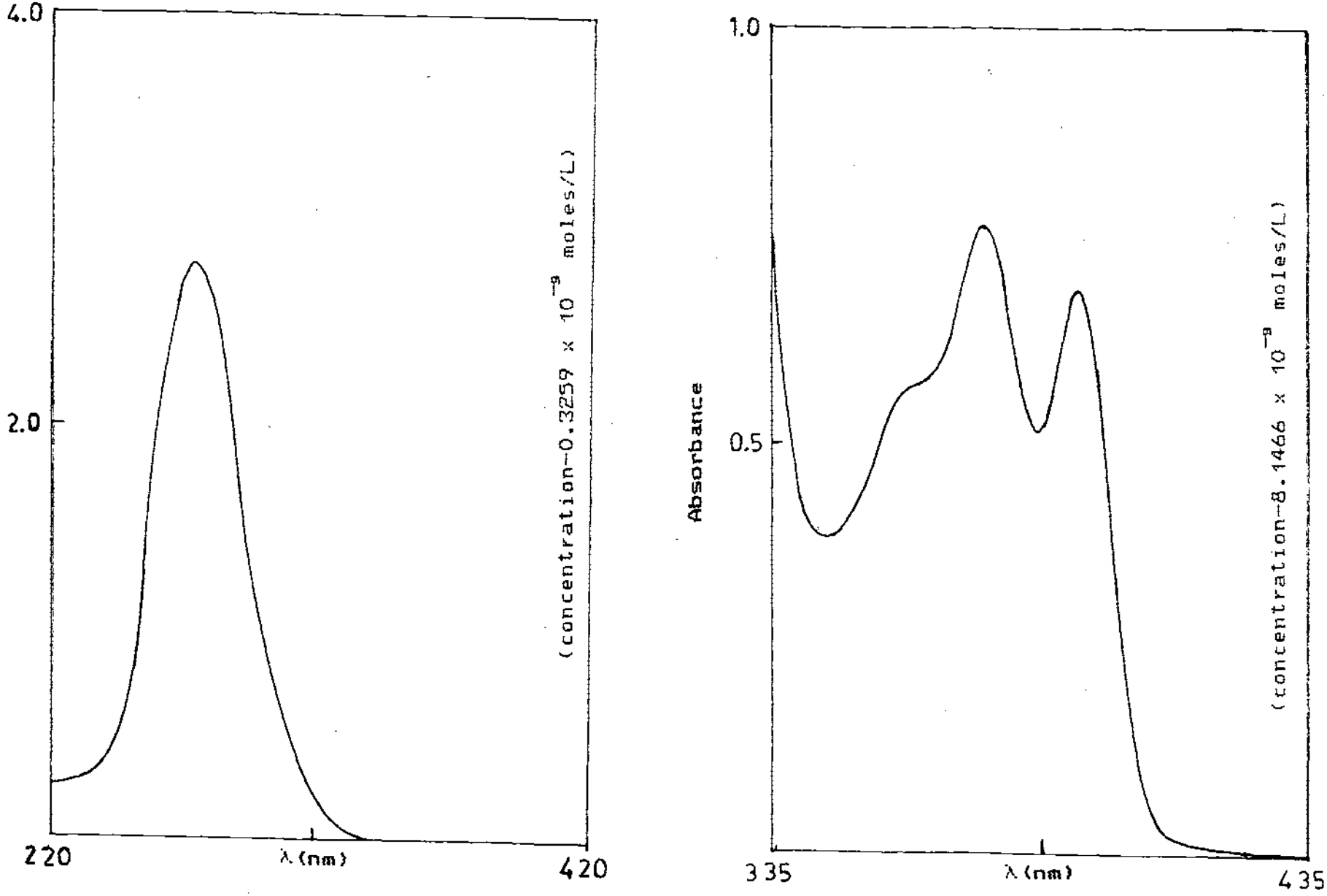


Fig.III.23. Electronic spectrum of BFH in CCl_4.

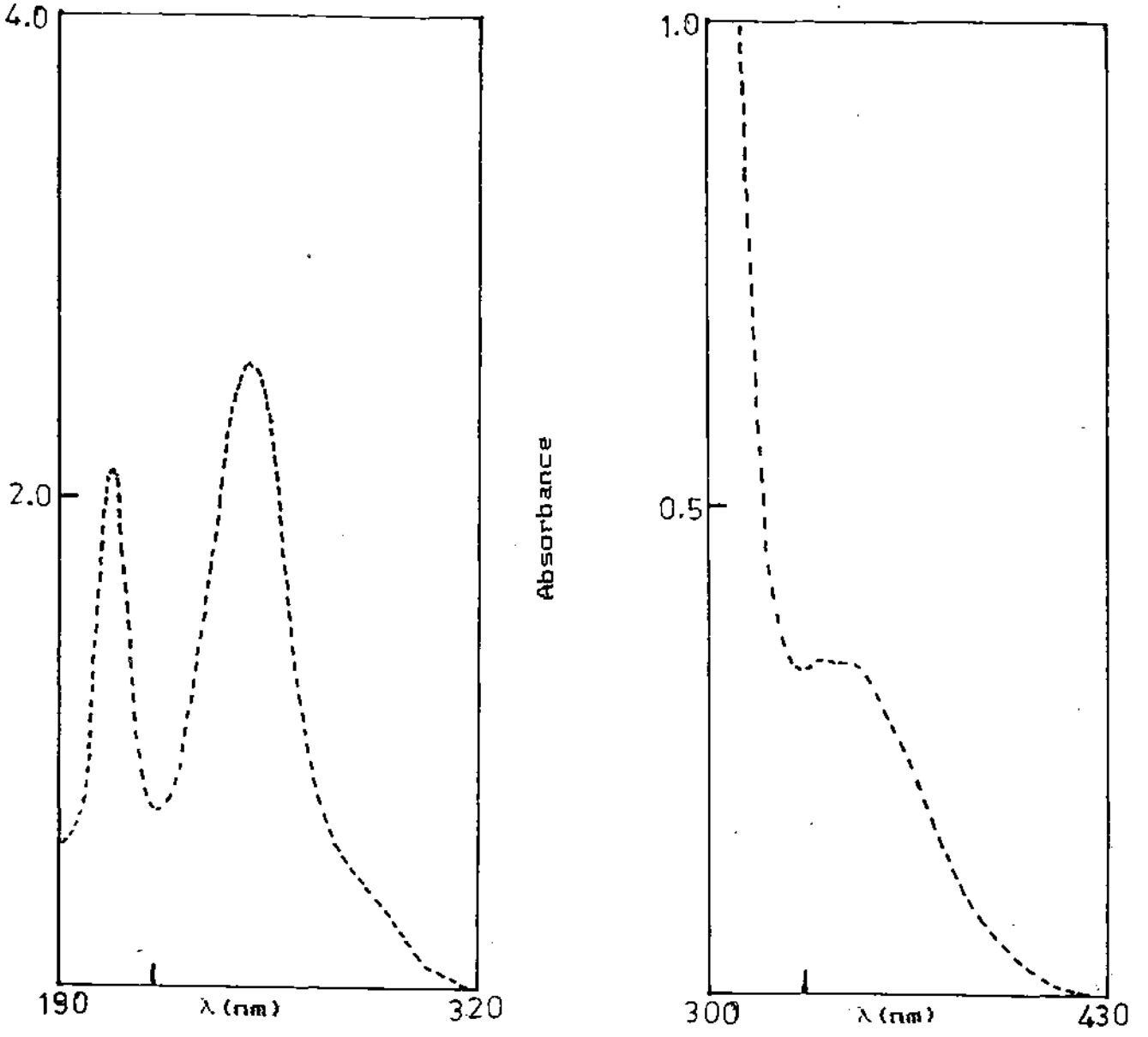


Fig.III.24. Electronic spectrum of BFH in MeOH.

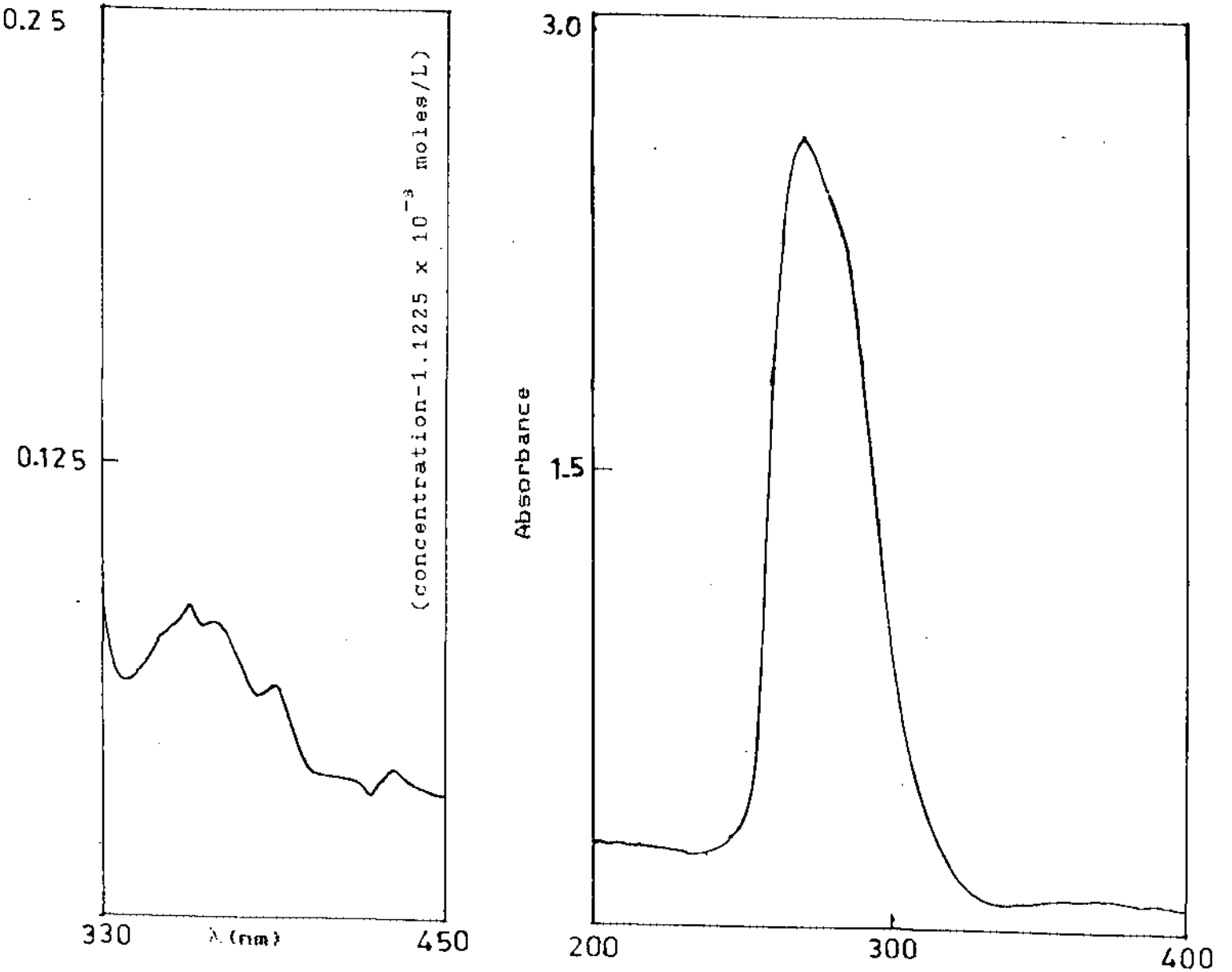


Fig.III.25. Electronic spectrum of Ph_3SnBF in CCl_4.

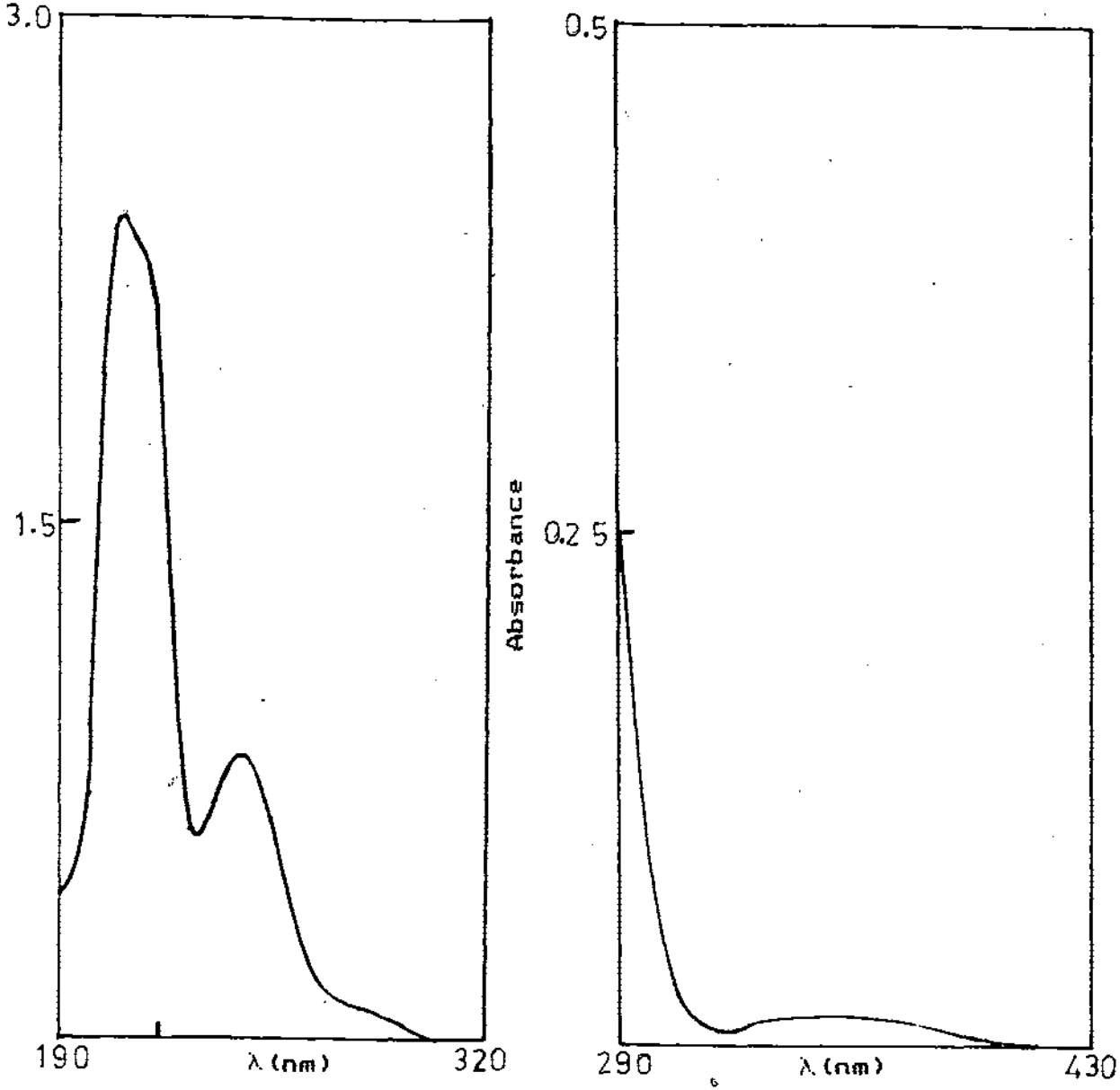


Fig.III.26. Electronic spectrum of Ph_3SnDF in MeOH.

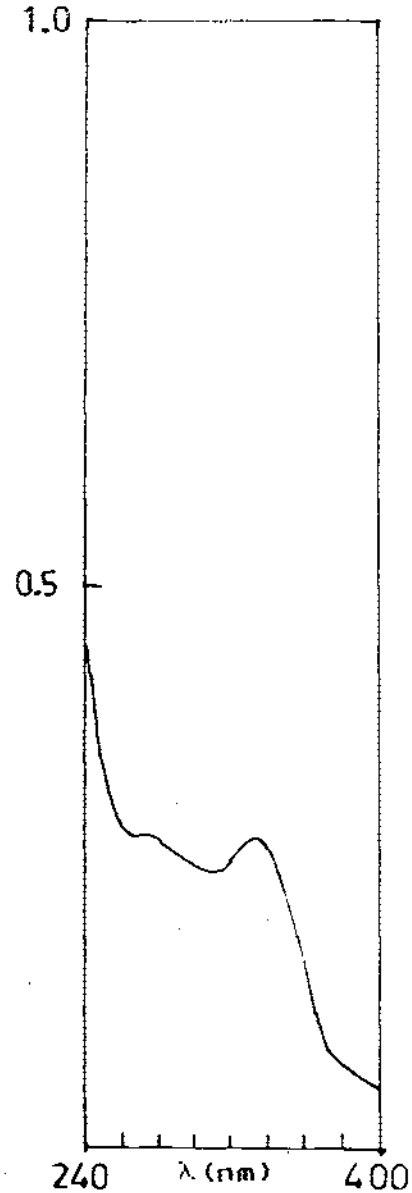


Fig.III.28. Electronic spectrum of $Bu_2Sn(Pv)_2$ in MeOH.

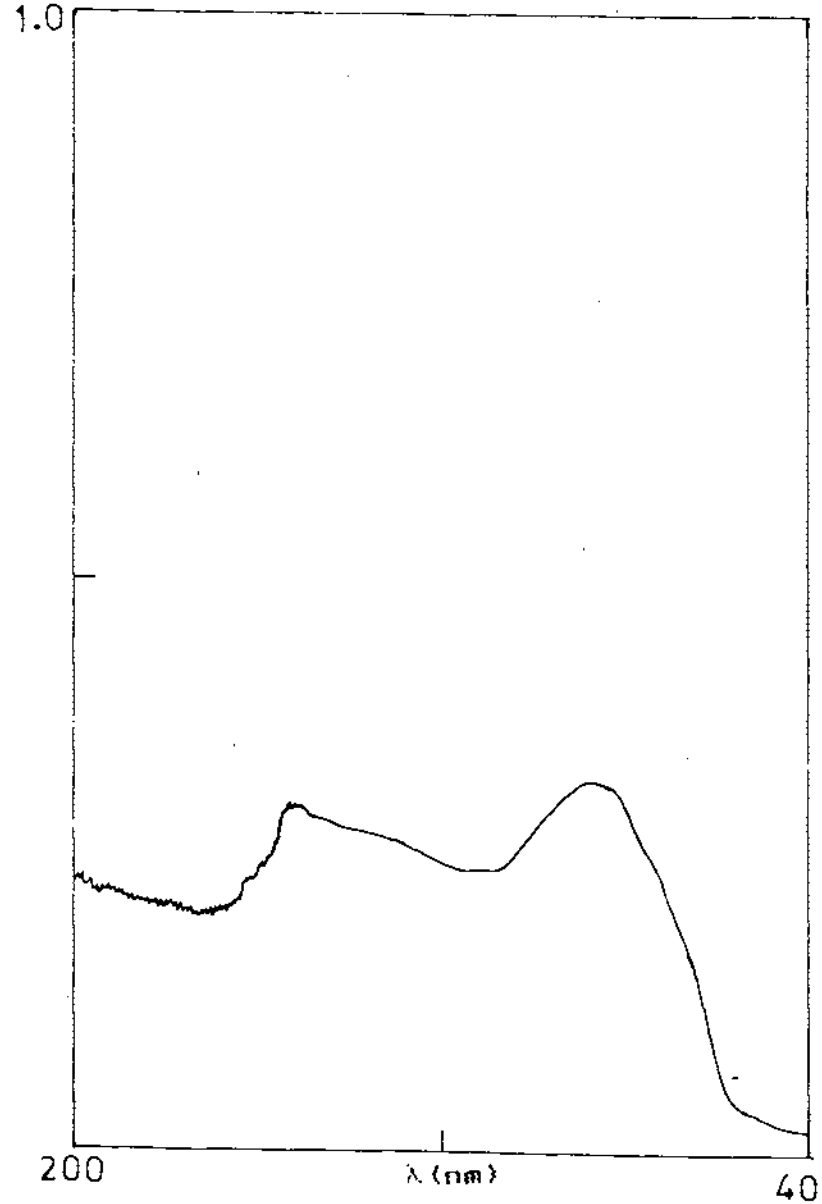


Fig.III.27. Electronic spectrum of $Bu_2Sn(Pv)_2$ in CCl_4.

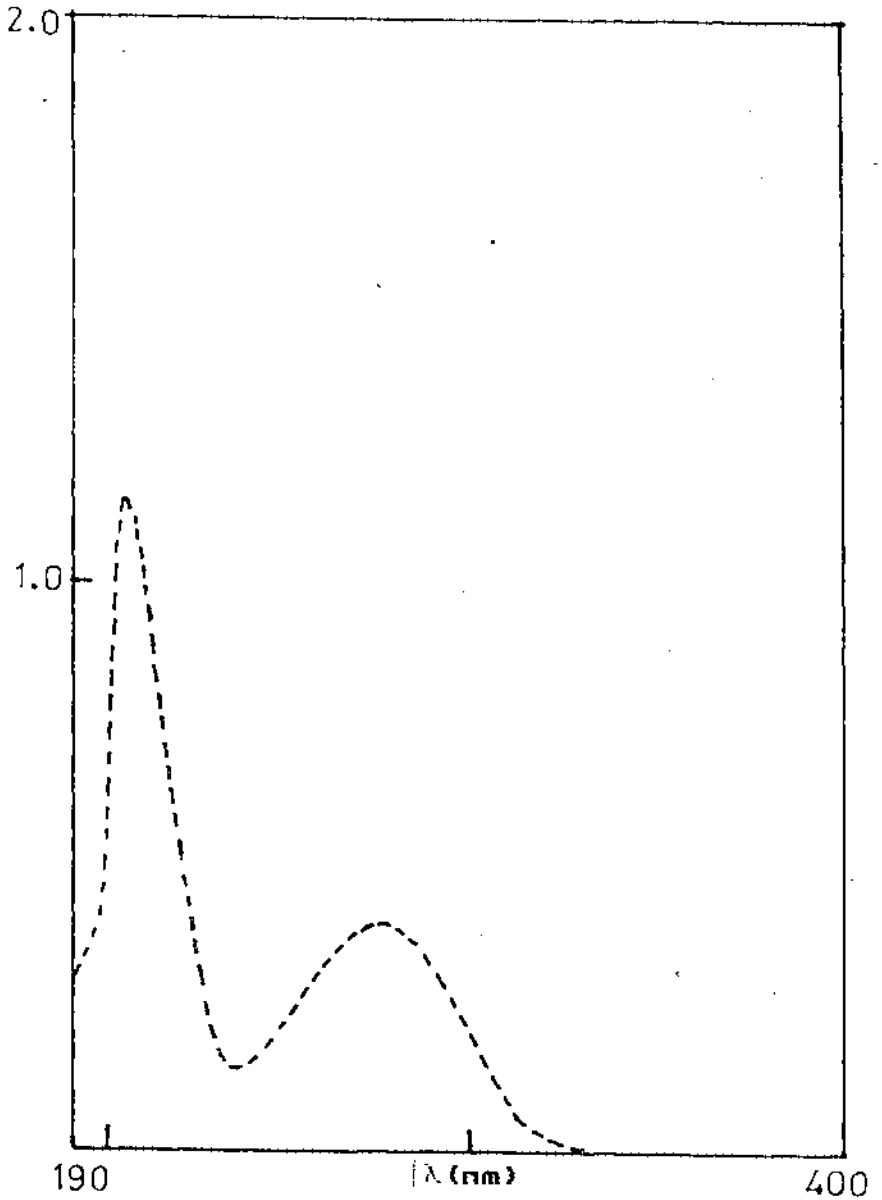


Fig.III.30. Electronic spectrum of $Oct_2Sn(PPv)_2$ in MeOH.

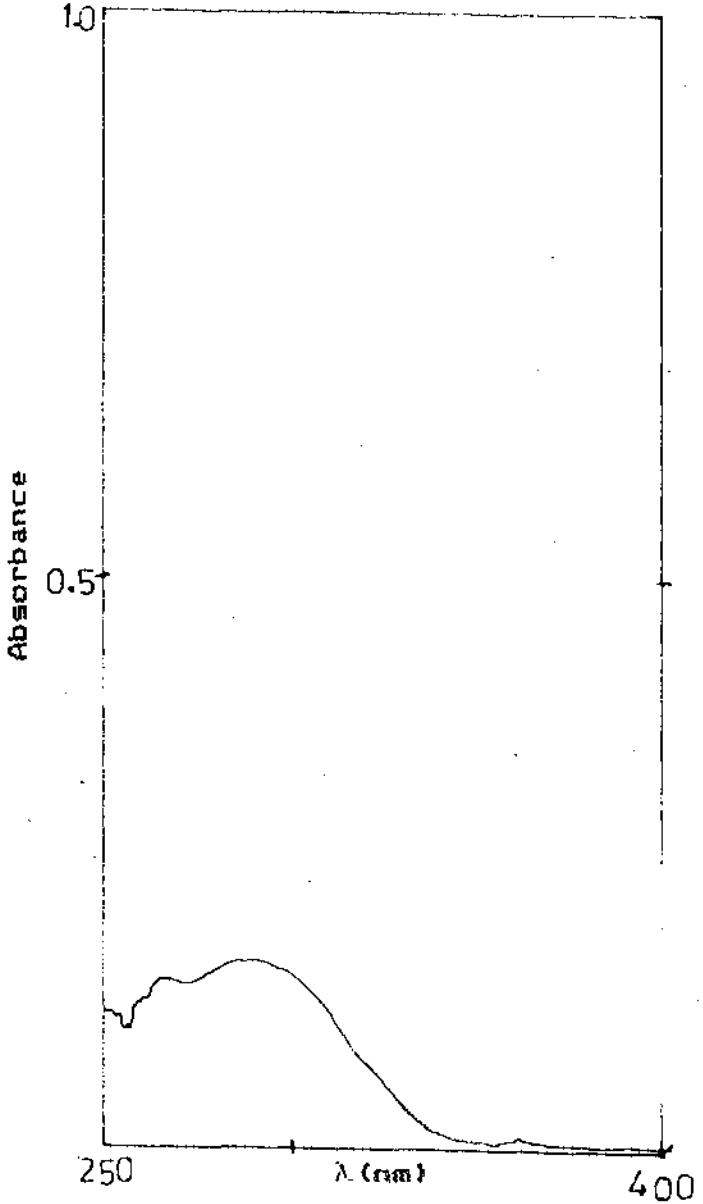


Fig.III.29. Electronic spectrum of $Oct_2Sn(PPv)_2$ in CCl_4.

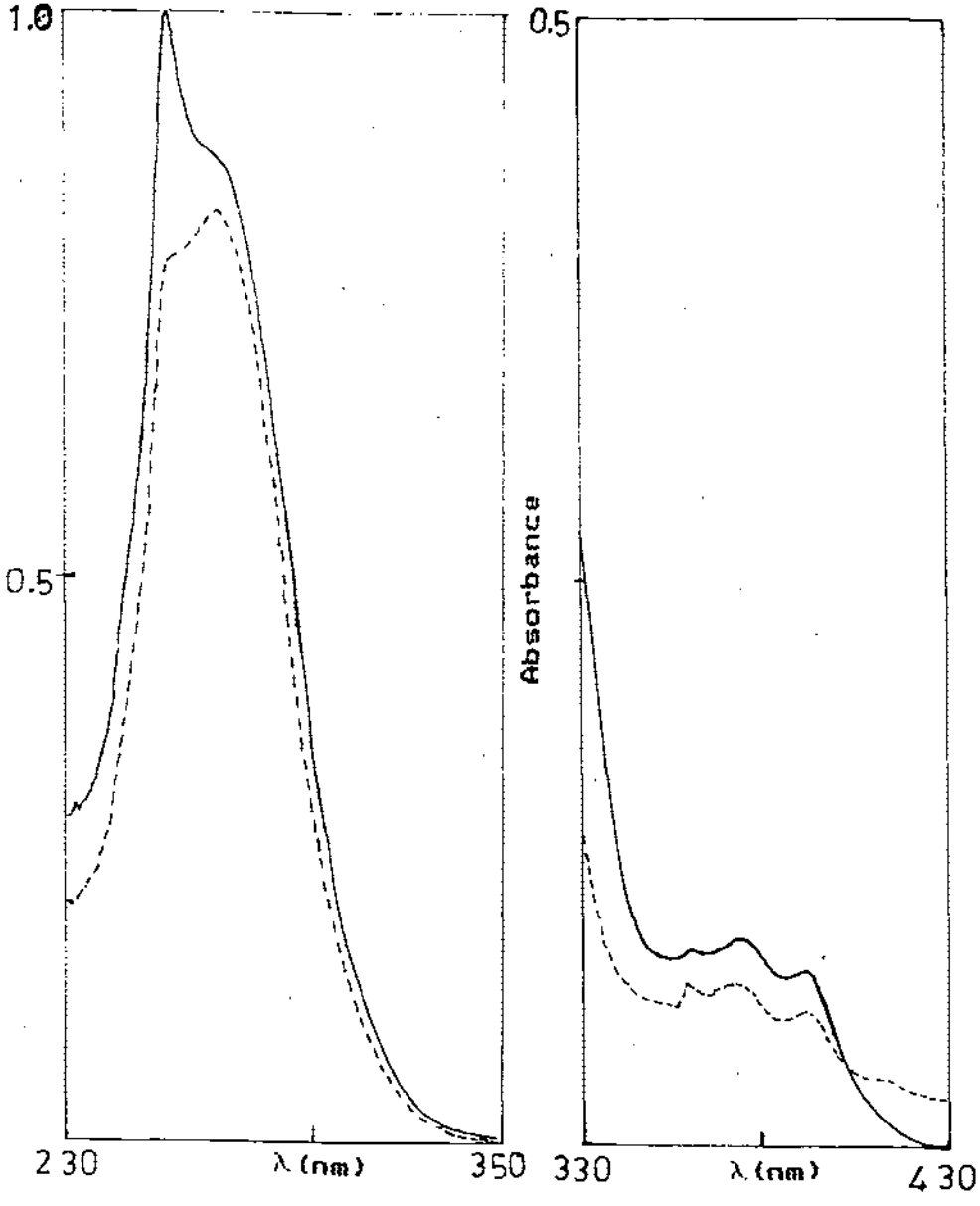


Fig.III.31. Electronic spectrum of $Bu_2Sn(BF)_2$ (———) and $Me_2Sn(BF)_2$ (- - - - -) in CCl_4.

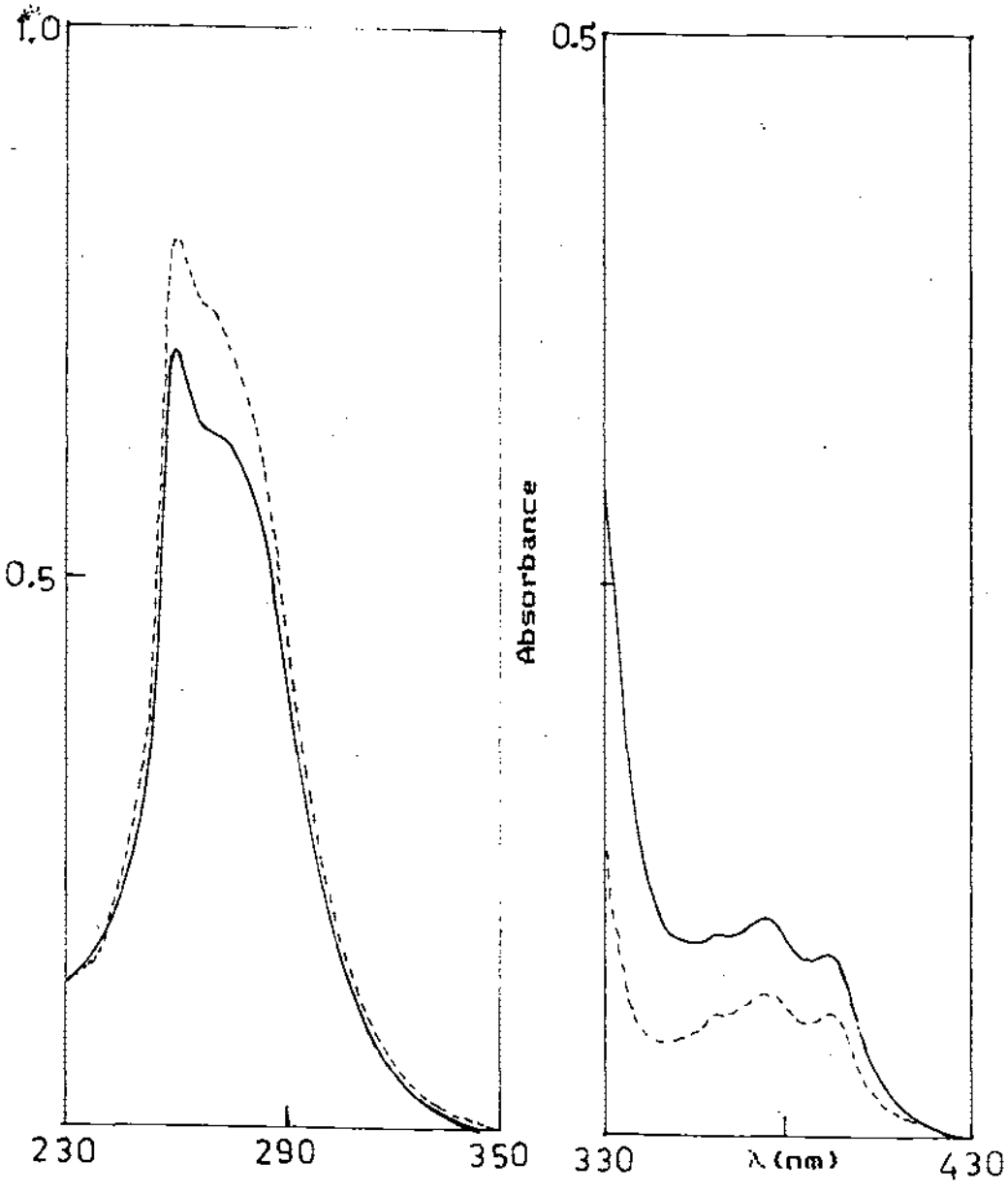


Fig.III.33. Electronic spectrum of $Oct_2Sn(BF)_2$ (———) and $Ph_2Sn(BF)_2$ (- - - - -) in CCl_4.

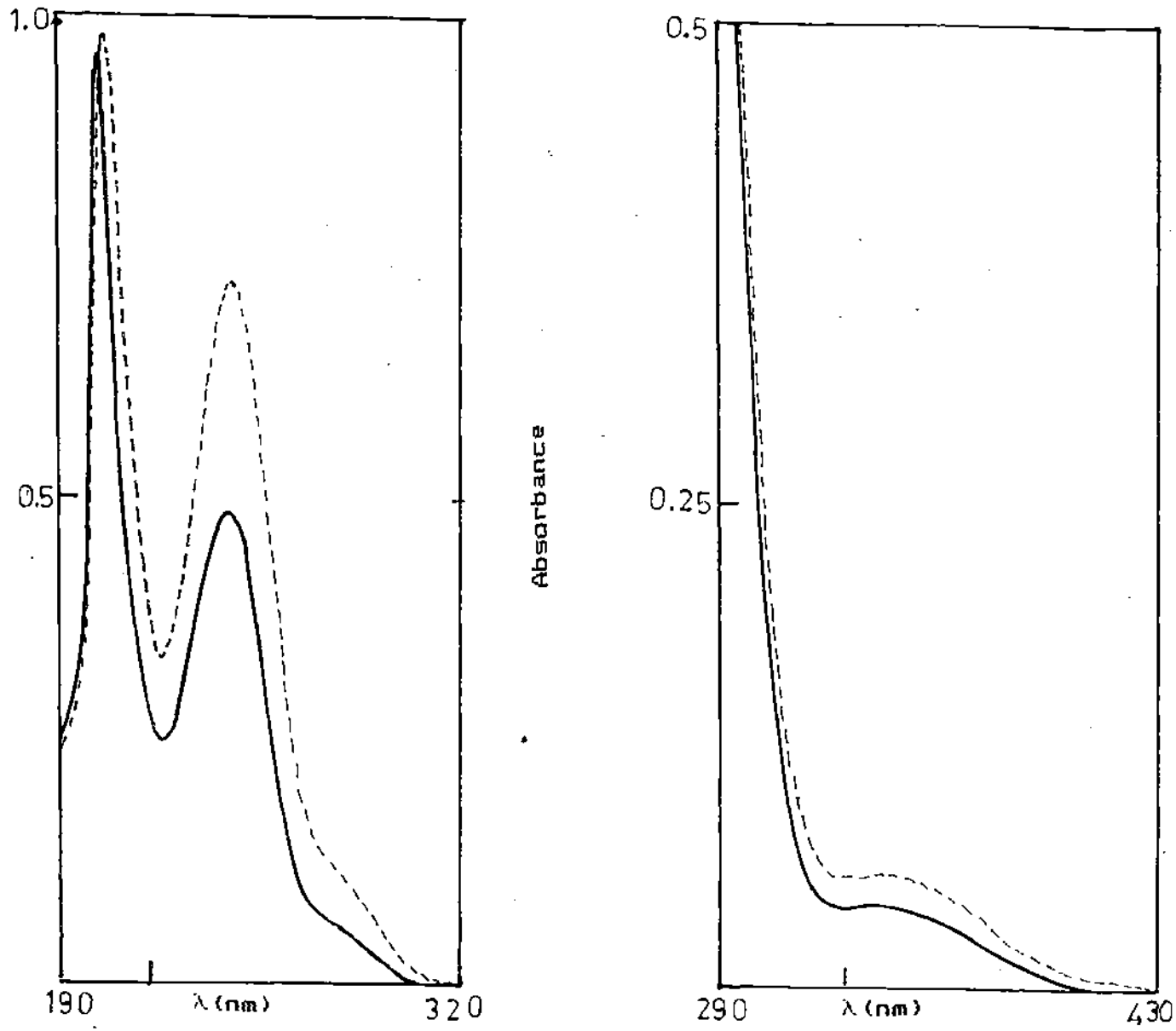


Fig.III.32. Electronic spectrum of $Bu_2Sn(BF)_2$ (——) and $Me_2Sn(BF)_2$ (------) in MeOH.

drawn from their IR spectra.

The π-π^* transitions of the carbonyl group in these organotin esters, occurring below 280 nm, are masked by the absorption bands of the Ph-ring , and therefore, provides little structural information.

(iv) ^{1}H NMR spectra :

The ^{1}H NMR spectra of the organotin keto carboxylates in $CDCl_3$ against the internal standard TMS (table-III.9.) are consistent with the structures assigned to them on the basis of IR and electronic spectral data. All the keto carboxylates exhibited expected peak multiplicities and intensities. Some of the spectra are shown in figures III.34-III.39.

Data from table-III.9. shows that the CH_3 protons in free pyruvic acid ($CH_3COCOOH$) appearing at δ 2.56ppm is only slightly shielded in ethyl pyruvate. But in the organotin pyruvates the CH_3 protons are considerably shielded due to the essentially polar nature of the Sn—O bond. The deshielding of the CH_3 protons by the adjacent C=O group is lowered due to the participation of the C=O group in intramolecular coordination. Hence, in all these compounds the CH_3 protons appear at sufficiently high field.

The signals for the resonances of the methyl and the methylene protons of the alkyl groups attached to tin appear in the same regions as reported for similar organotin

Table:-III.9

PMR data for the Organotin Keto Carboxylates:

Compounds.	Peak position (δ ppm) and assignments
$CH_3COCOOH$ (PvH)	2.56, (s), CH_3; 8.64, (s), COOH.
PvEt	1.22-1.49, (t), CH_3(Et); 2.5, (s), CH_3, (Pv); 4.13-4.5, (q), CH_2(Et).
Ph_3SnPv	2.13, (s), 3H, CH_3(Pv); 7.42-7.5, (m) and 7.68, (m), 15H, aromatic.
Bu_3SnPv	0.843-0.916, (t), (J 7.2Hz), 9H, CH_3(Bu); 1.142-1.355, (m), 15H, CH_2(Bu) and CH_3(Pv); 1.526-1.619, (m), 6H, Sn-CH_2.
$Bu_2Sn(Pv)_2$	0.834-0.906, (t), (J 7.2Hz), 6H, CH_3(Bu); 1.203-1.382, (m), (J 7 Hz), 8H, CH_2(Bu); 1.61, (s), 6H, CH_3(Pv); 2.415-2.917, (m), 4H, Sn-CH_2.
PhCOCOOH (BFH)	7.34-7.64, (m) and 8.04-8.12, (m), 5H, aromatic; 10.98, (s), COOH.
Ph_3SnBF	7.35-7.41, (m), 7.5-7.58, (m) and 7.79-7.86, (m) aromatic.
$Bu_2Sn(BF)_2$	0.89-0.96, (t), (J 7 Hz), 6H, CH_3(Bu); 1.38-1.5, (m), (J 8 Hz), 4H, Sn-CH_2; 1.68-1.92, (m), 8H, CH_2(Bu); 7.52-7.62, (m), 7.7-7.78, (m) and 8.28-8.4, (d), 10H, aromatic.
$Me_2Sn(BF)_2$	1.18, (s), 6H, CH_3(Me); 7.52-7.62, (m), 7.7-7.78, (m) and 8.28-8.4, (d), 10H, aromatic.
$Oct_2Sn(BF)_2$	0.8-0.92, (t), (J 7 Hz), 6H, CH_3(Oct); 1.1-1.48, (m), 24H, CH_2; 1.72-1.9, (m), 4H, Sn-CH_2; 7.52-7.62, (m), 7.7-7.78, (m) and 8.28-8.4, 10H, aromatic.

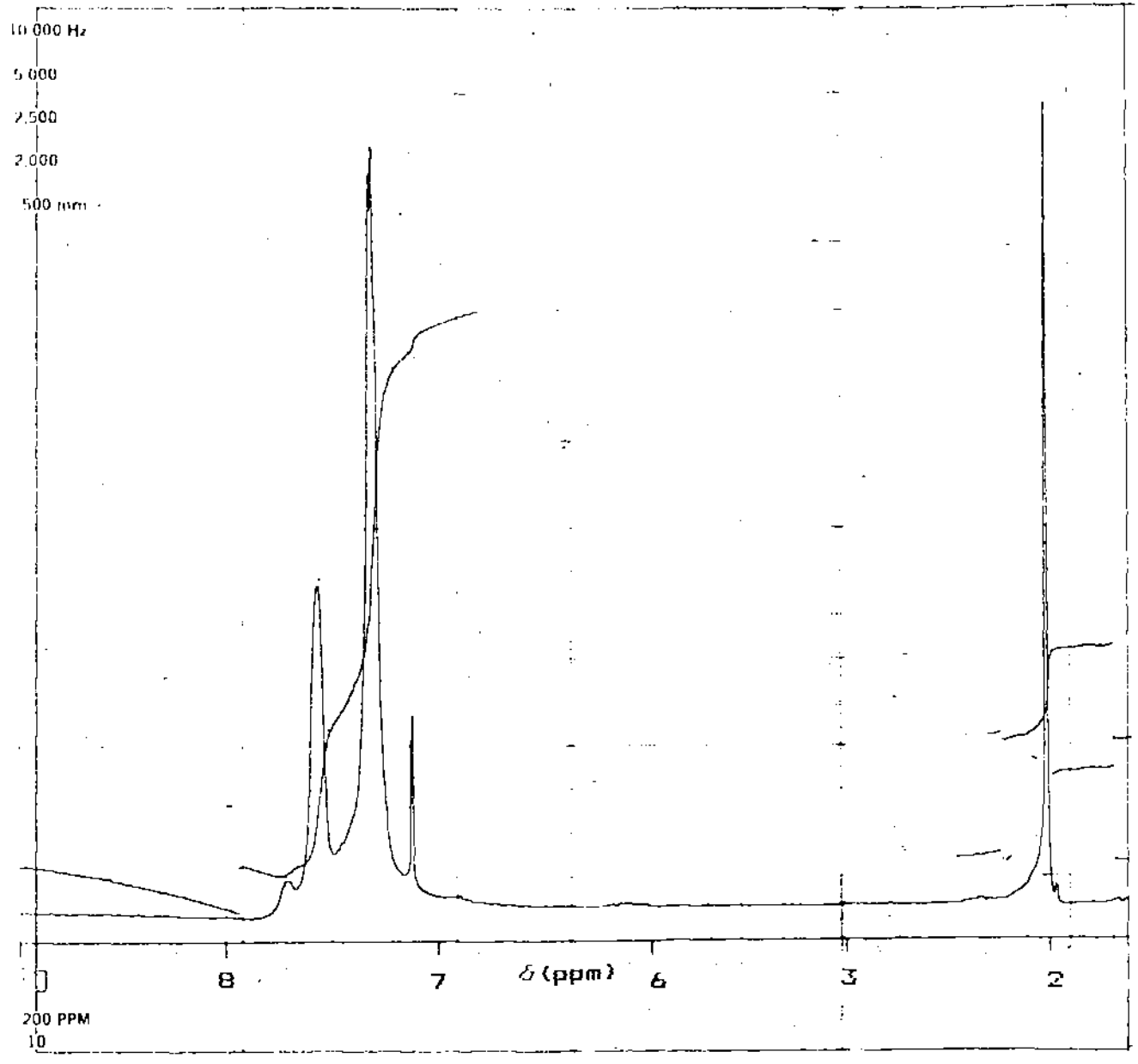


Fig.III.34. ^{1}H NMR spectrum of Ph_3SnPv in $CDCl_3$.

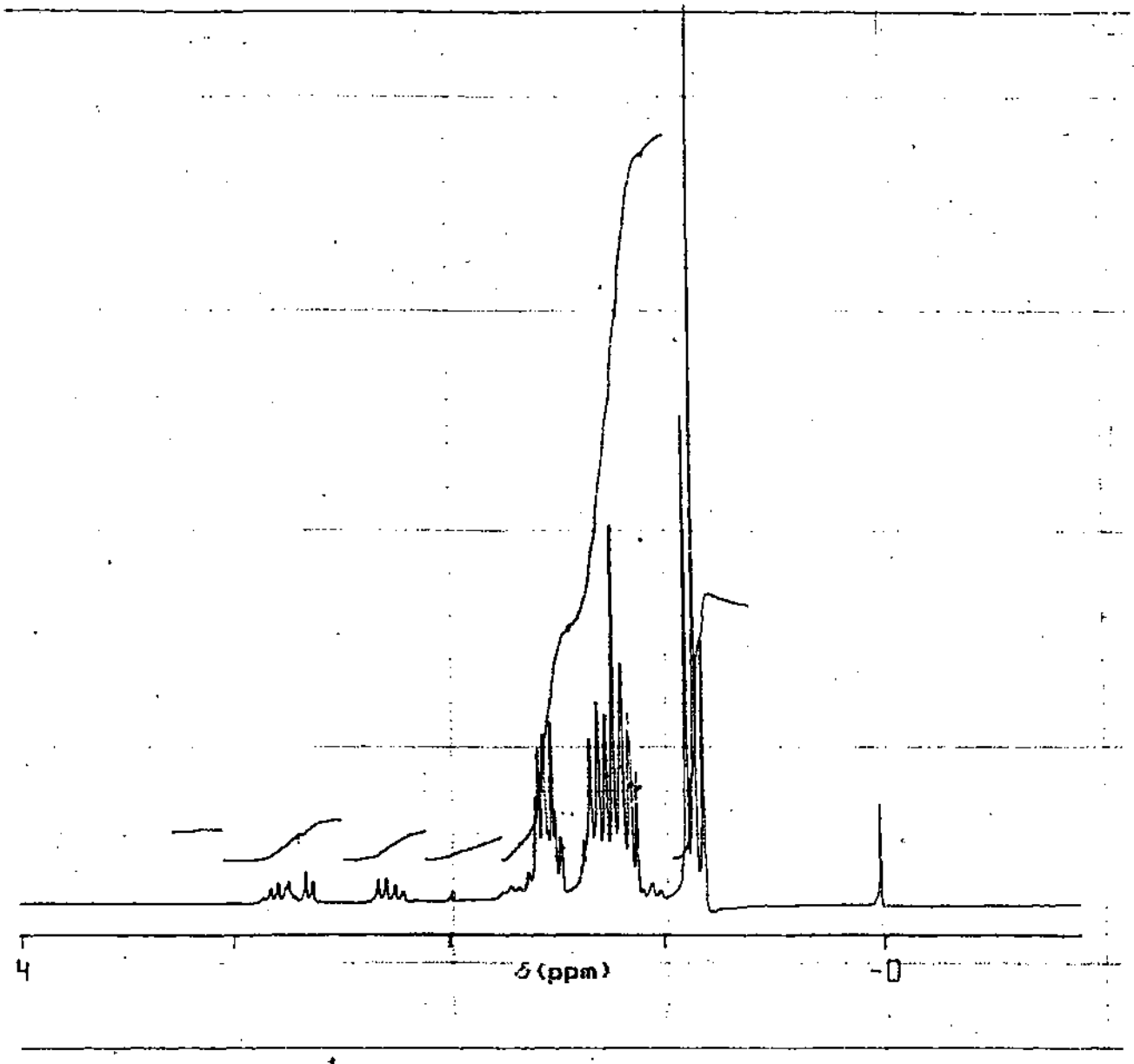


Fig.III.35. ^{1}H NMR spectrum of Bu_3SnPv in $CDCl_3$.

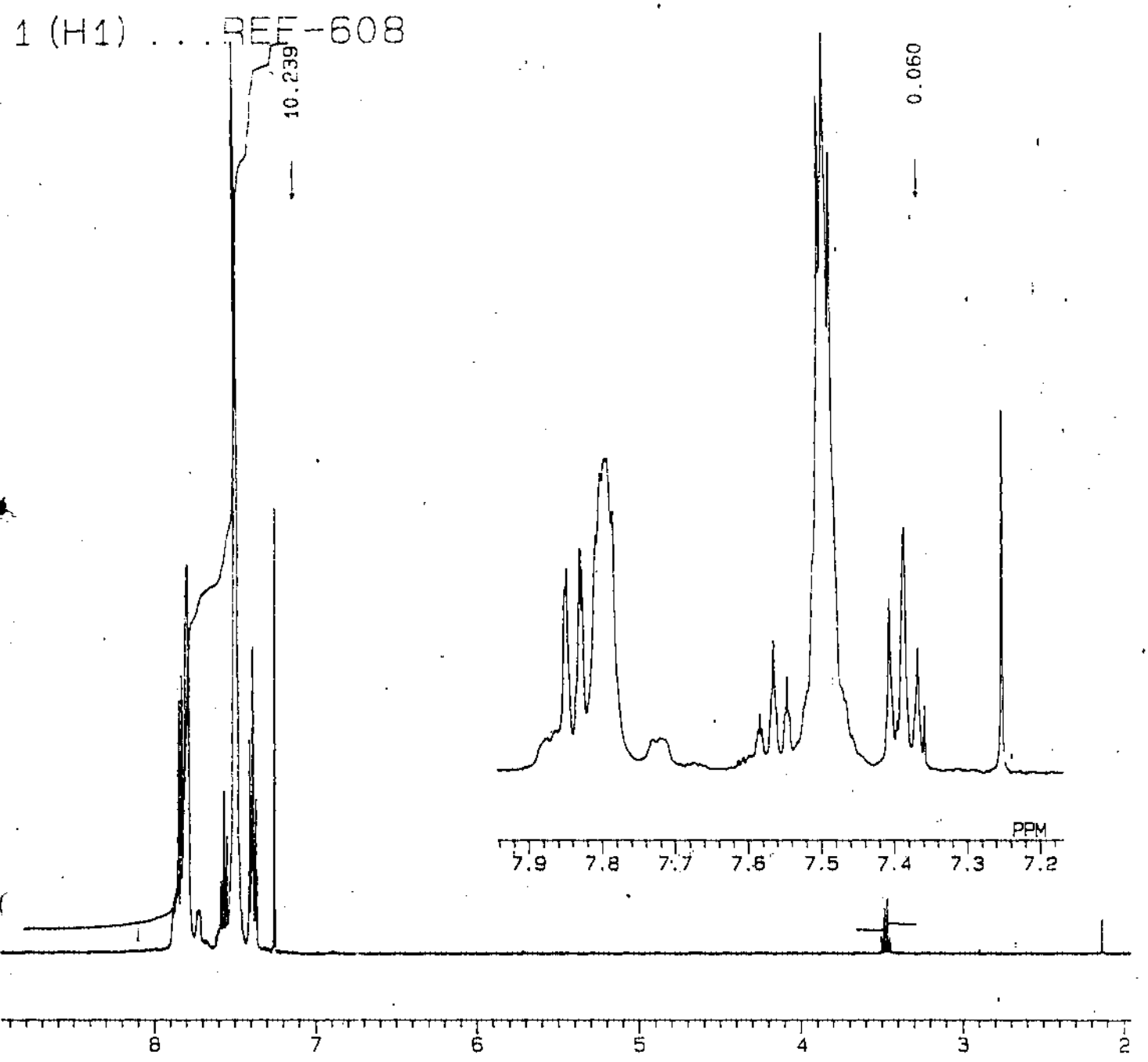


Fig.III.36. ^{1}H NMR spectrum of Ph_3SnBF in $CDCl_3$.

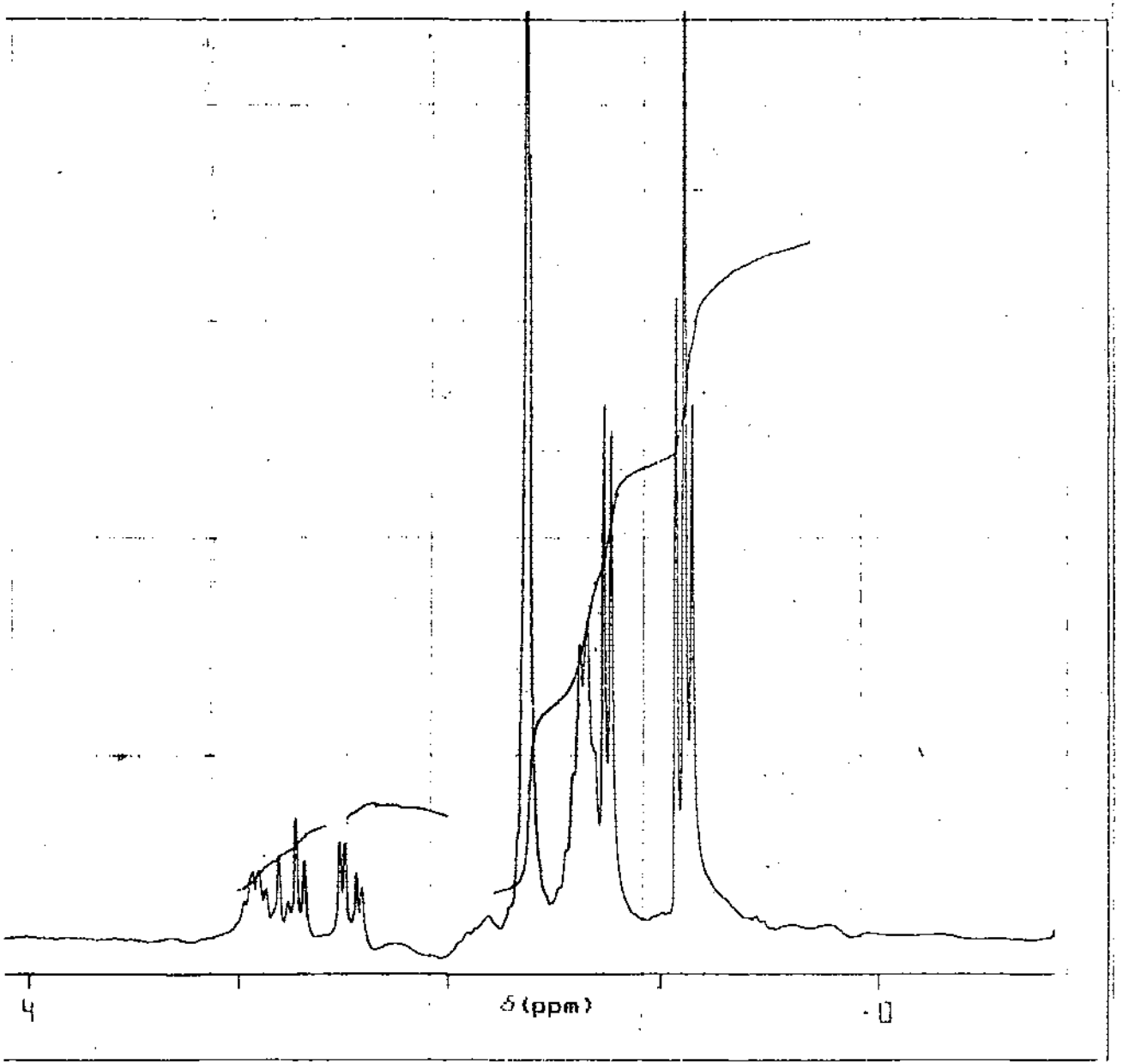


Fig.III.37. ^{1}H NMR spectrum of $Bu_2Sn(Pv)_2$ in $CDCl_3$.

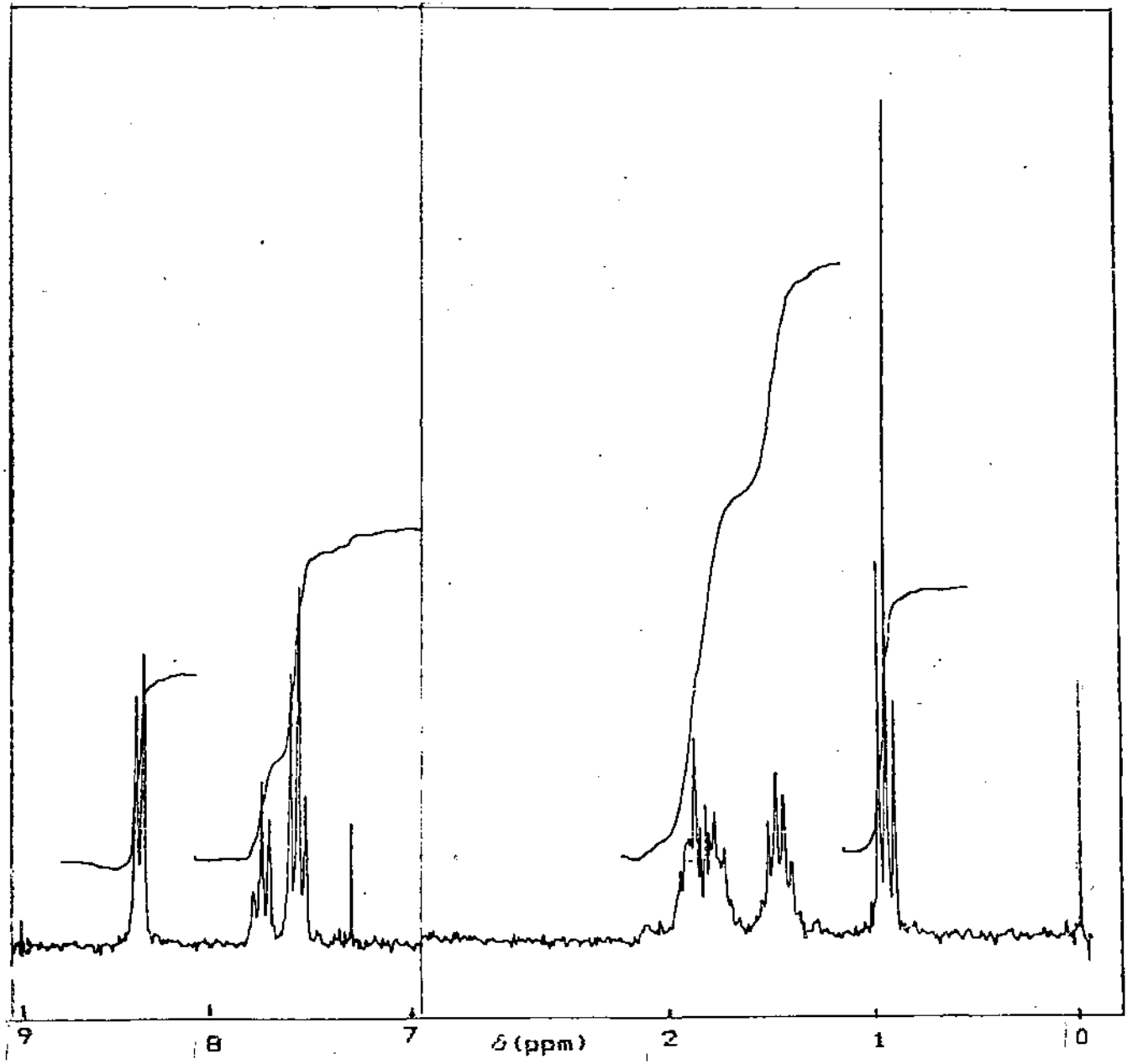


Fig.III.38. ^{1}H NMR spectrum of $Bu_2Sn(BF)_2$ in $CDCl_3$.

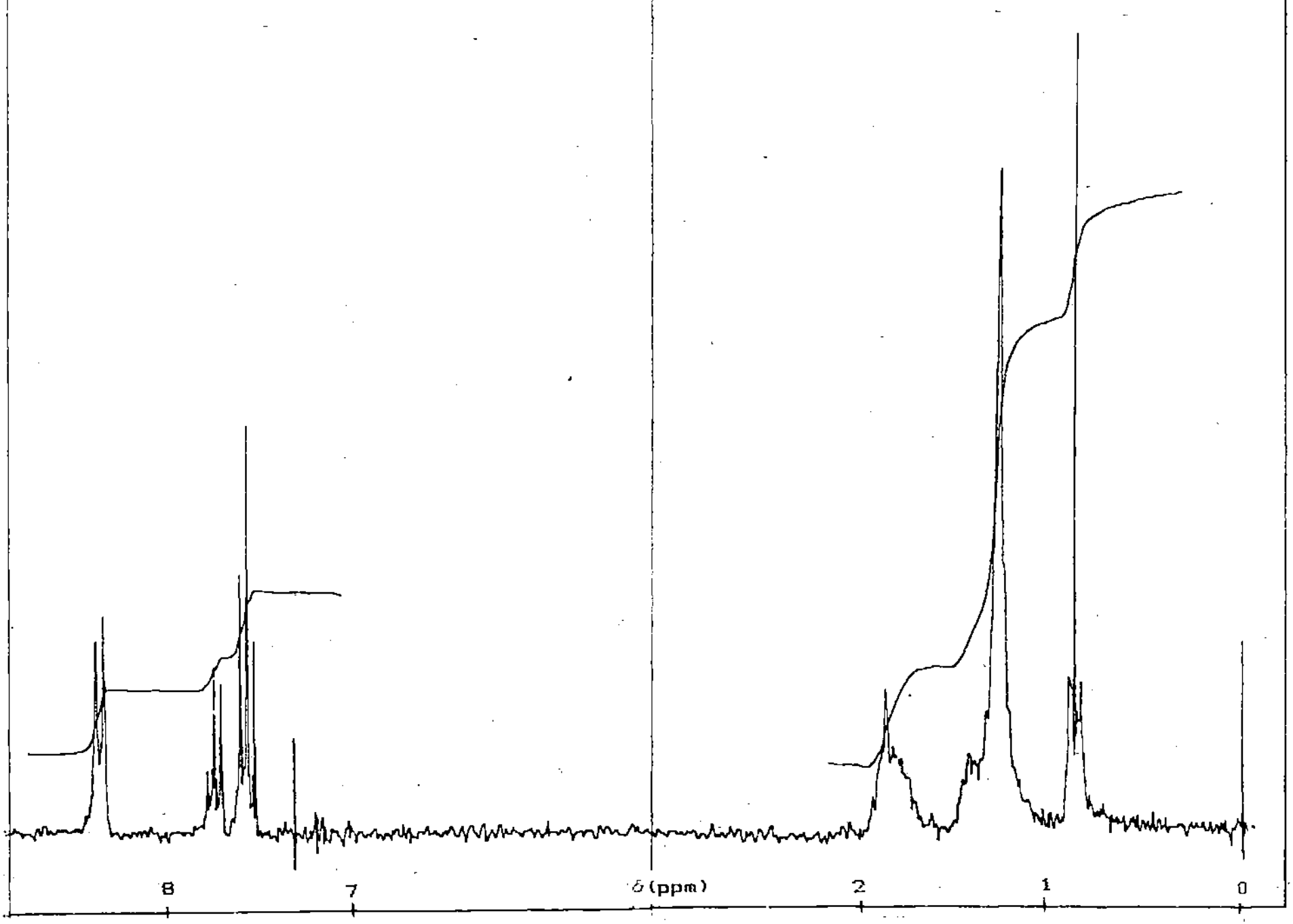


Fig.III.39. ^{1}H NMR spectrum of $Oct_2Sn(BF)_2$ in $CDCl_3$.

carboxylates[43,44].

In the derivatives of benzoyl formic acid (PhCOCOOH), due to the combined effect of the ring current and diamagnetic anisotropy of the C=O group, which remains free, the ring protons are slightly deshielded and appear as three separate groups of signals (meta, para, ortho) in the region δ 7.36-8.4 ppm.

III.3.1B. Diorganotin Di-keto carboxylates [$R_2Sn(OCOCOR')_2$] :

The diorganotin derivatives of the α-keto acids are similar to their triorganotin analogues in their solubilities, (table-III.2) melting points (table-III.1) and spectroscopic properties. For these compounds also the IR (table-III.6A) UV (table-III.10) and ^1H NMR (table-III.9) spectral data suggest intramolecular involvement of the keto group in the derivatives of PvH and PPvH, while in the derivatives of BFH the keto group remains free. Representative IR, UV and ^1H NMR spectra of these compounds are shown in figures III.10-III.14, III.27-III.33 and III.37-III.39. respectively.

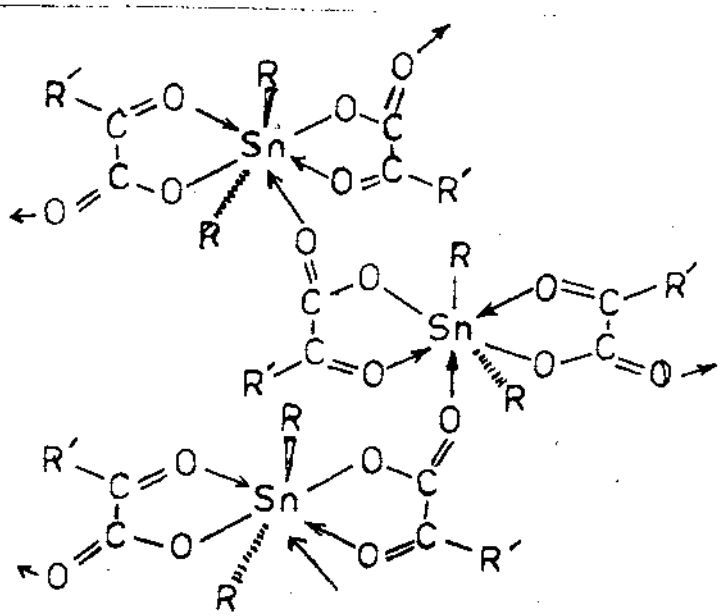
(i) IR spectra :

In the IR spectra of the diorganotin pyruvates the $\nu_{C=O}$ and ν_{asOCO} appear at around 1580 cm^{-1}, while ν_{sOCO} appears at around 1400 cm^{-1}, in the solid state. For the derivatives of PPvH the $\nu_{C=O}$ band occurs at slightly higher frequencies around 1620 cm^{-1}.

In $CHCl_3$ solution of the pyruvates the ν_{asOCO} and $\nu_{C=O}$ are raised to around 1680 and 1610 cm^{-1} respectively, while ν_{sOCO} is slightly lowered.

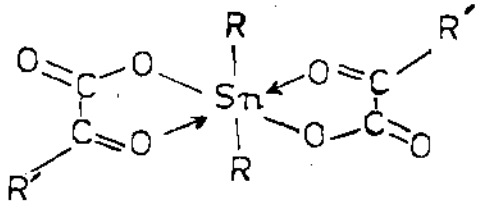
These may be interpreted in terms of the involvement of the keto group in coordination and a seven coordinate tin atom having a distorted pentagonal bipyramidal geometry in the solid state, similar to the polymeric dimethyltin dipicolinate[96].

This structure requires each molecular unit to be linked to three adjacent units through the carboxylate groups, which are most likely to function in the bridging mode, as their bite angle (—C<O O) is small (ca. 55°)[95]. Hence, the ketonic C=O group should be involved as depicted below.



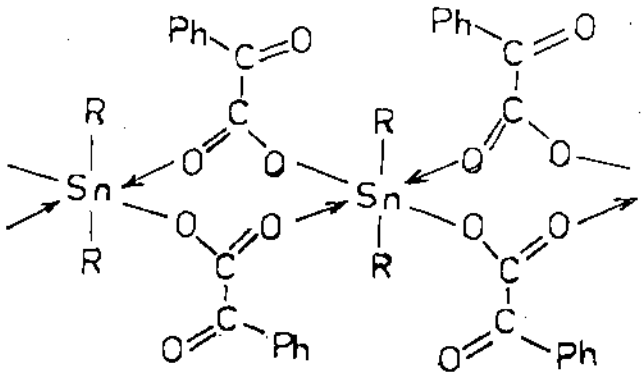
X

In solution depolymerisation is likely to occur leading to structure XI, involving monodentate carboxylate groups.



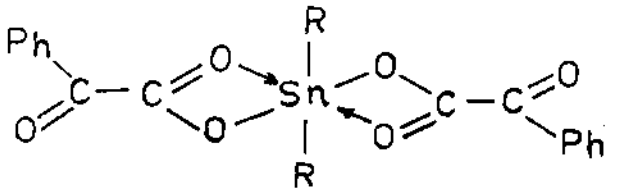
XI

In the diorganotin derivatives of BFH the $\nu_{C=O}$ frequency appears at 1686 cm^{-1}, i.e., the same as in the free acid, whereas, the ν_{asOCO} and ν_{sOCO} appear in the regions 1645-1620 cm^{-1} and 1375-1365 cm^{-1} respectively. Therefore, the keto group is not involved in coordination and this may be due to steric as well as electronic reasons as envisaged for the triorganotin benzoyl formates in section III.3.1.A. The structures of these compounds may then be represented as-



XII

In solution the ν_{asOCO} and ν_{sOCO} frequencies are only slightly changed and it is likely that chelated carboxylate groups are present, the keto group remaining free.



XIII

(ii) Electronic Absorption Spectra :

The electronic spectral data for the diorganotin esters of PvH and PPvH, shown in table-III.10, indicate that the n-π^* bands of these acids have undergone considerable blue shift on stannylation and appear in the region 300-330 nm in CCl_4 solution. As discussed for the triorganotin derivatives this shows the involvement of the keto group in coordination. Likewise, in the derivatives of BFH the n-π^* transition bands remain practically unchanged compared to the free acid, indicating the presence of non-interacting CO group.

From these observations it can be inferred that the electronic spectra further support the structures assigned to the diorganotin ketocarboxylates on the basis of IR spectra.

Table:-III.10.

Electronic spectral data of Diorganotin Keto Carboxylates:

Compounds.	$n-\pi^*$ peaks (nm) in CCl_4 Sol.	$n-\pi^*$ peaks (nm) in MeOH Sol.
PvH	370, 350, 335(sh)	330
$Bu_2Sn(Pv)_2$	340[b]	280
PPvH	385, 368, 306	345, 330, 300
$Bu_2Sn(PPv)_2$	320, 310, 296	305, 294(sh), 234
$Oct_2Sn(PPv)_2$	320, 290	278
BFH	393, 375, 360	346, 336, 292(sh)
$Bu_2Sn(BF)_2$	393, 375, 360	360, 280(sh)
$Oct_2Sn(BF)_2$	,,	,,
$Me_2Sn(BF)_2$	,,	344, 280(sh)
$Ph_2Sn(BF)_2$	,,	,,

sh-shoulder.

III.3.1.C. Carboxylato Diorganotin Hydroxides [$R_2Sn(OCOCOR')OH$] :

This group of compounds consists of organotin derivatives of PvH and PPvH, which are hydrolysates of diorganotin dicarboxylates. These highly polymeric products are obtained by heating, in benzene or solvent ether, stoichiometric amounts (1:1) of diorganotin oxide and acid for a few minutes to several hours. When oxide and acid are taken in 1:2 ratio these products are obtained along with the dicarboxylates.

On the basis of analytical data (table-III.2) these compounds can be formulated as $R_2Sn(OCOCOR')OH$. Only a few of

these compounds have well defined melting points, others decompose at high temperature. They are soluble in polar solvents like acetone or alcohol and therefore, are highly polar in nature.

Their IR spectra (table-III.6B) are characterised by the presence of broad bands below 3420 cm^{-1}, which are well below similar bands in the free acids. This bands should be attributed to OH groups which are either strongly hydrogen bonded or involved in intermolecular coordination. (Some typical IR spectra are given in figures III.40-III.44.).

Table:-III.6B.

Characteristic IR freguencies (Cm^{-1}) of some Keto Carboxylato Organotin Hydroxides (in Nujol/KBr).

Sl. no.	Compound	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
1.	$Bu_2Sn(Pv)OH$	3420-3380	1770	1605[b]	1412
2.	$Oct_2Sn(Fv)OH$	,,	1775	1604[b]	1412
3.	$Me_2Sn(Fv)OH$	3400-3300	1780	1660[b]	1385
4.	$Ph_2Sn(Fv)OH$	,,	1770	1600[b]	1452
5.	$Bu_2Sn(FPv)OH$	3260[b]	1684	1652 1630	1432
6.	$Oct_2Sn(FPv)OH$	3254[b]	1700	1653 1585	1400
7.	$Me_2Sn(PPv)OH$	3260[b]	1745[b]	1670 1605	1405
8.	$Ph_2Sn(PFv)OH$	3375[b]	1676	1612	1408

b-broad.

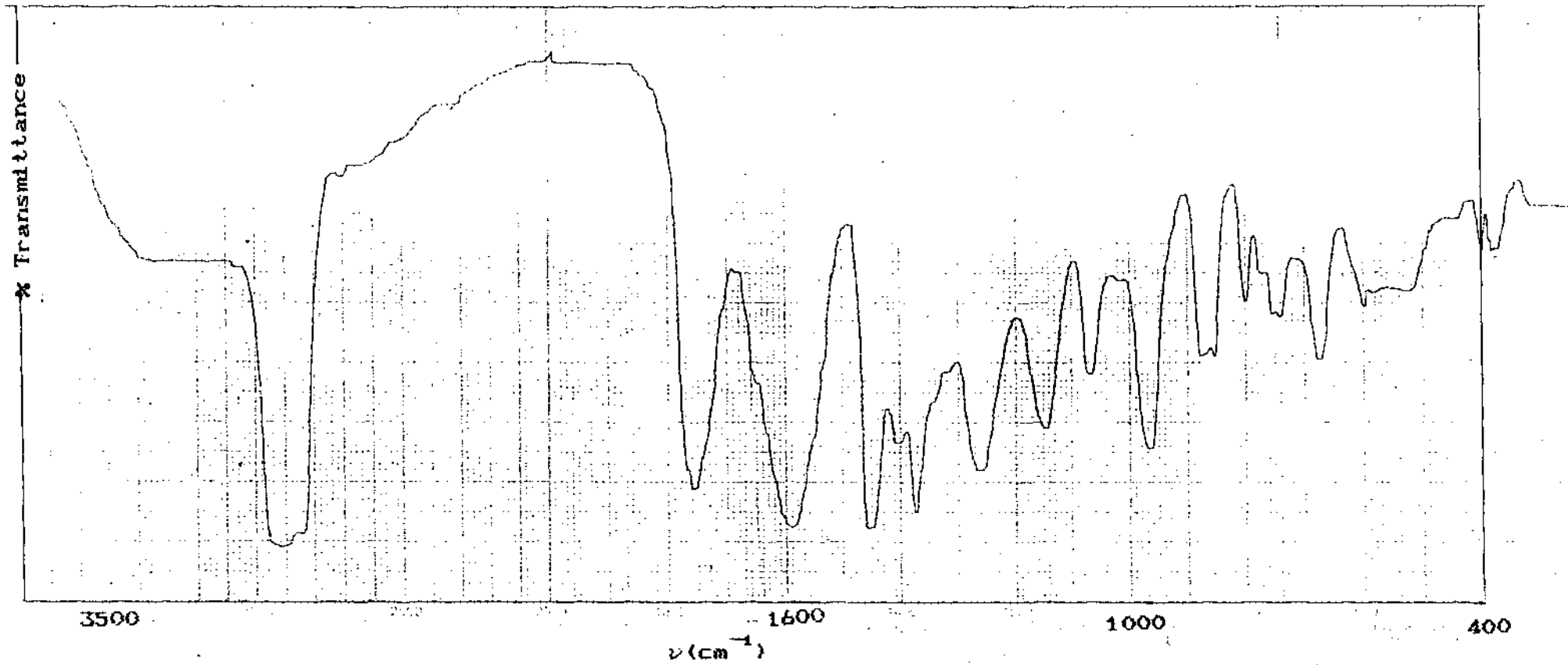


Fig.III.40. IR Spectrum of $Bu_2Sn(Pv)OH$ in Nujol.

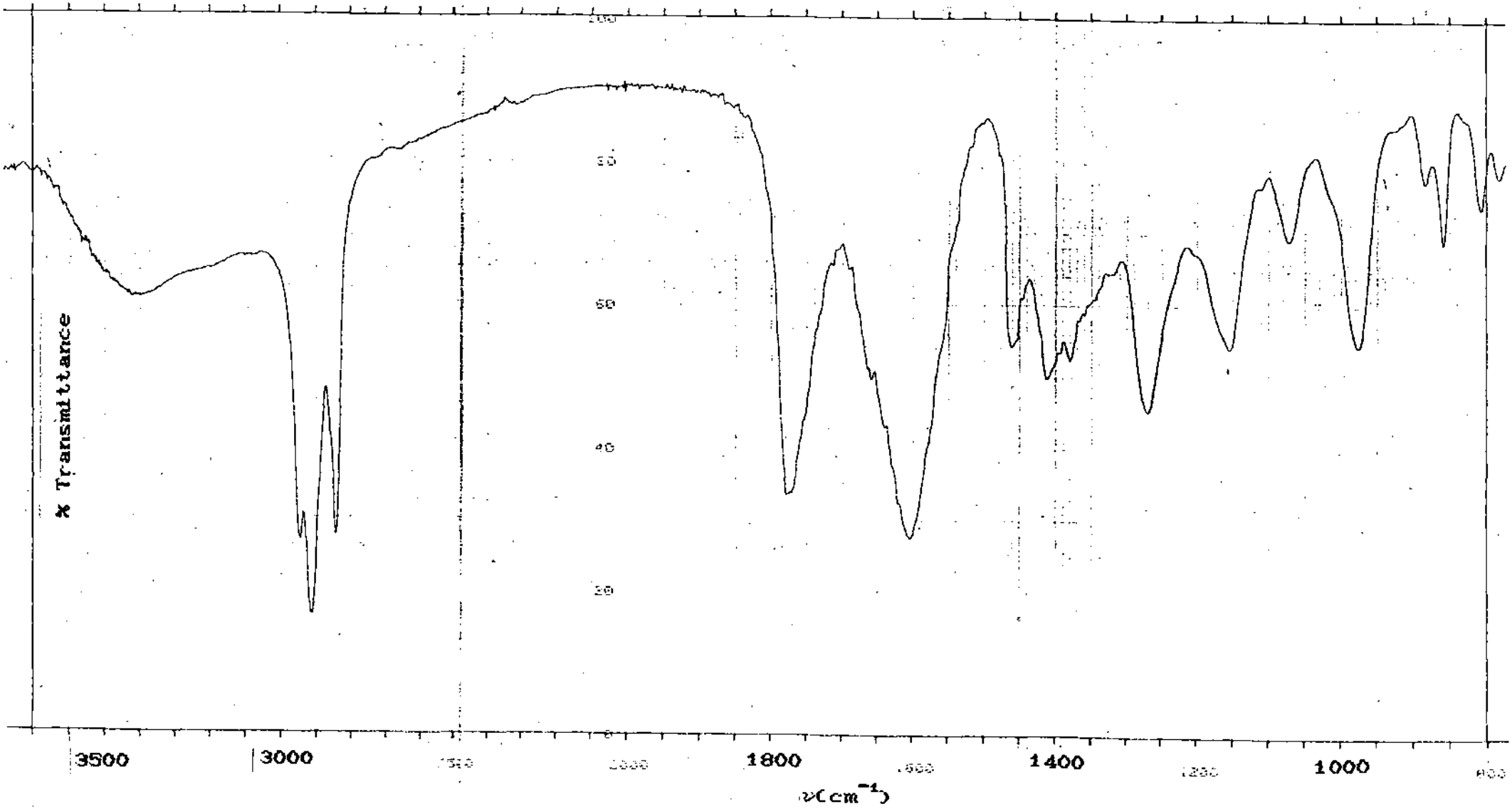


Fig.III.41. IR Spectrum of $Oct_2Sn(Pv)OH$ in KBr.

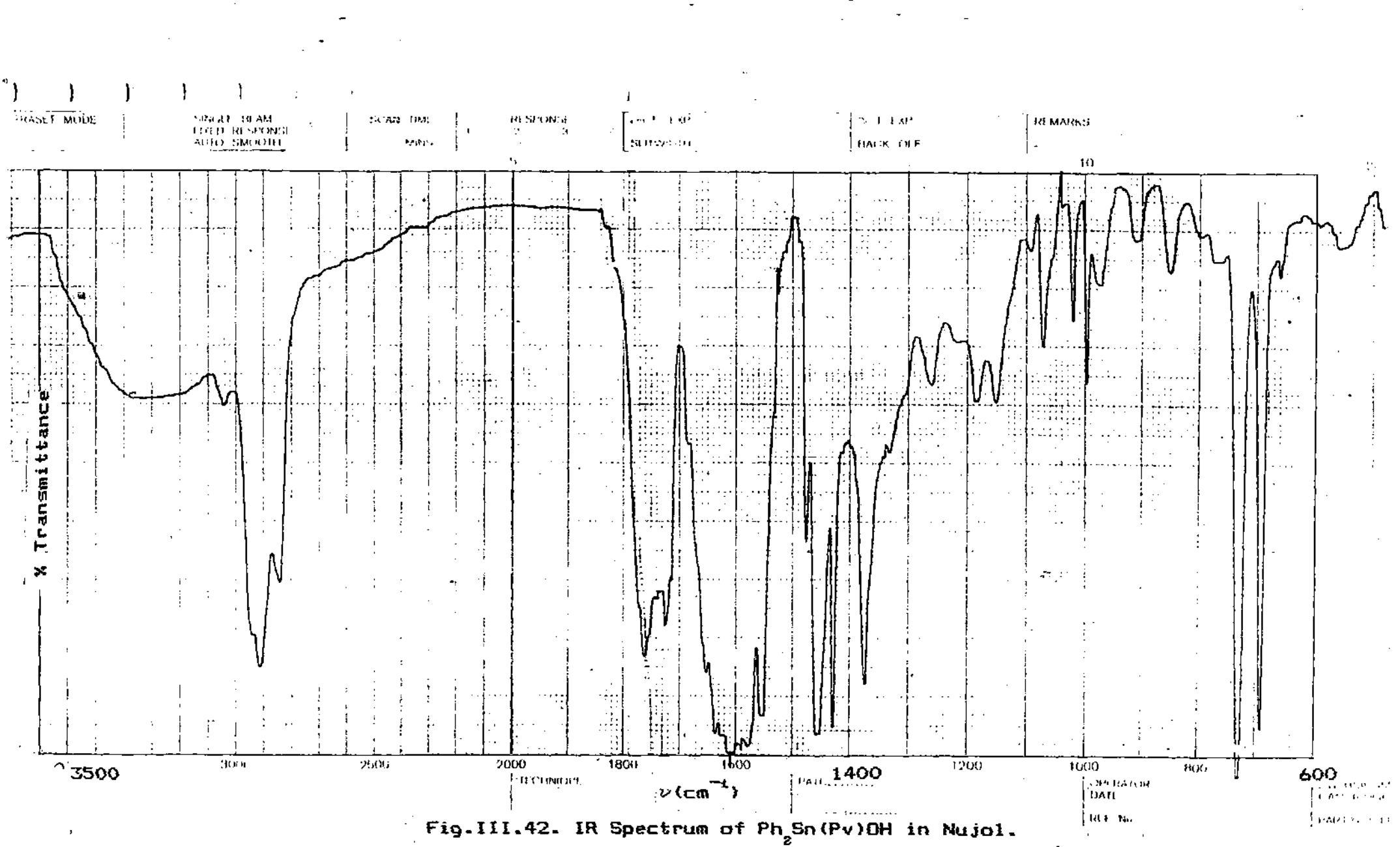


Fig.III.42. IR Spectrum of $Ph_2Sn(Pv)OH$ in Nujol.

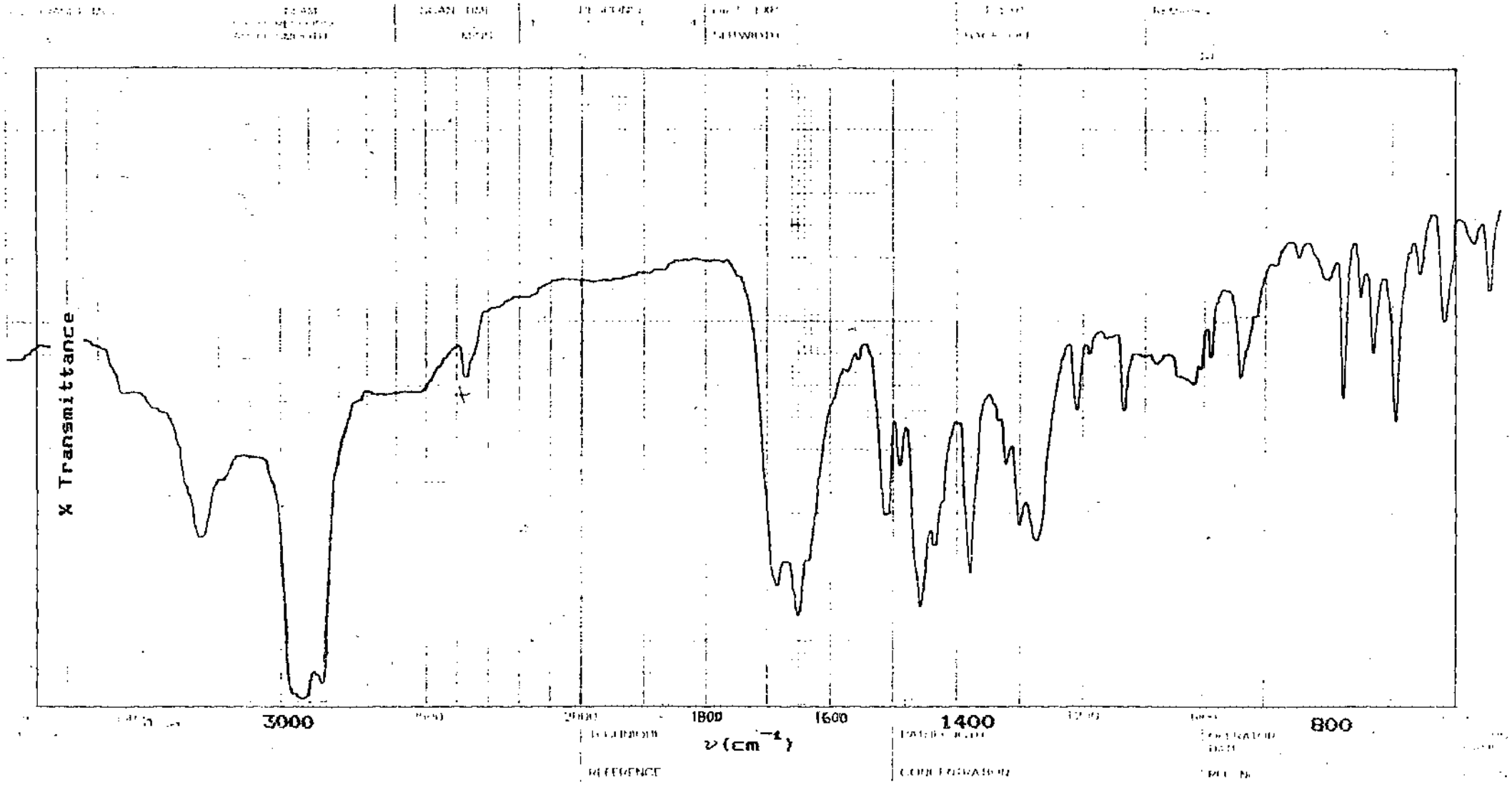


Fig.III.43. IR Spectrum of $Bu_2Sn(PPv)OH$ in Nujol.

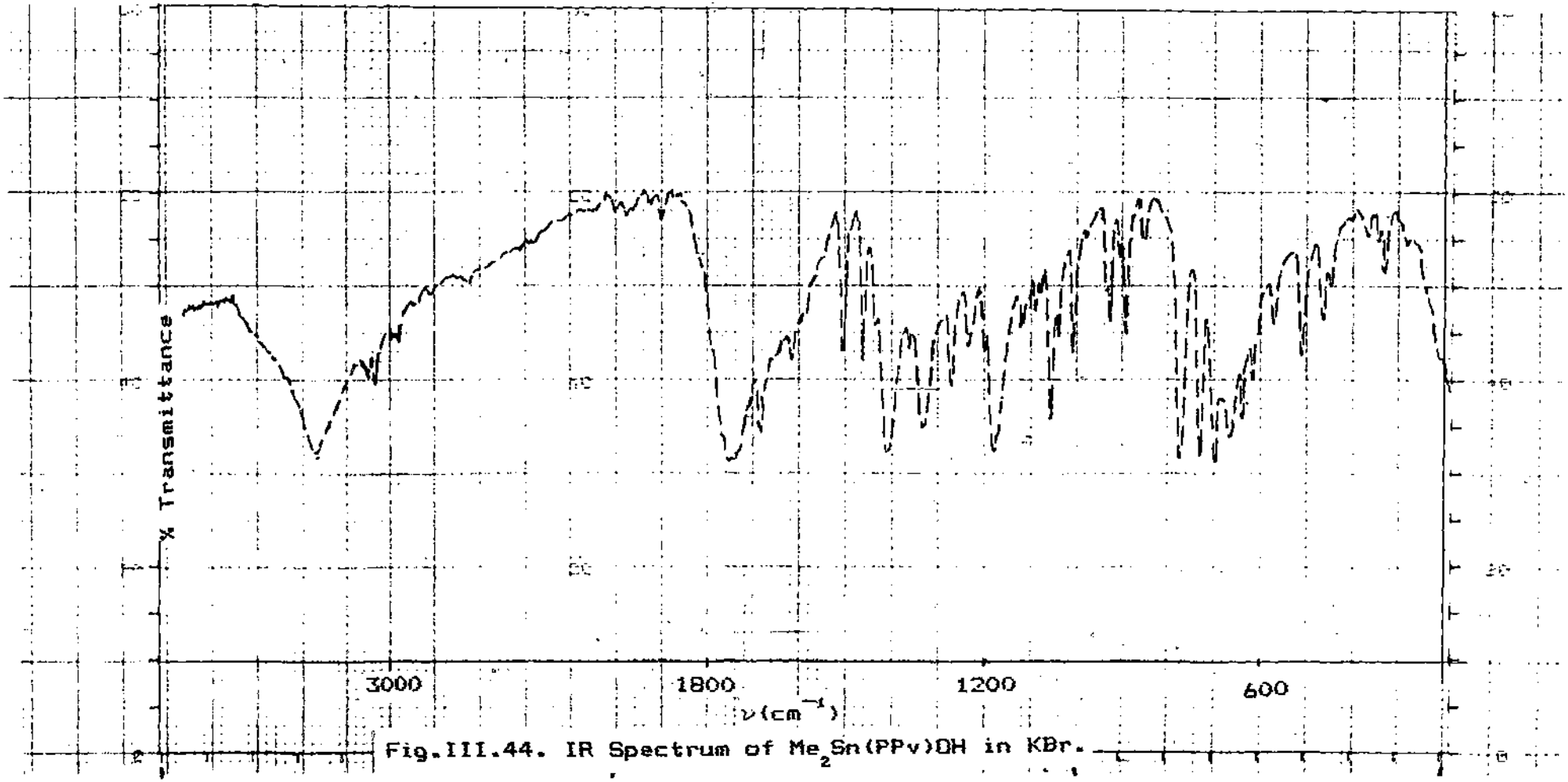
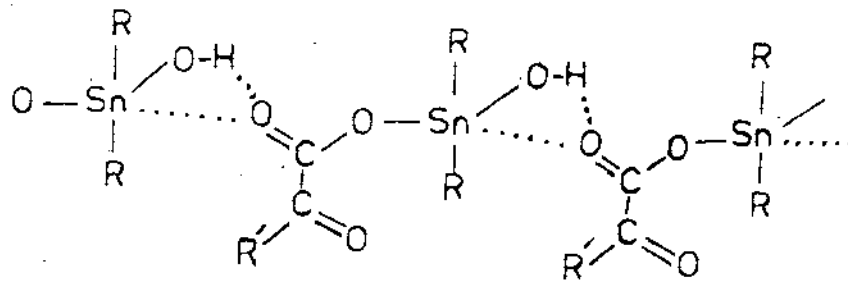
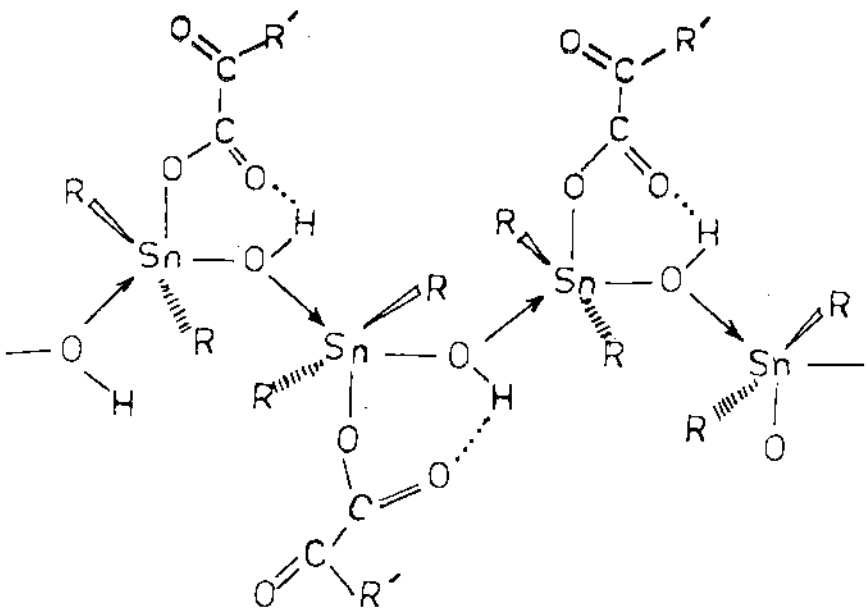


Fig.III.44. IR Spectrum of $Me_2Sn(PPv)OH$ in KBr.

Another peculiarity of these compounds is the occurrence of the $\nu_{C=O}$ bands at much elevated frequency compared to the free acids, viz., around 1770 cm^{-1} and 1700 cm^{-1} for the derivatives of PvH and PPvH respectively. These indicate the presence of free keto group comparable to the triorganotin derivatives of γ-keto carboxylic acids investigated by KumarDas et.al.[40]. The asymmetric and symmetric carboxyl stretching bands of these compounds appear in the region 1660-1600 cm^{-1} and 1430-1400 cm^{-1} respectively, in the solid state. These can be interpreted by assuming the presence of either, (a) hydrogen bonded carboxylate groups, involving trigonal bipyramidal tin atom geometry having the R groups above and below the equatorial plane of three O atoms as shown in structure XIV/XV below- or, (b) a bidentate carboxylate group involving 6-coordinate tin atoms as shown in structure XVI below, with the R groups occupying meridional positions as in the H-bonded structure XV.

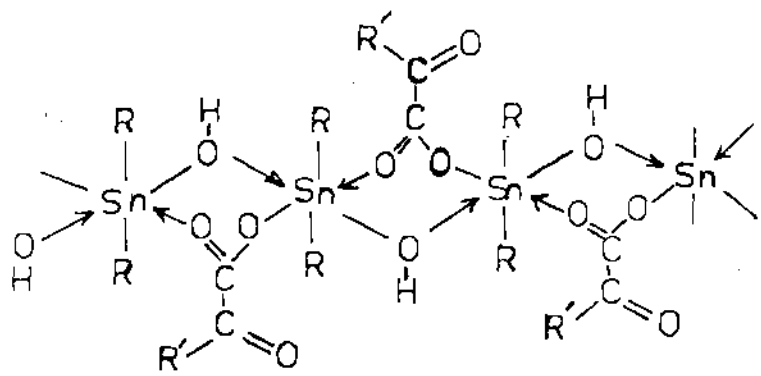


XIV



XV

The structures XV and XVI differ only slightly because one can be easily converted into the other by the simple rotation of the carboxylate moiety through 180° about the Sn—O (ester) bond.



XVI

The probable course of the reaction between diorganotin oxides and keto acids leading to the formation of the carboxylato diorganotin hydroxides may be represented as follows:

$$2\ R_2SnO + 4\ HOCOCOR' \xrightarrow{-2HOH} 2\ R_2Sn(OCOCOR')_2 \xrightarrow[-2\ R'COCOOH]{+HOH}$$

$$(R'COCOO)R_2SnOSnR_2(OCOCOR') \underset{-HOH}{\overset{+HOH}{\rightleftharpoons}} 2\ R_2Sn(OCOCOR')OH$$

It is also possible that the oxide and acid react directly to produce $R_2Sn(OCOCOR')OH$

$$R_2SnO + HOCOCOR' \longrightarrow R_2Sn(OCOCOR')OH$$

Apart from their reactions with Ph_2SnO, the keto acids produced $Ph_2(OCOCOR')OH$ from their reaction with $(Ph_3Sn)_2O$ also, probably through the cleavage of Ph-Sn bond, to be discussed in the next chapter.

III.3.2. *Conclusion :*

On the basis of spectroscopic evidences it can be inferred that the course of reaction between the α-keto acids and organostannoxanes is determined primarily by the nature of the $R'COCOO^-$ moiety and depending on the R' group, intra molecularly coordinated organotin carboxylate derivatives may be formed in some cases.

Spectroscopic data suggest that, in some of the keto carboxylates, the tin atom has apparently attained a coordination number of six through involvement of the carboxyl moiety in both inter and intra molecular coordination.

Bibliography.

1. Dunn P. and Norris T., *Austral. Comm. Dept. Suppl. Def. Std. Lab. Report.*, No-269, 1964. P-21.
2. Cummins R.A. and Dunn P., *Austral. Comm. Dept. Suppl. Def. Std. Lab. Report.*, No-266, 1963, P-106.
3. Japanese Patent., *Chem. Abstr.*, 1966, 65 ,12240c.
4. Graddon D.P. and Rana B.A., *J. Organomet. Chem.*, 1977, 136 ,19.
5. Huber F., Enders M. and Kaiser R., *Z. Naturforsch. B.*, 1966, 21B ,83.
6. Garner C.D., Hughes B. and King T.J., *J. Chem. Soc. Dalton Trans.*, 1975, 562.
7. Ford B.F.E. and Sams J.R., *Inorg. Chim. Acta.*, 1978, 28 ,L173.
8. Harrison P.G. and Phillips R.C., *J. Organomet. Chem.*, 1979, 182 ,37.
9. Siddiqui K.S., Zaidi F.R., Khan T.A. and Zaidi S.A.A., *Bull. Soc. Chim. Fr.*, 1983, 5-6 ,Pt-I, 140.
10. Srivastava T.N. and Sing J.D., *Ind. J. Chem.*, 1983, 22A(2) ,128; 1983, 22A(8), 674; 1986, 24A(6), 489.
11. Siddiqui K.S., Kureshi R.I., Khan P. and Zaidi S.A.A., *Ind. J. Chem.*, 1983, 22A(7), 616.
12. Narula S.P., Sharma R.K., Lata S., Kapur N. and Seth R., *Ind. J. Chem.*, 1983, 22A(3), 248.
13. Midha A. and Verma R.D., *J. Ind. Chem. Soc.*, 1985, 62(6), 421.

14. Srivastava T.N., Siddiqui M.A., Sing J.D. and Srivastava S., *Ind. J. Chem.*, 1987, 26A(2), 158.

15. Alcock N.W. and Rose S.M., *J. Chem. Soc. Dalton Trans.*, 1989(8), 1589.

16. Huber F., Preut H., Hoffman E. and Gielen M., *Acta. Crystallogr. Sect. C, Cryst. Struct. Commun.*, 1989, C45(1), 51.

17. Ng S.W., Chen W., Zainudin A., KumarDas V.G., Yip W.H., Wand R.J. and Mak T.C.W.., *J. Crystallogr. Spectrosc. Res.*, 1991, 21(1), 39.

18. KumarDas V.G., Chen W., Ng S.W. and Mak T.C.W., *J. Organomet. Chem.*, 1987, 322(1), 33.

19. Lockhart T.P., Calabrese J.C. and Davidson F., *Organometallics.*, 1987, 6 ,2479.

20. Molloy K.C., Blunden S.J. and Hill R., *J. Chem. Soc. Dalton Trans.*, 1988(5), 1259.

21. Speer R.J., Stewart D. and Rodgway H., *J. Clin. Hematol. Oncol.*, 1983, 13(4), 89.

22. Khan A., Tseng J. and Young R., *J. Clin. Hematol. Oncol.*, 1984, 14(2), 35.

23. Japanese Patent., *Chem. Abstr.*, 1984, 101 ,171102t.

24. Eur. Patent., *Chem. Abstr.*, 1984, 101 ,222710z.

25. Gilman H. and Rosenberg S.D., *J. Am. Chem. Soc.*, 1952, 74 ,5580.

26. Sisido K., Takeda Y. and Kinugawa Z., *J. Am. Chem. Soc.*, 1961, 83 ,538.

27. Vogel A.I., *A Text Book Of Practical Organic Chemistry.*; ELBS, 3rd Ed., Reprinted 1971.

28. (a) Gilman H. and Blatt A.H., *Organic Synthesis.*, John Wiley, N.Y., 1961, Col.Vol.-I, P-475.

(b) Blatt A.H., *Organic Synthesis.*, Col.Vol.-II, P-1,11,519.

29. Leusing D. and Stanfield C.K., *J. Am. Chem. Soc.*, 1964, 86 ,2805.

30. Colthup N.B., Daly L.H. and Wiberley S.E., *Introduction to InfraRed and Raman Spectroscopy.*, A.P.,N.Y., 1964, Ch-9.

31. Desk Top Molecular Modeller: Version 1.2, John Appleyard, Polyhedron Software; (c) Oxford Univ. Press., 1989.

32. Bellamy L.J. and Branch R.F., *J.Chem.Soc.*, 1954, 4491.

33. Okawara R., Webster D.E. and Rochow E.G., *J. Am. Chem. Soc.*, 1960, 82 ,3287.

34. Curtis N.F., *J.Chem.Soc.(A).*, 1968, 1579.

35. Ng S.W., KumarDas V.G., Skelton B.W. and White A.H., *J.Organomet.Chem.*, 1989, 377(2-3), 221.

36. Harrison P.G., Lambert K., King T.J. and Majee B., *J.Chem.Soc. Dalton Trans.*, 1983, 363, and references cited therein.

37. Swisher R.G., Vollano J.F., Chandrashekhar V., Day R.O. and Holmes R.R., *Inorg.Chem.*, 1984, 23 ,3147.

38. Vollan J.F., Day R.O., Rau D.N., Chandrashekhar V. and Holmes R.R., *Inorg.Chem.*, 1984, 23 ,3153.

39. Lockhart T.P. and Davidson F., *Organometallics.*, 1987, 6 ,2471.

40. Ng S.W., Chen W., Yap C.K., KumarDas V.G. and Mak T.C.W., *J.Organomet.Chem.*, 1986, 311 ,289.

1. Bent H.A., *Chem. Rev.*, 1961, 61, 275.

2. Majee B., *Rev. Silicon, Germanium, Tin, Lead Compds.*, 1975, Vol. II, No 1.

3. Muralidhara M.G. and Chandrasekhara V., *Ind. J. Chem.*, 1991, 30A, 487 and references cited therein.

4. Jain V.K. and Mokal V.B., *Ind. J. Chem.*, 1992, 31A, 861 and refernces cited therein.

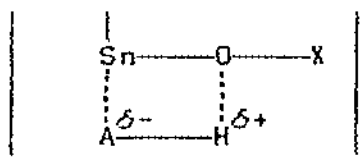
Chapter-IV

Carboxylic Acid Adducts.

CARBOXYLIC ACID ADDUCTS :

IV.1. *Introduction :*

The reactions between organostannoxanes and organic and inorganic acids, universally used for the preparation of organotin esters , are believed to proceed through the intermediate donor-acceptor transition state



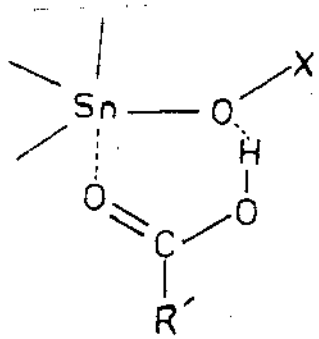
; X = Sn / H

I

Presumably, the intermediate complexes have very low stability and undergo intramolecular rearrangement leading to the final products, making it difficult to isolate the intermediate complexes in most cases. An evidence in favour of such an intermediate has been provided by Narula et.al.[1], who isolated the adduct $(Ph_3Sn)_2O{\longrightarrow}SO_3$ from the reaction of $(Ph_3Sn)_2O$ and SO_3 in CCl_4 at -20^oC. $(Ph_3Sn)_2O{\longrightarrow}SO_3$ converts into $(Ph_3Sn)_2SO_4$ on being refluxed in the same solvent.

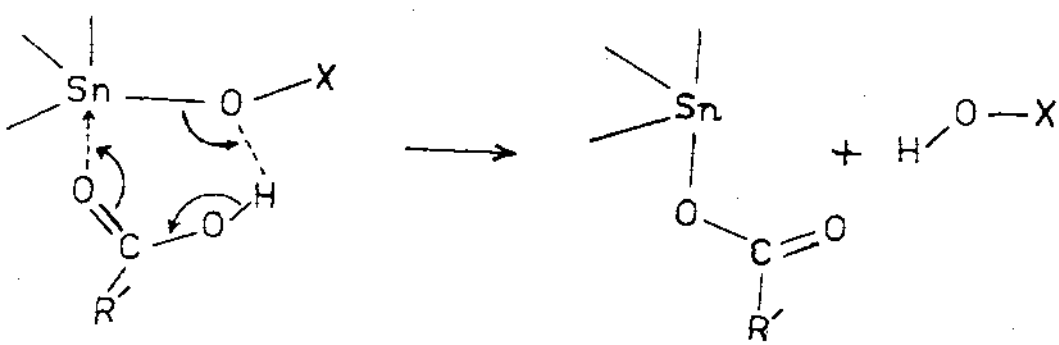
In the reaction between organotin oxides and carboxylic acids in non-ionising solvents, although there is no direct evidence, the following cyclic intermediate is expected to be formed through a H-bond between the Sn—O atom and the acidic

H-atom, assisted by a nucleophilic attack by the carbonyl O-atom at the tin atom.



II

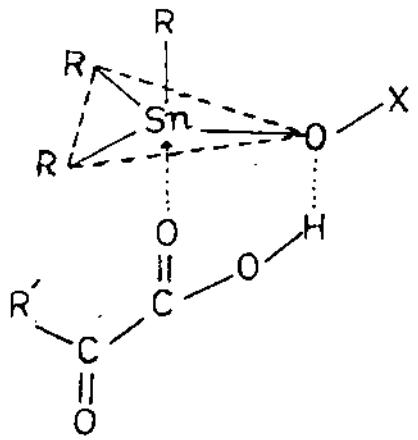
This is quite similar to the transition state proposed for the reaction of siloxanes with $AlCl_3$[2] and the reaction of $(Ph_3Sn)_2O$ with HgX_2[3], and does not seem very unlikely in view of the known donor property of the stannoxanes, discussed in chapter-1. Normally, such an intermediate [II] should undergo instantaneous electron shifts as shown below, leading to the organotin carboxylates.



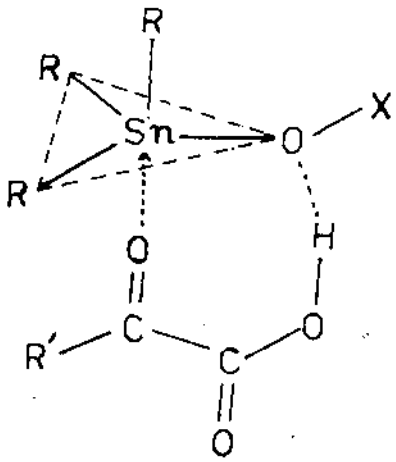
Obviously, the stabilisation of the intermediate II, if at all formed, will depend not only upon the donor-acceptor property of the oxo-organotin compounds, but also upon the presence of other potential donor sites in the $R'COO^-$ moiety, electronegativity and steric factors.

In this context the α-keto carboxylic acids, used in the present investigation, seem to be suitable for the isolation of the intermediate addition product, since they have the right acidity (pK_α <3.0) and suitably placed additional donor group. Since the nucleophilicity of the oxygen bonded to tin in the stannoxanes, is also important in the formation of the intermediate, bis(triorganotin) oxide are most likely to be the right choice for realisation of such addition products. In fact, stirring of a mixture of bis(triorganotin) oxide /hydroxide and α-keto acids led to the precipitation of compounds corresponding to addition complexes in a few cases. The intermediate involving the bis(triorganotin) oxides /hydroxide and α-keto acids may be represented by either of the structures IIIA or IIIB, where the nucleophilic and electrophilic interactions are mutually supportive, as shown below.

It may be noted that the proposed structures IIIA and IIIB of the transition state, involve the trans form of the keto acids. Although, the cis form of the acid can be utilised to draw a



III A

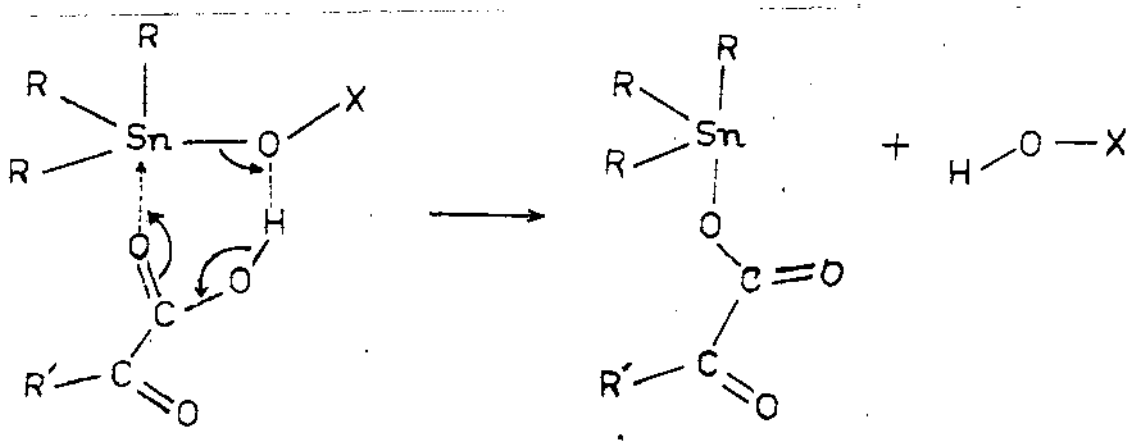


III B

structure analogous to IIIA, no structure similar to IIIB can be visualised using the cis form, because that would involve excessive steric strain making the structure improbable. Moreover, molecular modelling and energy calculations [see section III.3.1.A(i)] have shown that the cis form of the keto acids are less stable than the trans forms.

If the intermediate is represented by structure IIIA its stability should not differ much from that of structure II, because for structure IIIA, neither the additional donor group, nor the field effects originating at the R' group, can influence the electromeric effects leading to the immediate conversion into the carboxylate derivative as shown below.

On the other hand, the formation and stability of structure IIIB will be greatly influenced by the electronic and steric factors



dependent on the R' group. Moreover, rearrangement leading to the formation of the carboxylate derivative is not likely in IIIB. The latter is thus, expected to behave differently and its rearrangement will lead to different products. Therefore, although the product represented by structure IIIB may be isolable, it should not be regarded as the intermediate in the reaction between organostannoxanes and carboxylic acids leading to the formation of the organotin carboxylates, rather, it should be termed as carboxylic acid adduct of organostannoxanes/organotin hydroxides.

IV.2. *Experimental :*

The organotin compounds and the α-keto acids were prepared according to methods described in chapter-III. All the solvents were purified by standard methods[4]. The methods for the preparation of the addition products are described below :

1. Reaction of PvH with $(Ph_3Sn)_2O$:

1.79 g (0.0025 mole) of $(Ph_3Sn)_2O$ was dissolved in about 10 ml dry benzene/solvent ether by warming. To the clear, warm solution 0.44 g (0.005 mole) of PvH was added drop wise with shaking. Allowed to stand for 1-2 minutes, when solid began to separate. The benzene/ether solution was carefully poured into another flask containing 5 ml pet.ether. Allowed to stand for 10-20 minutes and the supernatant liquid decanted leaving the solid behind. The solid was then washed repeatedly with cold benzene and ether and dried, first in air and then under vacuum over $CaCl_2$.

Yield : 2.01 g (90 %). Mp. 146^{o}C (d).

Analysis :	% Sn	% C	% H
Found :	25.86	56.5	4.5
Calculated for $Ph_3SnOH.PvH$:	25.98	55.5	4.4

2. Reaction of PvH with Ph_3SnOH :

0.35 g (<0.001 mole) of freshly prepared and air dried Ph_3SnOH was suspended in 10 ml ether and 0.09 g (0.001 mole) PvH added drop wise and stirred for about 10 minutes using a magnetic stirrer, when Ph_3SnOH gradually went into solution. Stirring was continued and within a few minutes precipitation of product started. Precipitation was complete in about another 15 minutes. Allowed to settle for a while and the supernatant liquid

decanted. The solid was washed several times with ether and dried. 0.425 g (96 %) of a white product, melting at 146°C(d), were obtained. It was identified with $Ph_3SnOH.PvH$ by mixed melting point and comparison of IR spectra and analytical data.

3. Reaction of PvH with $(Bu_3Sn)_2O$:

1.49 g (0.0025 mole) of $(Bu_3Sn)_2O$ was dissolved in 10 ml pet.ether and 0.44 g (0.005 mole) of PvH was added drop wise with shaking. 2 drops more of PvH were added and shaking continued for another 5 minutes. The pet.ether solution was then carefully decanted, leaving the unreacted PvH behind, into a large watch glass and solvent removed by blowing hot air gently. The watch glass containing the semisolid mass was then placed in a vacuum desiccator and dried under pump for 2-3 minutes. The wax-like white solid was then transferred to a small conical flask and dried further under vacuum over $CaCl_2$.

Yield : 1.93 g (98 %). Mp. 72-74°C (d).

Analysis :	% Sn	% C	% H
Found :	30.8	47.69	7.9
Calculated for $Bu_3SnOH.PvH$:	29.94	46.69	8.1

4. Reaction of PvH with $[(PhCH_2)_3Sn]_2O$:

1 g (0.00125 mole) of $(Bz_3Sn)_2O$ was dissolved in 10 ml dry benzene and to the warm solution 0.24 g (>0.0025 mole) of PvH was

added drop wise with shaking. Shaking continued for 2-3 minutes more, when solid began to separate. The solution was decanted into another flask leaving the unreacted PvH behind. Precipitation was completed by addition of pet.ether and allowed to settle. The clear supernatant liquid was decanted and the residue was washed with benzene. The yellowish white residue was dissolved in ether and reprecipitated with pet.ether, filtered and dried.

Yield : 0.9 g (75 %). Did not melt.

Analysis :	% Sn	% C	% H
Found :	23.2	58.36	4.6
Calculated for $Bz_3SnOH.PvH$:	23.79	58.06	5.24

5. Reaction of PPvH with $(Bu_3Sn)_2O$:

0.3 g (0.0005 mole) of $(Bu_3Sn)_2O$ was dissolved in 5 ml pet.ether and shaken with 0.18 g (>0.001 mole) of PPvH for 5-6 minutes. The light yellow solution was filtered and kept overnight at 5°C. The slight precipitate formed was removed by filtration and the filtrate stored at 5°C for several days. The white product obtained melts at 88°C and weighed 0.28 g (60 %).

Analysis :	% Sn	% C	% H
Found :	25.3	54.6	7.5
Calculated for $Bu_3SnOH.PPvH$:	25.1	53.61	7.66

6. Treatment of $R_3SnOH.R'COCOOH$ with dil NaOH solution : (Estimation of organotin to acid ratio).

(i) An accurately weighed mass of the triorganotin compound was dissolved in methanol and titrated against a dilute NaOH (aq) solution having accurately known strength of N/100 order using phenolphthalein as indicator. The burette reading (V_1) was noted. A blank titration of the bis(triorganotin) oxide vs. NaOH was then carried out and on its basis the volume of NaOH consumed by the amount of stannoxane, expected to be present in the triorganotin compound taken, was calculated. This volume was deducted from V_1 to get the volume of NaOH (V_2) apparently consumed by acid present in the triorganotin compound. From V_2 the amount of acid was calculated and was found to agree well with the formulation $R_3SnOH.HL$ (where, HL = R'COCOOH).

(ii) A benzene solution of an accurately known amount of the triorganotin compound $Ph_3SnOH.PvH$ was shaken with calculated volume (required for complete hydrolysis of the complex) of N/50 NaOH (aq) solution. and the aqueous layer was separated. The concentration of NaPv in the aqueous solution was calculated on the basis of the above formulation. Another aqueous solution of NaPv, having exactly the same concentration, was prepared by neutralising PvH with N/50 NaOH solution. The absorption spectrum of the two solutions in the UV region were recorded using a

Shimadzu UV240 spectrophotometer and were found to be reasonably matching.

IV.3. *Results and Discussion :*

Perhaps, the most interesting results of the present study is the separation of addition products of the type $R_3SnOH.HL$, where HL denotes the keto acids. These products are obtained simply by mixing the keto acid with $(R_3Sn)_2O$ (or R_3SnOH) in appropriate proportion in benzene or solvent ether under very mild conditions. Pyruvic acid (PvH) exothermally adds on to $(Bu_3Sn)_2O$ at room temperature, even when the two liquids are just mixed in appropriate ratio in the absence of any solvent, to give a waxy solid product. The reaction conditions and other details for the preparation of the addition products are given in the table-IV.1.

A reference to the table-IV.2., showing the percentage yield of the products, reveal that their formation depends both on the nature of the keto acid and the organic group R on the stannoxane. The data from table-IV.2. also show that the Taft's constant value of the substituent R', which gives a measure of their ability to influence the electron flow to the adjacent atoms in R'COCOOH, strongly effects the yield of the addition products. Increasing Taft's constant decreases the possibility of formation of these

Table:-IV.1.

Summary of reaction conditions and products :

Sl. no.	Reactants and mole ratio.	Reaction Conditions	Time	Product	% Yield , Mp.
1.	$(Ph_3Sn)_2O$ + PvH (1:2)	Solution of stannoxane in ether/bez. shaken with acid. Soln. diluted with pet. ether. Product washed with ether.	2-3 min.	$Ph_3SnOH.PvH$	90, 146°C(d)
2.	Ph_3SnOH + PvH (1:1)	Stirred in cold ether with slight excess acid. Product washed with cold ether.	30 min.	$Ph_3SnOH.PvH$	96, 146°C(d)
3.	$(Bu_3Sn)_2O$ + PvH (1:2)	Shaken in pet.ether with slight excess acid. Pet.ether layer decanted and evaporated.	5 min.	$Bu_3SnOH.PvH$	98, 72-74°C
4.	$(Bz_3Sn)_2O$ + PvH (1:2)	Benzene soln. of stannoxane shaken with slight excess acid. Bez. layer decanted into pet.ether. Solid dissolved in ether and reprecipitated with pet.ether.	5 min.	$Bz_3SnOH.PvH$	75, -
5.	$(Bu_3Sn)_2O$ + PPvH (1:2)	Stannoxane and acid shaken in warm pet.ether, filtered and stored at 5°C. Product washed with cold pet.ether.	5 min.	$Bu_3Sn.PPvH$	60, 88°C
6.	Ph_3SnOH + BFH (1:1)	Stirred in cold ether with slight excess acid. Product washed with cold ether.	30 min.	Ph_3SnBF	95, 149°C

products. This is quite reasonable, since the formation of addition product is expected to be facilitated by electron releasing groups (low Taft's constant).

With the same keto acid, the yield depends on the organic group attached to tin and decreases in the series n-Bu >Ph >$PhCH_2$. This pattern is not related to the electronic factors, e.g., inductive or mesomeric effect of the group. On the other hand, this clearly reflects a correlation between the size of the group and the ease of formation of the addition complex. Thus, both steric factors and electronic factors govern the formation of these products. High Taft's constant values combined with the presence of bulky group at the tin atom, as can be seen from table-IV.2., prevents the formation of such complex.

Table-IV.2.

Reaction of $(R_3Sn)_2O$ with R'COCOOH producing $R_3SnOH.R'COCOOH$:

	% yeild of product.		
R' (Taft's const.) \ R	n-Bu	Ph	$PhCH_2$
CH_3 (-0.05)	98	90	75
$PhCH_2$ (0.04)	60	-	-
Ph (0.1)	-	-	-

Significantly, the keto acid where the substituent has high Taft's constant, e.g., PhCOCOOH (benzoyl formic acid) gives high yield of the carboxylate of the type $R_3SnOCOCOR'$, by reacting with either $(R_3Sn)_2O$ or R_3SnOH, even under very mild condition.

IV.3.1. Characterisation of the Products :

All these compounds differ considerably from the ketocarboxylates and their hydrolysates in their stability, solubility, chemical and spectroscopic properties and have been characterised on the basis of analytical data, their IR, UV and ^{1}H-NMR spectra and reactivities.

Although these compounds have been obtained by the reaction of $(R_3Sn)_2O$ and HL (HL = R'COCOOH) in 1:2 ratio, they should be formulated as $R_3SnOH.HL$ on the basis of analytical data (table-IV.3.) and other evidences discussed below.

(i) Titrimetric determination of acid to organotin ratio in the addition product :

These complexes are highly susceptible to cleavage by OH^- ions. The reaction between the triorganotin derivatives and very dilute alkali solution, such as 0.01(N) NaOH, (eqn-1) leading to the organostannoxane and alkali metal salt of the acid is so fast and complete that this reaction can be utilised in quantitative estimation of the acid present in the complex.

Table:-IV.3.

Analytical data and solubilities of the products :

Sl. no.	Compounds.	% Found / (Calculated). Sn	C	H	Solubilities.
1.	$Ph_3SnOH.PvH$	25.86 (25.99)	56.5 (55.5)	4.5 (4.4)	Ace., Alc. Sl.sol. in Bez., Et_2O, $CHCl_3$.
2.	$Bu_3SnOH.PvH$	30.8 (29.94)	47.69 (45.69)	7.9 (8.1)	Bez., Pet.eth., CCl_4, $CHCl_3$, Et_2O, Ace., Alc.
3.	$Bz_3SnOH.PvH$	23.2 (23.79)	58.36 (58.06)	4.6 (5.24)	Et_2O, Ace., Alc.
4.	$Bu_3SnOH.PPvH$	25.3 (25.1)	55.6 (53.61)	7.5 (7.66)	Bez., $CHCl_3$, Et_2O, Ace., Alc.

$$R_3SnOH.HL + MOH \longrightarrow R_3SnOH + ML + HOH \text{ -------[1]}$$

Thus, a methanolic solution of triphenyl/tributyl tin derivative of PvH was titrated against a standard NaOH (aq) solution of 0.01(N) order using phenolphthalein indicator. Even a benzene solution of the tributyl derivative could be titrated in the same manner with vigorous shaking. Results of typical titrations are presented in the table-IV.4. below. The equivalence point of these titrations corresponds to 1:1 mole ratio of organotin to acid, which agrees well with analytical data.

These results are further supported by the reasonable identity of the absorption spectrum (fig-IV.1) of an aqueous NaPv

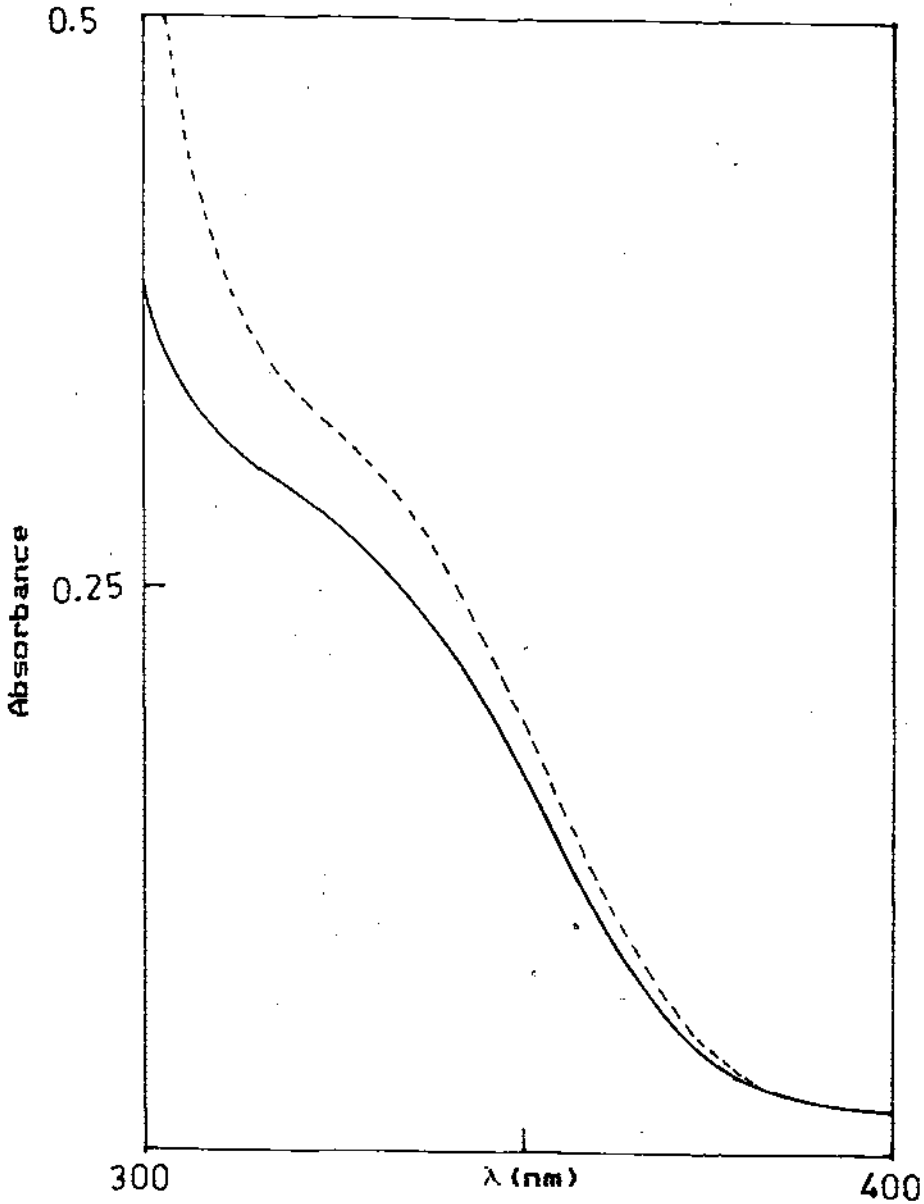


Fig.IV.1. Electronic spectrum of NaPv (in water) from neutralisation of PvH (-------) and decomposition of $Ph_3SnOH.PvH$ (———).

Table :- IV.4.

Titration of Addition Complex against Std.NaOH Solution :

Sl. no.	Addition product.	Amount in grams.	Vol.& Strength of NaOH Soln. consumed.	Amt.of PvH found (g)	Amt.of PvH (g) calculated for $R_3SnOH.PvH$.
1.	$(Bu_3Sn)_2O$		21.0 cc		
	+ PvH	0.086803	1.111525 N/100	0.02054	0.019387
2.	$(Ph_3Sn)_2O$		21.3 cc		
	+ PvH	0.101113	1.111525 N/100	0.020824	0.019599

solution, obtained by shaking a benzene solution of a known amount of $Ph_3SnOH.PvH$ with calculated volume (calculated on the basis of the aforesaid formulation) of 0.02(N) NaOH (aq) solution, with that of another aqueous solution of NaPv, having the same concentration, prepared by neutralising PvH with 0.02(N) NaOH solution.

(ii) Solubility :

The formulation, viz. $R_3SnOH.HL$, arrived at on the basis of analytical data and the above titrimetric estimation of organotin to acid ratio, implies that the compounds should be highly polar in nature, which is reflected in their solubilities. Of the four compounds isolated the two tributyl compounds are soluble in both polar and nonpolar solvents, but the triphenyl and tribenzyl derivatives of pyruvic acid (PvH) have very poor solubility in

nonpolar solvents (table-IV.3.). But in all cases the solubility in polar solvents is much higher indicating the presence of highly polar structure in these compounds.

(iii) Spectroscopic evidence :

Spectroscopic data support the formulation of the addition complexes as $R_3SnOH.HL$ and provides an insight into the structure of these compounds.

(a) IR spectra :

The IR spectra of the ligands have been discussed and assignments for the various absorption bands made in section III.3.1.A. IR spectral data for the addition complexes are presented in table-IV.5., along with relevant data for the free acids. Some typical IR spectra are given in figures IV.2.-III.7.

It can be seen from table-IV.5. that in free PvH there is a very broad band in the region 3600-2900 cm^{-1} and in PFvH a sharp medium intensity band at 3460 cm^{-1}. In the addition complexes a broad band, indicative of the presence of hydrogen bonded OH group occurs in the region 3425-3400 cm^{-1}. In $Ph_3SnOH.PvH$ there is a low intensity band at 3620 cm^{-1} which is characteristic of the Sn—OH grouping. This band is slightly broadened in the complex compared to the same band in Ph_3SnOH.

As may be seen from the table, PvH shows two $\nu_{C=O}$ stretches at 1728 and 1740 cm^{-1} respectively, of which the former may be

Table:-IV.5.

Characteristic IR freguencies (Cm^{-1}) of some Addition Complexes :

Sl. no.	Compounds.	Solid Phase (in Nujol/KBr)					Soln. Phase (in CCl_4)			
		ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}	$\nu_{C=O}$ (wag)	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
1.	PvH	3600-2900[b]	1728	1740	1285 1160	615	3420	1725	1790	1280 1200
2.	PvEt	-	1745	1755	1370 1300	618	-			
3.	PvNa	-	1710	1625	1405	625	-			
4.	$Ph_3SnOH.PvH$	3620 3400[b]	1612	1715	1428 1410	635	3400[b]	1620	1710	1398
5.	$Bu_3SnOH.PvH$	3425[b]	1620	1722	1415 1395	625	-	1620	1735	1398
6.	$Bz_3SnOH.PvH$	3400	1610	1715	1408	632	-			
7.	PPvH	3460	1686[b]	1688[b]	1248 1195	695	-			
8.	$Bu_3SnOH.PPvH$	3425	1620	1725	1402	680 635	-			

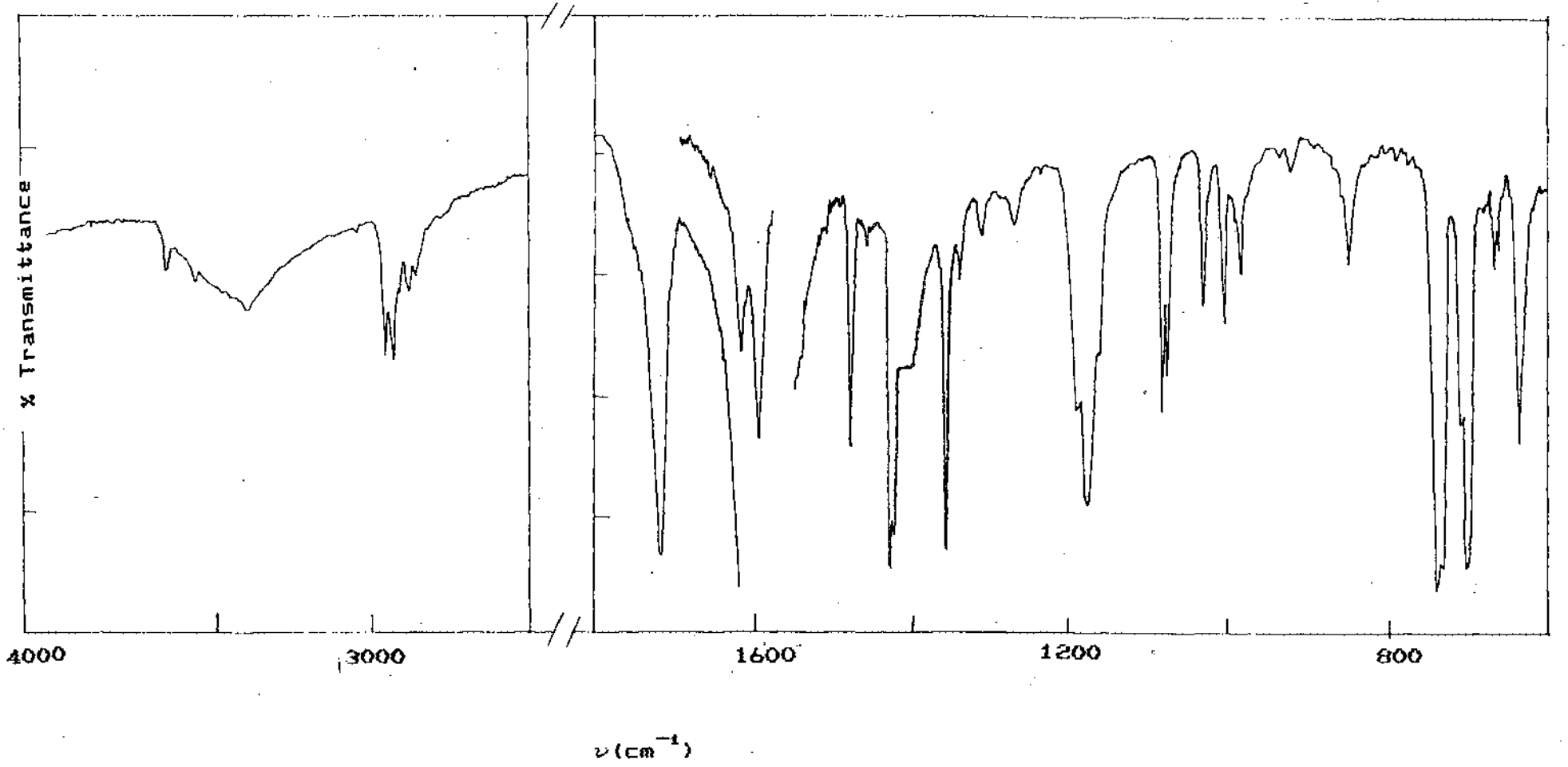


Fig.IV.2. IR Spectrum of $Ph_3SnOH.PyH$ in KBr.

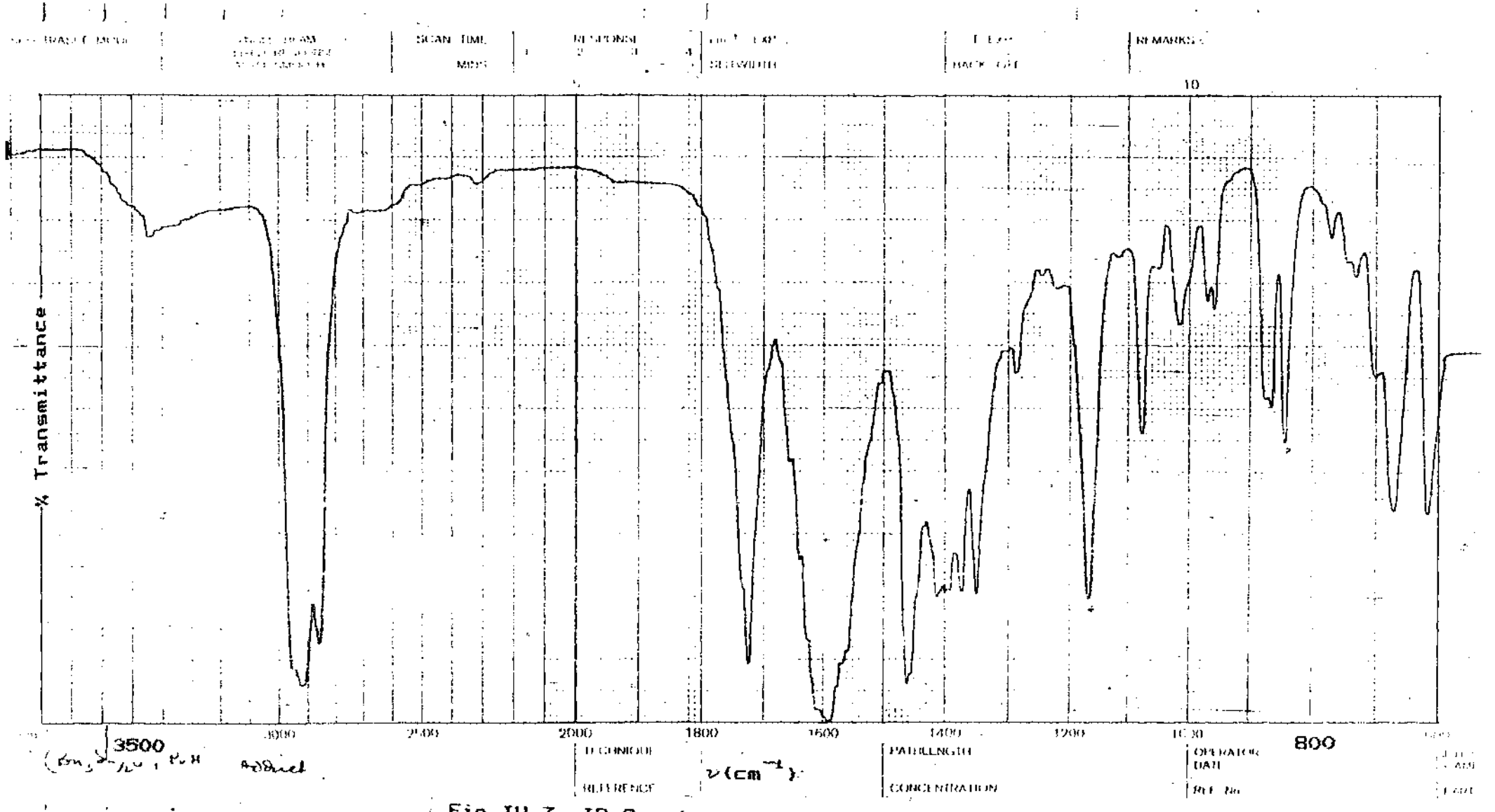


Fig.IV.3. IR Spectrum of $Bu_3SnOH.PvH$ in Nujol.

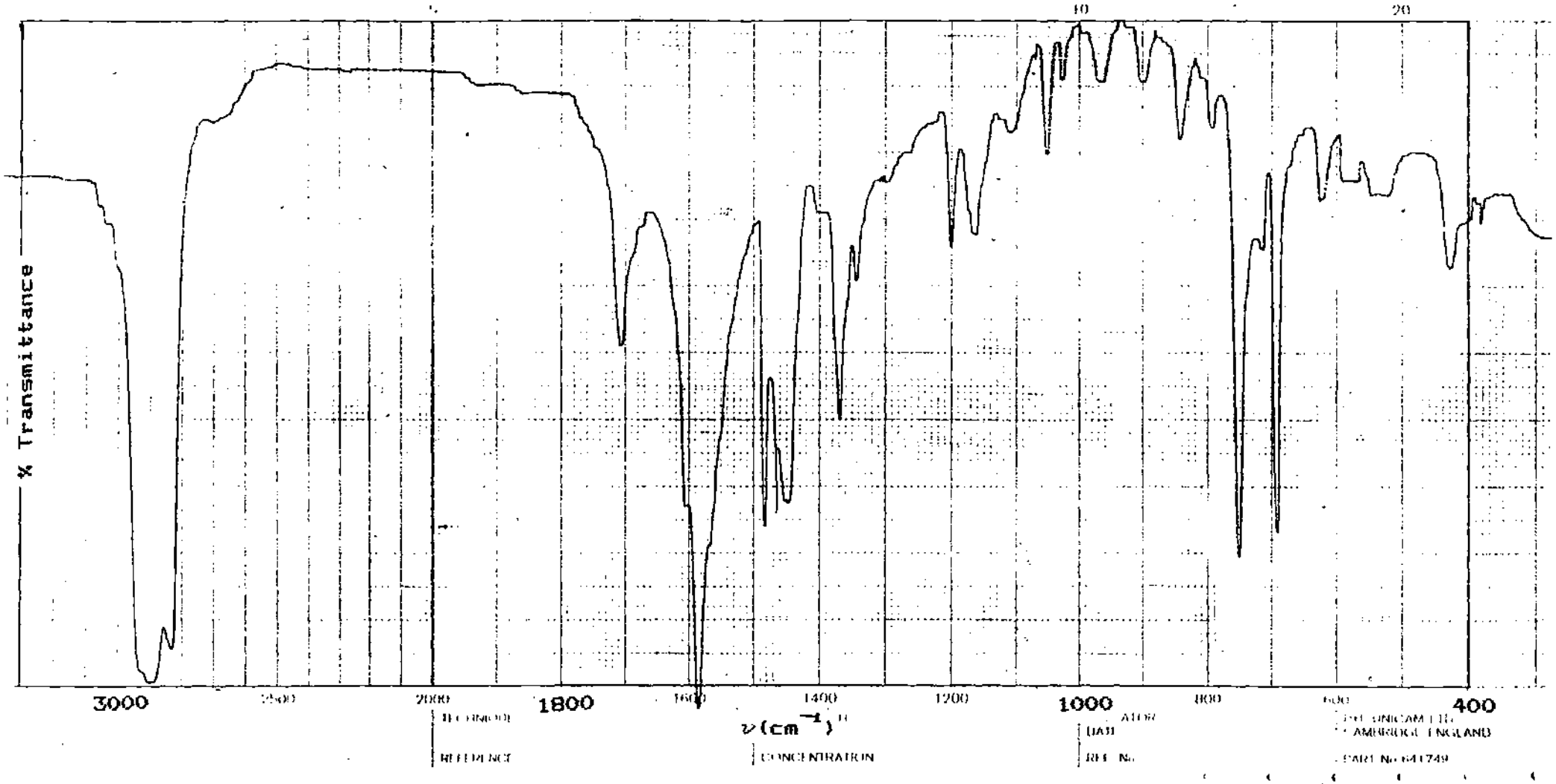


Fig.IV.4: IR Spectrum of $Bz_3SnOH.PvH$ in Nujol.

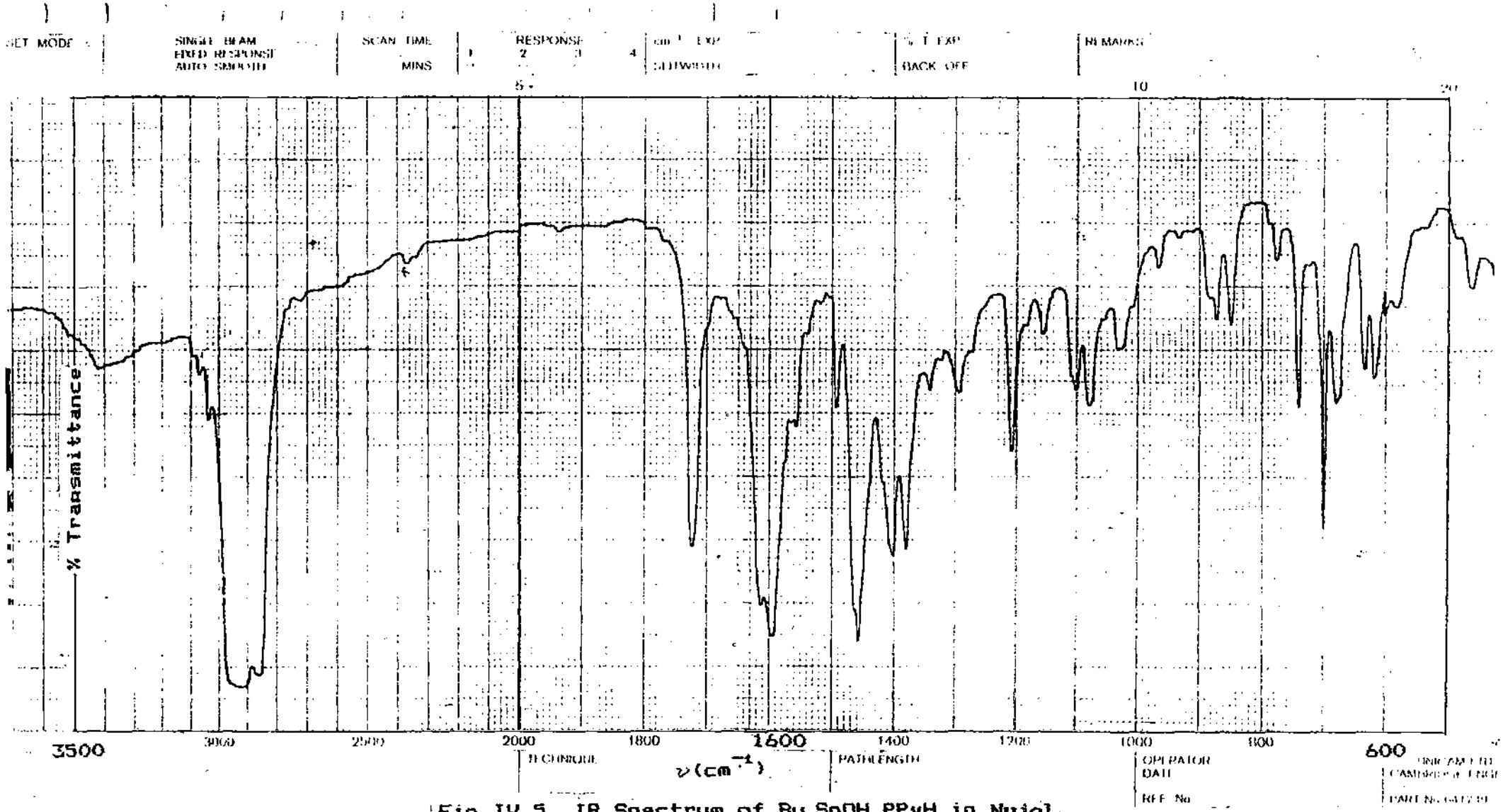


Fig.IV.5. IR Spectrum of $Bu_3SnOH.PPvH$ in Nujol.

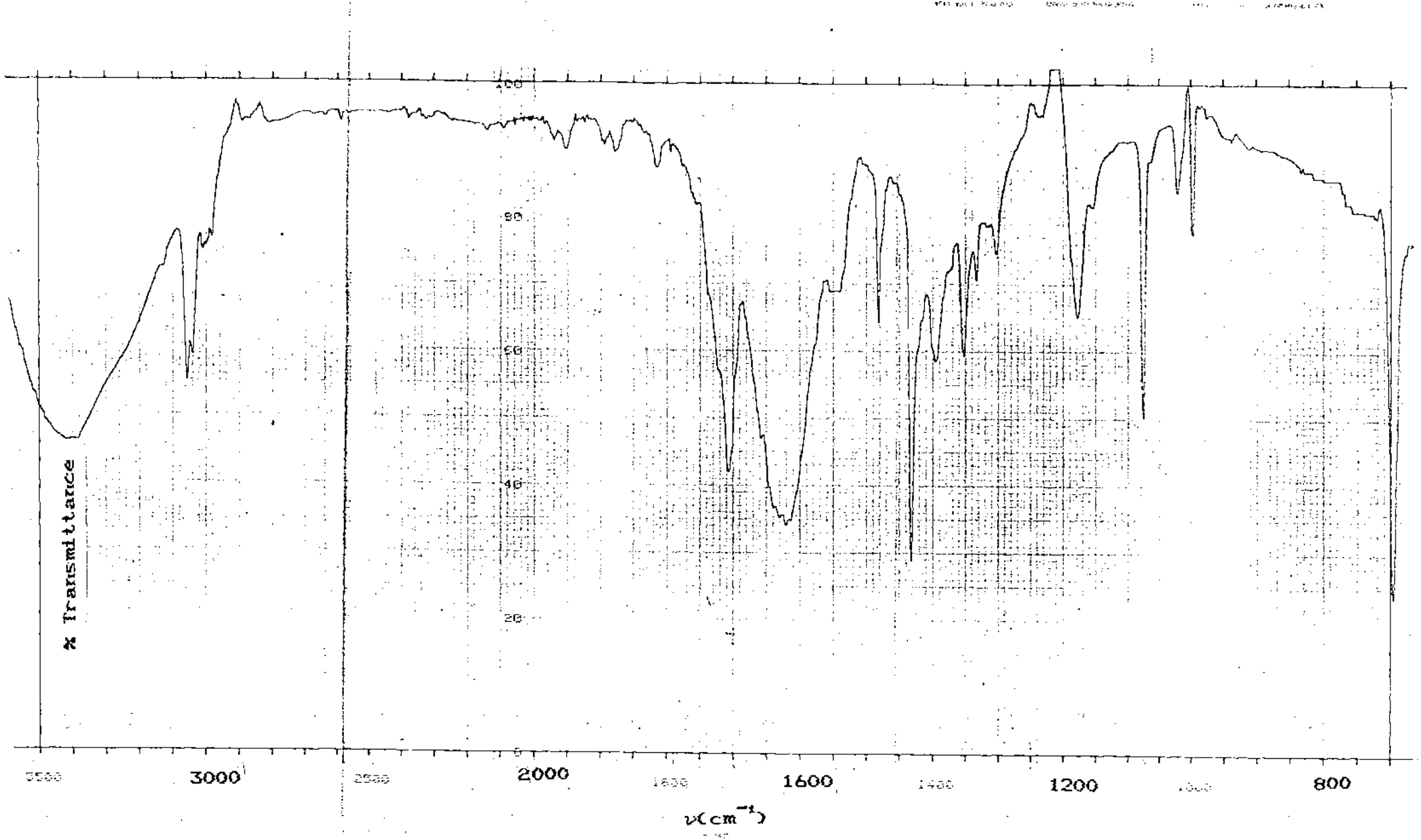


Fig.IV.6. IR Spectrum of Ph_3SnOH PvH in CCl_4.

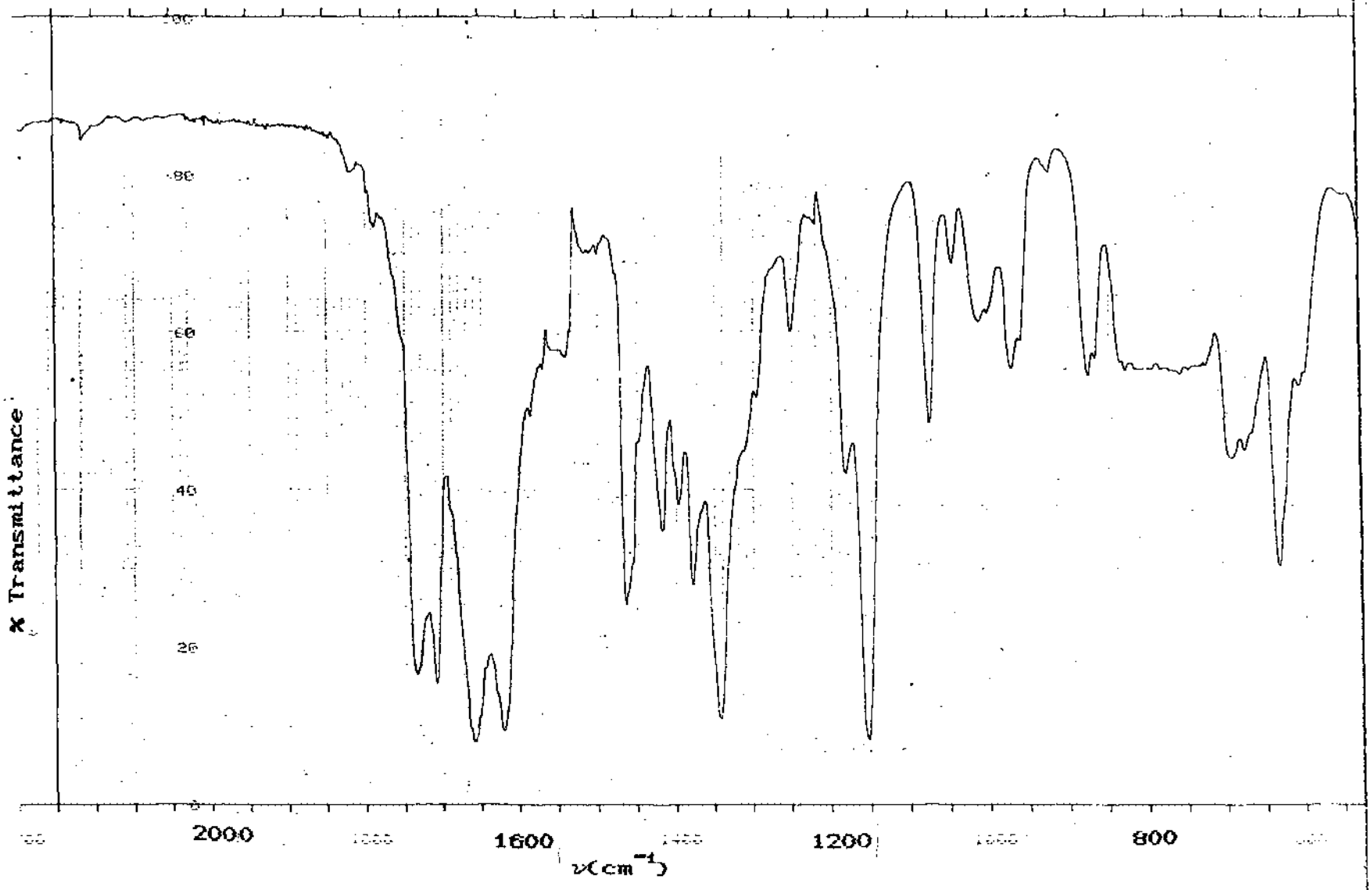


Fig.IV.7. IR Spectrum of $Bu_3SnOH.PyH$ in CCl_4.

assigned to the ketonic C=O and the latter to the C=O group of the carboxylate moiety from a comparison of the spectra of the neat acid, its CCl_4 solution, its Et-ester and that of its Na-salt (figures-III.1,1a,1b, and 1c). In PPvH these bands merge into a broad band around 1688 cm^{-1} because of intramolecular H-bonding.

In each of the addition complexes there is an intense sharp band at 1722-15 cm^{-1} region and several strong peaks near 1600 cm^{-1}. Thus the formation of the addition complex has resulted in a small change in one of the two carbonyl stretch frequencies and a considerably large change in the other compared to the free acid. Of these two frequencies the one undergoing large negative shift should be assigned to $\nu_{C=O}$, because the addition complex can not be stable without the involvement of the ketonic C=O group as pointed out in section IV.1., and if involved, $\nu_{C=O}$ would be expected to be considerably lowered. In the event of nonparticipation of the ketonic C=O group the $\nu_{C=O}$ should remain unaltered relative to the free acid, as has been found in the case of the carboxylate derivatives of benzoyl formic acid (BFH) [section III.3.1.A(ii)] and may even be shifted to higher frequencies as observed for the carboxylato diorganotin hydroxides discussed in section III.3.1.C. Such +ve shift of $\nu_{C=O}$, where the C=O group is nonparticipating, has also been reported by KumarDas et.al.[5] for the triorganotin derivatives of some γ-keto acids.

The band at around 1720 cm^{-1} is, therefore, assigned to ν_{asOCO} and the ν_{sOCO} band in these compounds shows at around 1400 cm^{-1} in the solid state. In $CHCl_3/CCl_4$ solution all these peaks remain almost unaltered.

Thus the IR spectra of these derivatives of PvH and PPvH differ from those of the corresponding organotin ketocarboxylates for which both $\nu_{C=O}$ and ν_{asOCO} appear well below 1600 cm^{-1} in the solid state and both are considerably raised in solution. It may be mentioned here that in the derivatives of BFH, although one of the carbonyl frequencies remains unaltered compared to the free acid, a comparison with its Na-salt reveals that it is the $\nu_{C=O}$ that remains unchanged and the ν_{asOCO} gets sufficiently lowered. Therefore, the derivatives of BFH are regarded to be normal carboxylates and not addition products. This conclusion is also supported by their stability, solubility and chemical reactivity.

The addition compounds also differ from the carboxylato diorganotin hydroxides in that, the $\nu_{C=O}$ frequency is substantially lowered in the former but considerably raised in the latter compounds in comparison to the respective free acids.

The addition complexes also show a strong band around 630 cm^{-1}, which may be assigned to out of plane C=O wag. This is also indicative of the involvement of the keto group in coordination. For $Bu_3SnOH.PPvH$ the apparent lowering in this frequency is due to

the fact that in the free acid the C=O group is involved in intramolecular H-bonding and the carbonyl wag appears at considerably higher frequency (690 cm^{-1}) compared to noninteracting C=O group.

Thus, on the basis of IR spectra it can be said that both the ketonic C=O and the acidic hydrogen of the ligands interact with the organostannoxane in forming the addition complex. It is also interesting to note that the IR frequency, characteristic of the Sn-O-Sn linkage in the stannoxanes, occurring around 780 cm^{-1} is absent in all these derivatives, thereby suggesting the cleavage of this bond during the formation of the addition complexes. Therefore, IR spectra also suggest that the addition complex should be formulated as $R_3SnOH.HL$ and not as $(R_3Sn)_2O.2HL$.

(b) Electronic spectra :

The electronic spectral data of PvH and PPvH shown in table-IV.6. reveal that for both the acids very weak transition bands (ε 10-25) occur in the region 350-385 nm in CCl_4 solution. As pointed out in section III.3.1.A(iii) these bands have been identified as due to $n-\pi^*$ transition of the C=O group, from a comparison of the spectra in polar (MeOH) and nonpolar (CCl_4) solvents.

It can be seen from the table-IV.6. that in the addition complexes the $n-\pi^*$ bands have undergone considerable hypsochromic

Table:-IV.6.

Electronic spectral data of the Addition Complexes :

Compounds.	$n-\pi^*$ peaks (nm) in CCl_4 Sol.	ε_{max}	$n-\pi^*$ peaks (nm) in MeOH Sol.
$CH_3COCOOH$	370, 350,	9, 13	330
(PvH)	335(sh)		
$Ph_3SnOH.PvH$	335	22.5	310
$Bu_3SnOH.PvH$	345	59.5	305
$PhCH_2COCOOH$	385, 368,	16.5, 23	340
(PPvH)	306, 293		
$Bu_3SnOH.PPvH$	360,306,293		

sh-shoulder.

shift and appear in the region 335-345 nm. This can be accounted for only by assuming the involvement of the C=O group in binding, which stabilises the n-orbital. This suggests that the addition complexes are formed through a nucleophilic attack by the carbonyl oxygen on a tin centre of the stannoxane. Thus, electronic spectra also support the inference drawn on the basis of IR spectral data.

It should also be noted that the blue shift of the $n-\pi^*$ band in an addition complex, though large, is not as large as in the corresponding keto carboxylate [section III.3.1.A(iii)). Therefore, it may be inferred that the Sn—O (carbonyl) bond in an addition compound is weaker than the same bond in the keto

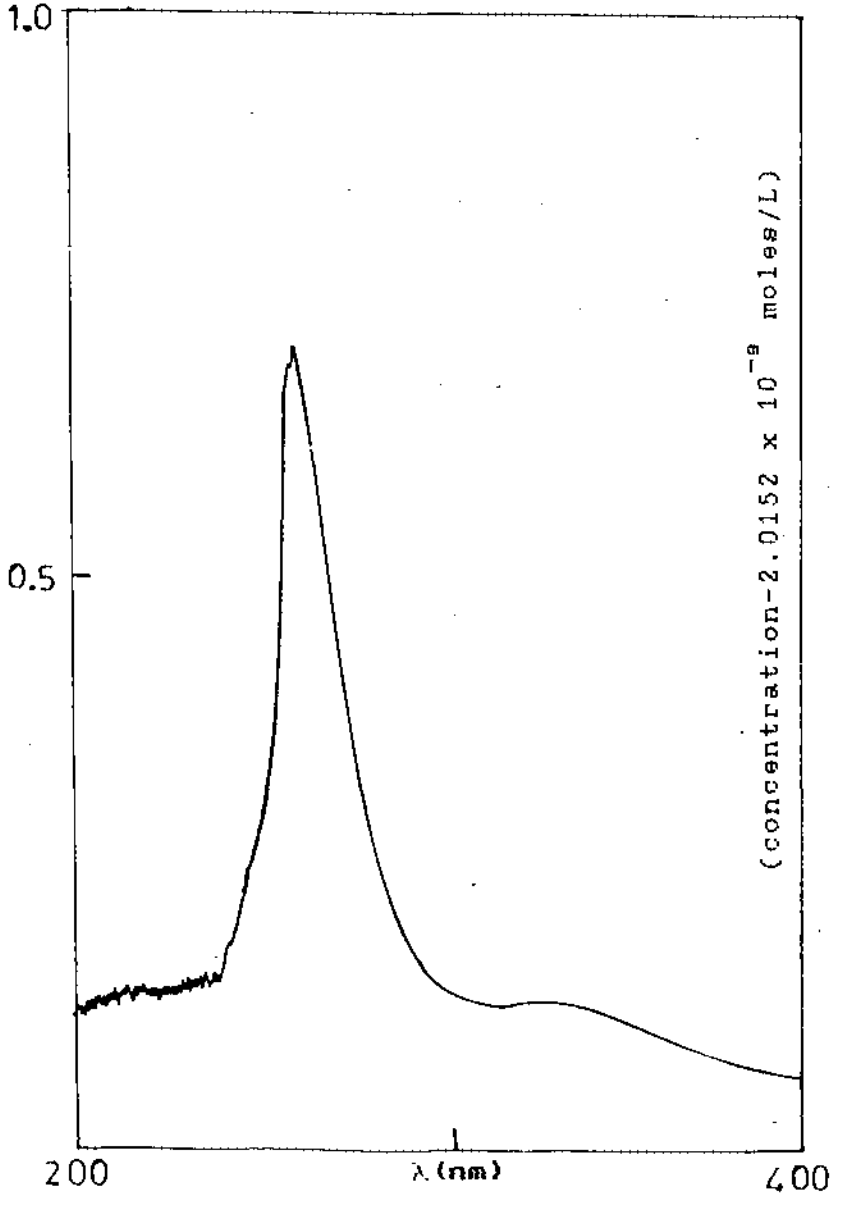


Fig.IV.9. Electronic spectrum of $Bu_3SnOH.PvH$ in CCl_4.

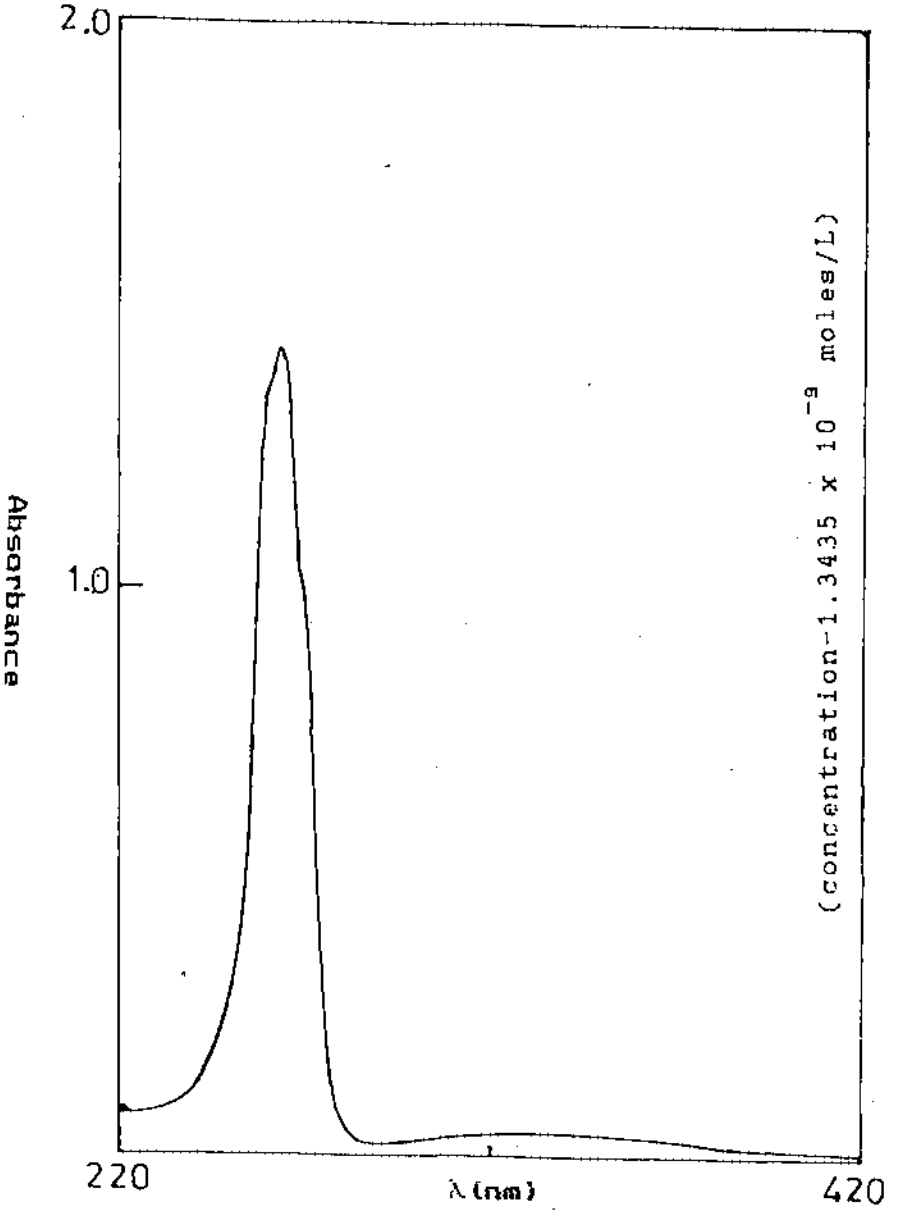


Fig.IV.8. Electronic spectrum of $Ph_3SnOH.PvH$ in CCl_4.

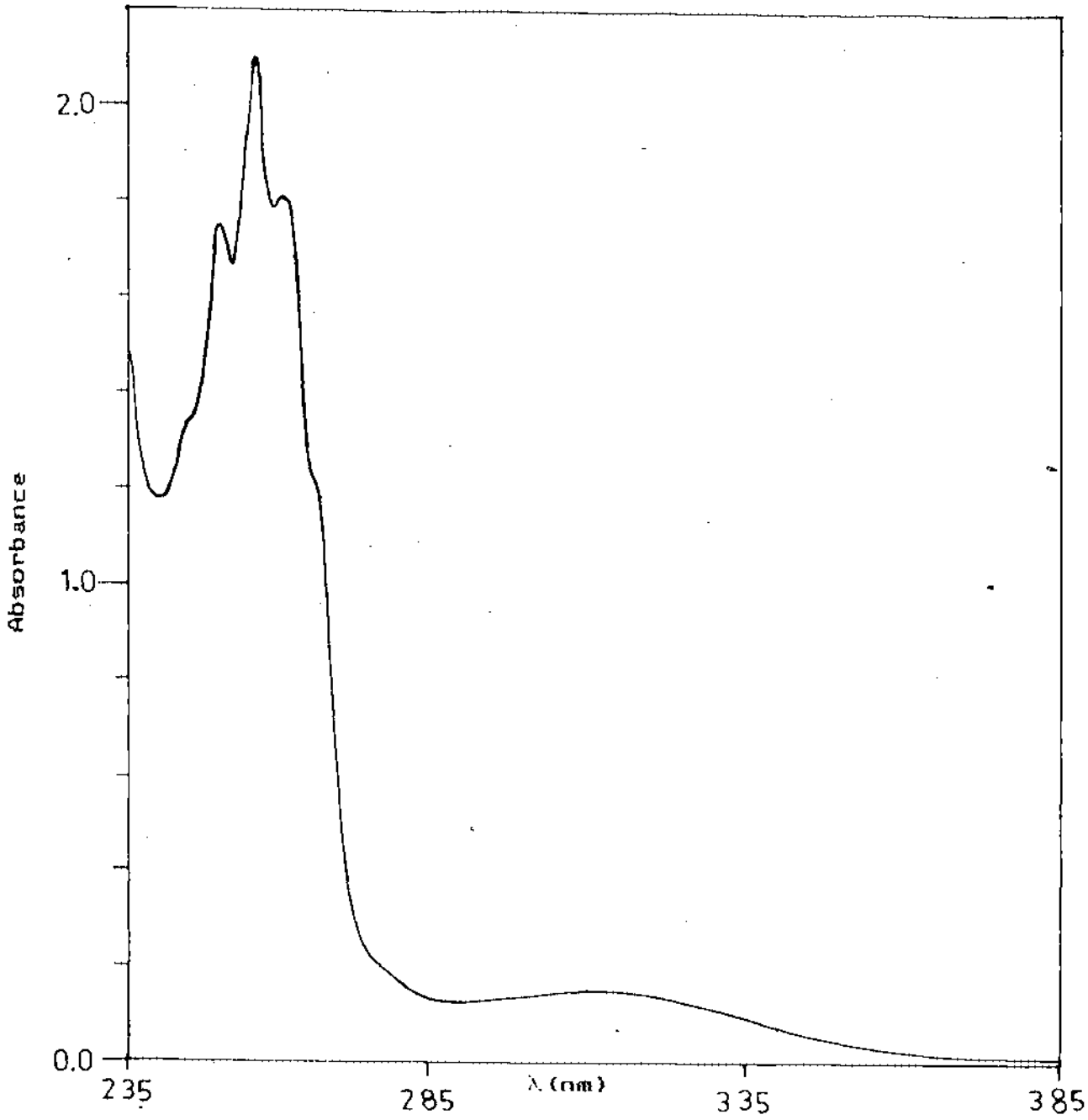


Fig. IV. 8a. Electronic spectrum of $Ph_3SnOH.PyH$ in MeOH.

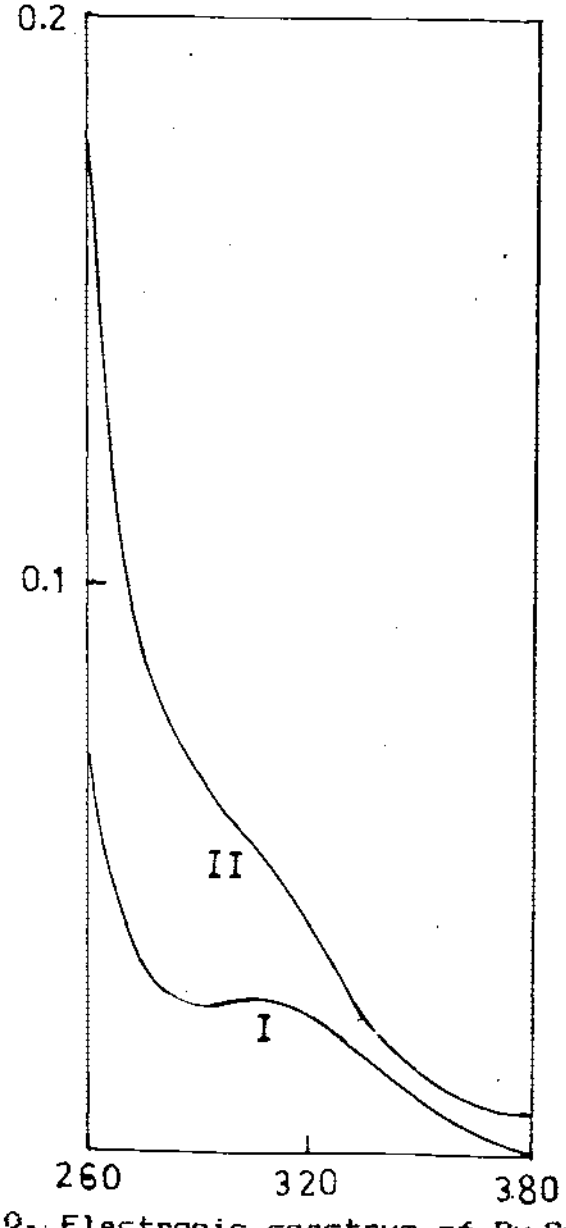


Fig.IV.10. Electronic spectrum of $Bu_3SnOH.PvH$ (I) and Bu_3SnPv (II) in MeOH.

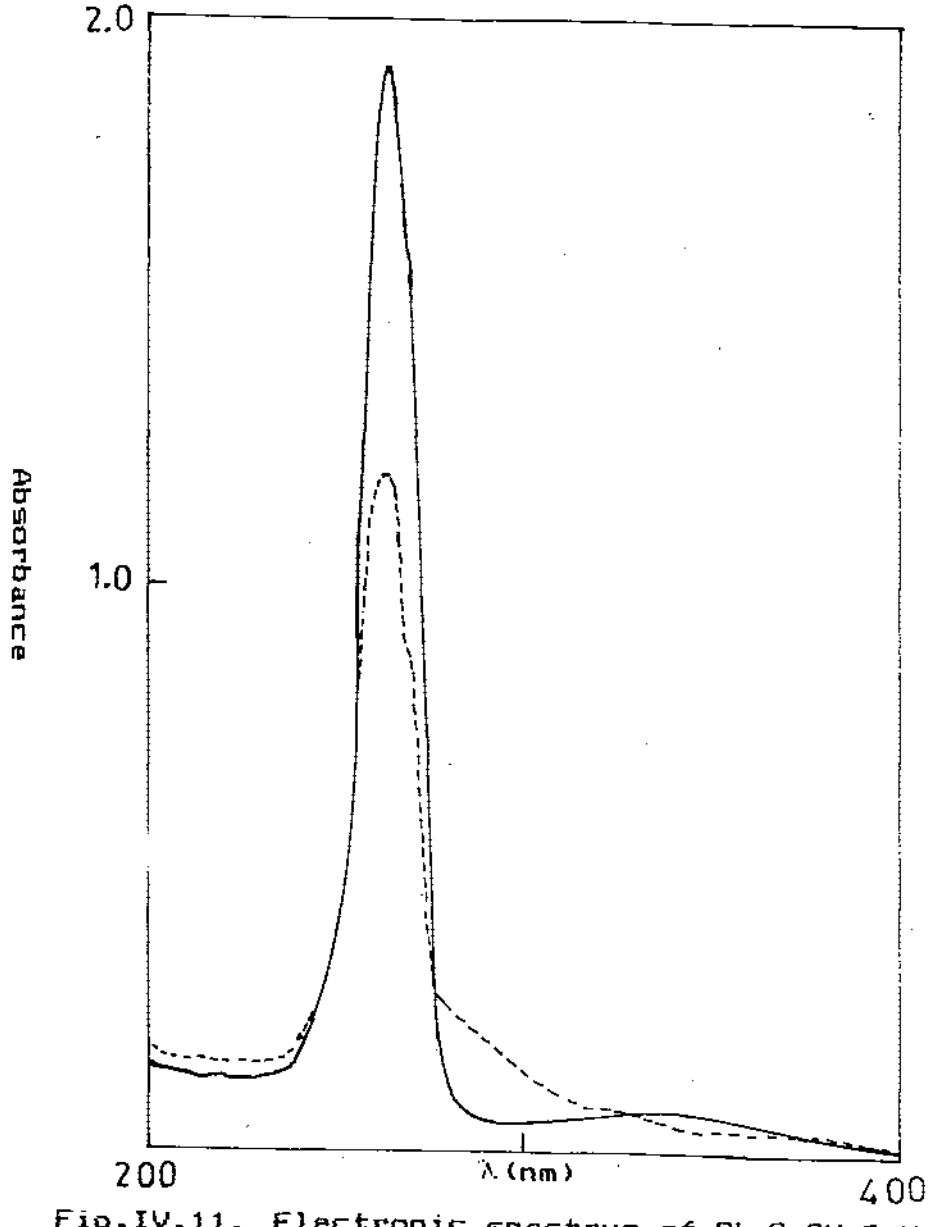


Fig.IV.11. Electronic spectrum of $Ph_3SnOH.PvH$ (———) and Ph_3SnPv (- - - - - - -) in CCl_4.

carboxylate and may be cleaved during the transformation of the former into more stable compounds.

In the addition compounds also, the short wave length bands originating from the π-π^* transition of the carbonyl group and n-π^* transition of the acid get superimposed among themselves as well as with the vibrational fine structures of the Ph-ring and are of little diagnostic value.

Absorption spectra in the UV region of the ligands and some of their derivatives are given in figures IV.8.-IV.11.

(c) PMR Spectra :

The PMR spectra, recorded for the two addition complexes $Ph_3SnOH.PvH$ and $Bu_3SnOH.PvH$, provide further supporting evidence for the inferences already drawn.

In the ^1H NMR spectra of $Ph_3SnOH.PvH$ [fig-IV.12] the COOH proton appears at δ 7.132ppm as a sharp singlet. Although in the uncomplexed acid this proton appears at δ 8.64ppm, the IR spectra of the acid and its ethyl ester clearly show that the acid exists as a hydrogen bonded dimer and the proton signal is expected to appear at low field. These data suggest that in the addition complex the acidic proton is relatively weakly hydrogen bonded to the Sn—O oxygen.

In the case of the tributyl tin adduct of pyruvic acid a sharp peak at δ = 2.43ppm (1H) is observed which can be assigned

to the COOH proton. It is well known that, the electronegativity of the oxygen in tributyltin oxide is lower than that of triphenyltin oxide. The former is, therefore, expected to form weaker hydrogen bonding than the latter, in its adduct and the appearance of the COOH proton at high field agrees well with this.

It can be seen from table-IV.7. that triphenyltin hydroxide in $CDCl_3/DMSO\text{-}d_6$ shows a NMR absorption at δ 3.6ppm corresponding to one proton. On deuterium exchange, this peak vanishes, confirming the peak to be due to OH proton. The adduct $Ph_3SnOH.PvH$ shows a peak due to single proton at δ 1.582ppm. Although this peak is at considerably higher field compared to that of Ph_3SnOH, this could reasonably be assigned to the Sn—OH in the adduct. The reason for such upward shift may be attributed to the following factors.

Due to the low solubility of Ph_3SnOH in $CDCl_3$ the NMR spectra was taken in $CDCl_3/DMSO\text{-}d_6$ mixture. Without doubt, there would be interaction between DMSO and Ph_3SnOH. DMSO can coordinate to Sn-atom and also it is almost certain to form H-bond with the Sn—OH proton. It is well known that H-bond formation shifts the signal considerably downfield. The adduct, on the other hand, is not expected to form any such H-bond, firstly because, the solvent was $CDCl_3$ and secondly, the proposed structure precludes the possibility of H-bond without a structural change. Therefore, the

peak at δ 1.582ppm, corresponding to a single proton, is reasonably assigned to Sn—OH. This is also consistent with the evidences obtained through IR and UV spectra as well as chemical reactivities of the adducts, presented earlier.

Although the position of the Sn—OH proton in the tributyl tin adduct of PvH cannot be precisely ascertained, the relative intensity of the peaks in the methylene region (δ 1.3—1.566ppm, 19H) shows the presence of an extra proton. This may be attributed to the Sn—OH by comparison with the position of the same proton in the triphenyl tin complex.

The CH_3 proton of the ligand part in the tributyl and triphenyl complexes appear at δ 1.03 and 2.34ppm respectively. Although the chemical shifts of the CH_3(ligand) protons in these complexes are large, they are significantly different from those of the corresponding keto carboxylates (δ 1.142-1.355ppm for the tributyl and δ 2.13ppm for the triphenyl tin pyruvate). This is presumably, due to the larger polarity of the Sn—O bond in the carboxylates than in the addition complexes. In both the cases the ability of the adjacent C=O group to deshield the CH_3 protons is lowered due to the involvement of the carbonyl group in coordination and cannot drastically influence the peak positions.

Table :- IV.7.

PMR data of addition complexes :

Compounds.	Peak position (δ ppm) and assignments.
$Ph_3SnOH.PvH$	1.582, (s), 1H, Sn-OH; 2.34, (s), 3H, CH_3(PvH) 7.132, (s), 1H, COOH; 7.34-7.37, (m), and 7.6-7.65, (m), 15H, aromatic.
$Bu_3SnOH.PvH$	0.967, (t), 9H, CH_3(Bu); 1.03, (s), 3H, CH_3(Pv) 1.3-1.56, (m), (18+1)H, CH_2(Bu) and Sn-OH 2.43, (s), 1H, COOH.
PvH	2,56, (s), 3H, CH_3; 8 64, (s), 1H, COOH
Ph_3SnOH	3.6[a], (s), 1H, Sn-OH; 7.2-7.65, 15H, aromatic.

a-concentration dependent.

(iv) Reaction of Ph_3SnOH with $CH_3COCOOH$ (PvH) :

In view of the aforesaid formulation of the addition complex one would expect that the compounds should be produced from the reaction of R'COCOOH (HL) with R_3SnOH as well as with $(R_3Sn)_2O$. We have observed exactly the same by allowing $CH_3COCOOH$ (PvH) to react with Ph_3SnOH.

When Ph_3SnOH and pyruvic acid in 1:1 ratio were stirred in cold ether for about 30 minutes, the product was found to be identical with the product obtained from $(Ph_3Sn)_2O$ and PvH, on the

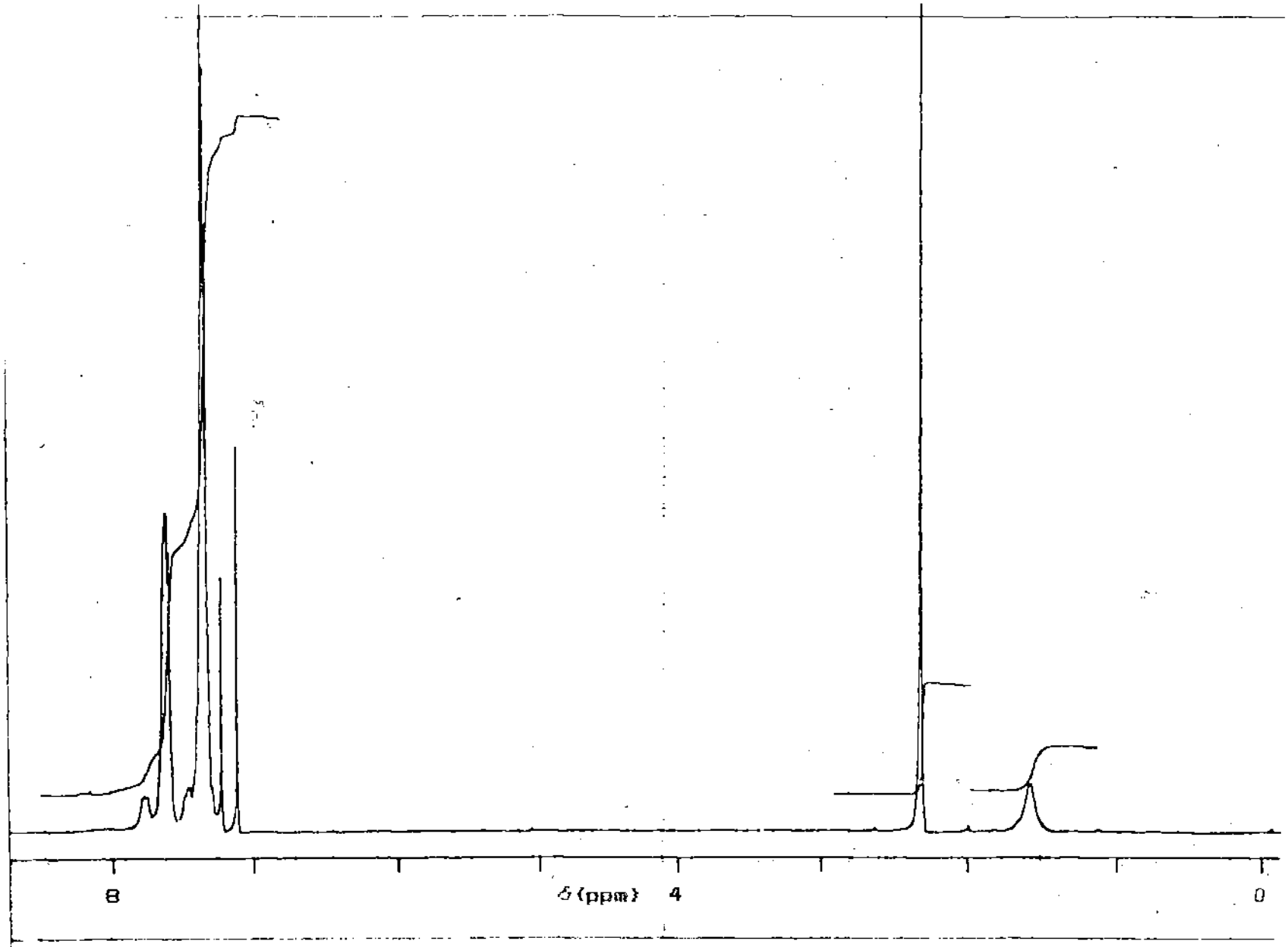


Fig.IV.12. ^{1}H NMR spectrum of $Ph_3SnOH.PyH$ in $CDCl_3$.

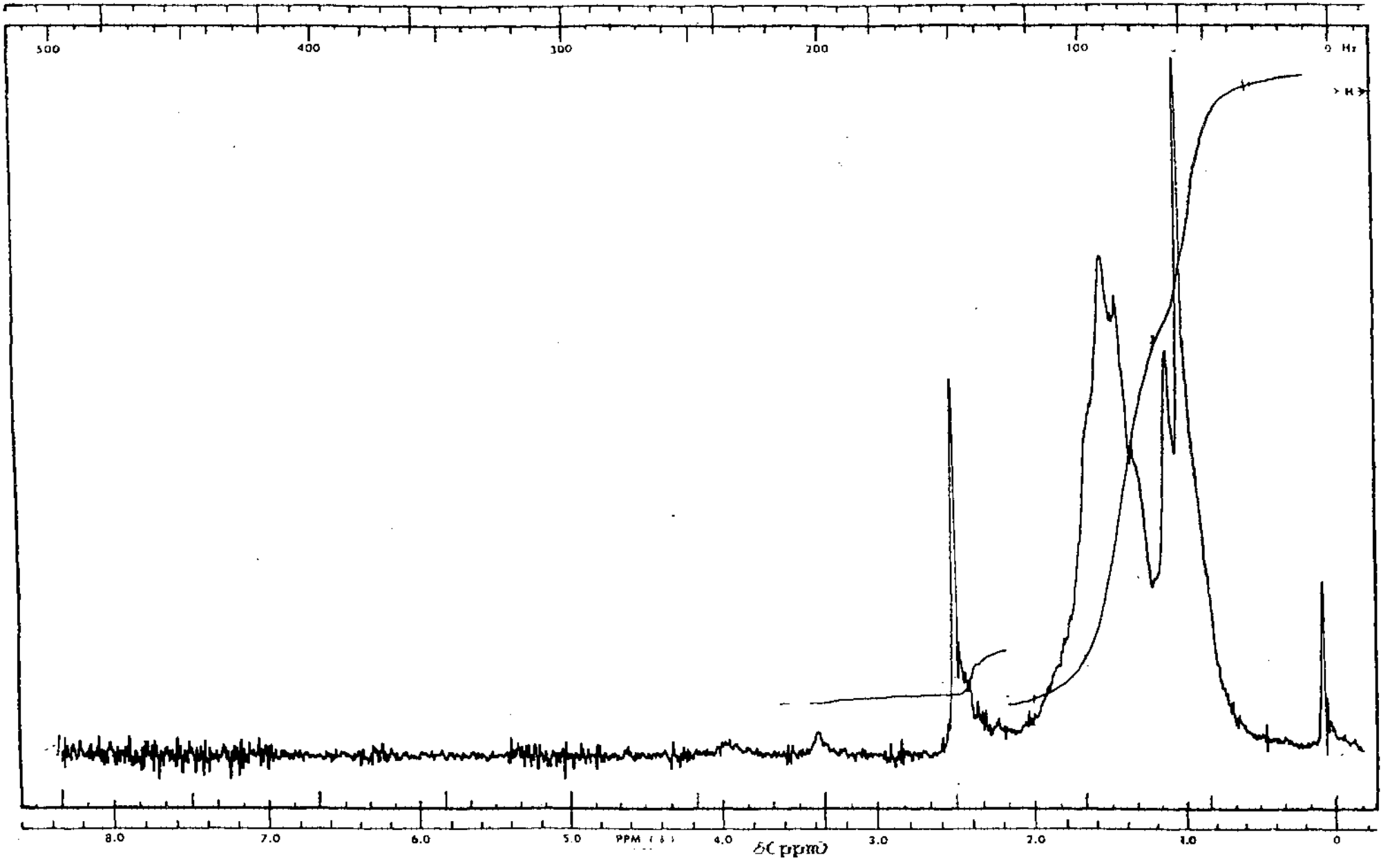
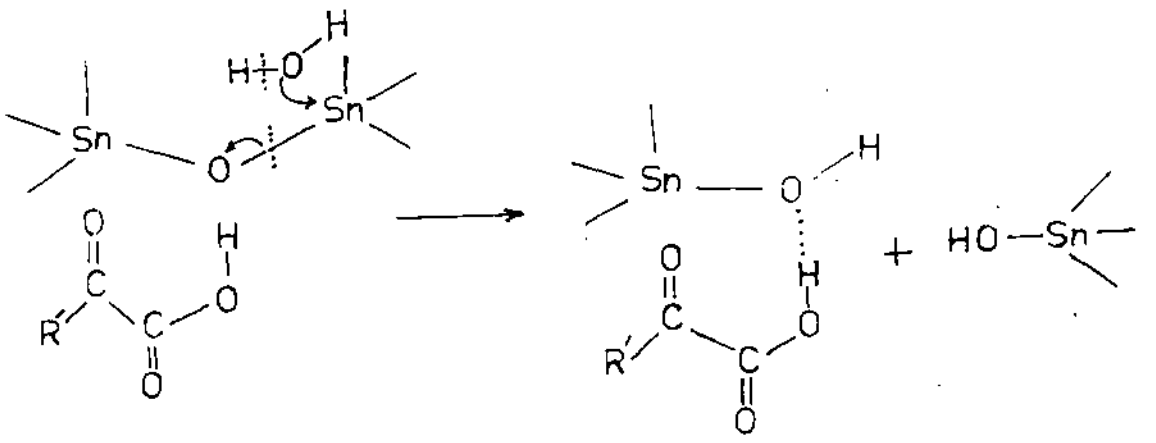


Fig.IV.13. ^{1}H NMR spectrum of $Bu_3SnOH.PvH$ in $CDCl_3$.

basis of mixed melting point, elemental analysis and IR data. The formation of the same compound through the two routes and absence of any Sn-O-Sn band in the IR spectrum of the said compound suggest that it should be formulated as $Ph_3SnOH.PvH$. This is also supported by the presence of Sn-OH band at 3620 cm^{-1} in the IR spectrum of this compound.

This reaction, therefore, corroborates the IR spectral evidence that the Sn-O-Sn bond of the stannoxane must have been broken during the electrophilic attack on it by the carboxylic acid as shown below, without regard to the role played by the keto group.



The water necessary for such a cleavage becomes readily available because pyruvic acid invariably remains associated with some water and the reactions could not be carried out under anaerobic conditions.

Although the nature and stability of the product is not determined solely by the aforesaid electrophilic attack, as has already been pointed out in section IV.1, the above reaction clearly shows the role played by the acidic H-atom in initiating the process. The importance of the presence of the acidic H-atom and its involvement in the reaction is also brought out by the following observation.

(v) Treatment of $CH_3COCOOEt$ with Ph_3SnOH / $(Ph_3Sn)_2O$:

A well known method for the preparation of organotin carboxylates involves the reaction of either the organotin hydroxide or oxide with the esters of carboxylic acids[6,7] according to the following equations :

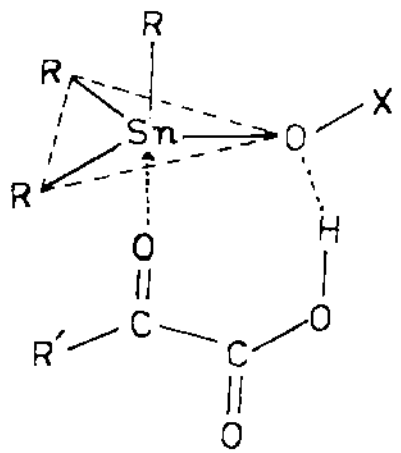
$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH \text{ -------[2]}$$

$$(R_3Sn)_2O + R'COOEt \longrightarrow R_3SnOCOR' + R_3SnOEt \text{ -----[3]}$$

Accordingly, ethyl pyruvate was allowed to react with organotin hydroxides or oxides either by stirring or by refluxing in benzene/solvent ether. But neither the carboxylate nor the addition product was obtained in any case. The not so well-defined products obtained in some cases gave the organotin oxides back on recrystallisation from benzene.

The failure of these reactions suggest that the OH group of the carboxylic function must be involved in the formation of the addition complex.

In the light of the spectroscopic and other evidences cited so far, one must be inclined to infer that these derivatives of PvH and PPvH are a unique class of addition compounds of the organostannoxanes and keto acids and the only probable structure that can explain all the observations is shown in III.B.



III B

However, such a structure is not expected to be highly stable, because of unfavourable ring size and high affinity of tin for oxygen. This is reflected in the fact that the addition complexes are particularly unstable towards heat and when refluxed in benzene or solvent ether undergo gradual transformation giving several products, accompanied by Sn—C bond cleavage.

(vi) Transformation of the addition product when refluxed :

The transformation reactions for the most typical of the addition products, the triphenyl tin derivative of PvH, has been

investigated in some detail and the cleavage products have been identified, For the other addition products the separation and characterisation of the cleavage products could not be achieved.

Thus, when the triphenyl tin derivative of PvH was refluxed in dry ether for about an hour, a white solid, which could be formulated as $Ph_2Sn(Pv)OH$ on the basis of elemental analysis and IR spectrum, separated. When the solvent was carefully distilled off, the distillate was found to contain benzene, which was identified spectrophotometrically. When heating under reflux was continued for long periods, the separated light yellow solid could be formulated as $[PhSn(Pv)O]_n$. The same sequence of reactions was also observed when $(Ph_3Sn)_2O$ and PvH, in 1:2 mole ratio, were refluxed in benzene or solvent ether under the same conditions. Minute quantities of another product, viz., Ph_3SnPv was also obtained, when after refluxing for about half an hour the supernatant liquid was evaporated at room temperature and extracted with petroleum ether. When prolonged heating was done in benzene small amount of Ph_4Sn was obtained in addition to the other products, but Ph_3SnPv could not be obtained.

From these observations it may be inferred that the principal mode of interaction between $(Ph_3Sn)_2O$ and PvH always leads to the formation of the addition product, which transforms into the other compounds through cleavage reaction, under more

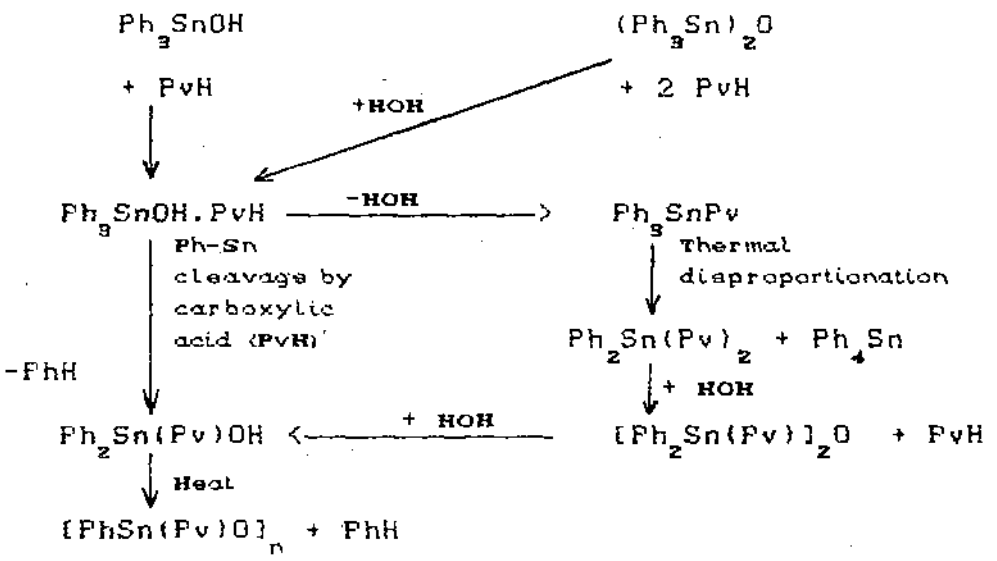
drastic condition. The direct reaction between the stannoxane and PvH leading to Ph_3SnPv seems to be less favoured.

The structure III.B, proposed for the addition product, accounts for its high susceptibility to cleavage and suggest that it would behave as a precursor to more stable compounds such as $Ph_2Sn(Pv)OH$ or the keto carboxylate. The formation of $Ph_2Sn(Pv)OH$, which is the principal mode of transformation of the addition product, requires the cleavage of the Sn—Ph bond, largely known to be induced by protic[8-11] and chelating[12] agents. The loosely bound keto acid molecule in the addition complex is most likely to provide an ideal protic agent, which causes phenyl-tin cleavage, that accounts for the production of benzene when $Ph_3SnOH.PvH$ is refluxed.

The formation of Ph_4Sn from prolonged heating under reflux in benzene, of the addition complex, may be attributed to thermal disproportionation of Ph_3SnPv, formed in the course of the reaction. Considering the very low yield of this product it can be concluded that only a small fraction of the addition complex pass through these changes. This would also explain the non availability of Ph_3SnPv when heating is continued for long. Although thermal disproportionation of triorgano tin carboxylates are known to occur at their melting points[13] and when refluxed in pyridine (Bp. 115°C)[14], a definite comment on the thermal

disproportionation of Ph_3SnPv would require more detailed investigation.

Considering all the above facts the formation and the subsequent transformations of the typical addition complex $Ph_3SnOH.PvH$ may be represented by the following scheme.



IV.3.2. *Conclusion :*

On the basis of the foregoing discussions it can be concluded that some α-keto carboxylic acids react with triorgano tin oxides and hydroxides forming a unique class of addition complexes, which may be represented by structure III.B, and that their formation is governed predominantly, among various factors, by the basicity of the ketonic oxygen atom, which is profoundly

influenced by the electronic and steric factors originating at the R' group.

Since these complexes are inherently unstable and are transformed into more stable products when heated, probably in several different ways, understanding their structures may help in designing new carboxylate ligands, which can possibly be helpful in the isolation of intermediate complexes, believed to be the first step in the reaction between the stannoxanes and carboxylic acids.

Bibliography.

1. Paul R.C., Sharma R.K., Walia R. and Narula S.P., *Ind. J. Chem.*, 1978, 16A, 544.
2. Eaborn C., *Organotin Compounds.*, Butterworth, London, 1960, P-103.
3. Dutta D.R., Majee B. and Ghosh A.K., *J. Organomet. Chem.*, 1971, 29, 251.
4. Vogel A.I., *A Text Book of Practical Organic Chemistry.*, ELBS, 3rd.Ed., Reprinted 1971.
5. Ng S.W., Chen W., Yap C.K., KumarDas V.G. and Mak T.C.W., *J. Organomet. Chem.*, 1986, 311, 289.
6. Biswas G., Ph.D. Thesis, North Bengal Univ., India, 1977.
7. Anderson H.H., *Inorg. Chem.*, 1964, 3, 912.
8. Sasin R. and Sasin G., *J. Org. Chem.*, 1955, 20, 770.
9. Koton M.M., *Zh. Obshch. Khim.*, 1956, 26, 3581.
10. Clark H.C., O'Brien R.J. and Fickard A.L., *J. Organomet. Chem.*, 1965, 4, 43.
11. Peruzzo V., Plazzogna G. and Tagliavini G., *J. Organomet. Chem.*, 1972, 40, 121.
12. Nelson W.H. and Martin D.F., *J. Organomet. Chem.*, 1965, 4, 67 and references cited therein.
13. Seyferth D. and Burlitch J.M., *Z. Naturforsch.*, 1967, 22B, 1358.
14. Deacon G.B. and Farquharson G.J., *J. Organomet. Chem.*, 1977, 135, 73.

NORTH BENGAL
University Library
Raja Rammohunpur