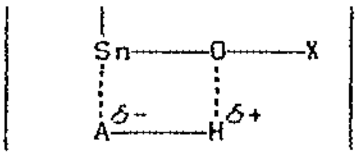
CHAPTER-IV

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



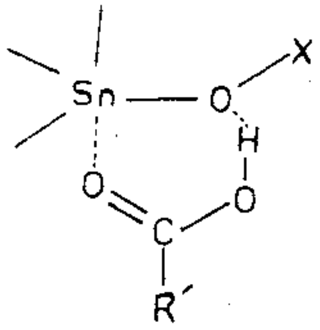
; X = Sn / H

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 $-20^{\circ}C$. $(Ph_3Sn)_2O \longrightarrow SO_3$ converts into $(Ph_3Sn)_2SO_4$ on being refluxed in the same solvent.

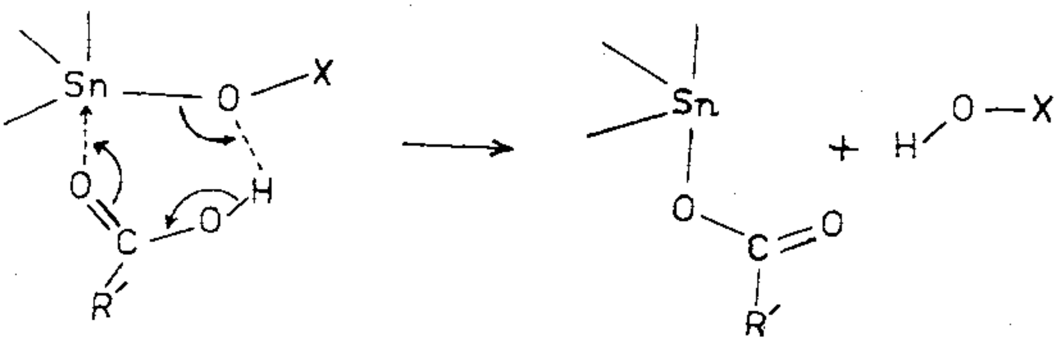
In the reaction between organotin oxides and carboxylic acids in non-ionising solvents, although there is no direct evidence, the following cyclic intermediate is expected to be formed through a H-bond between the Sn—O atom and the acidic

H-atom, assisted by a nucleophilic attack by the carbonyl O-atom at the tin atom.



II

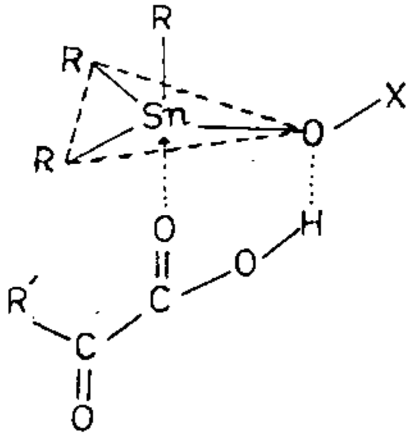
This is quite similar to the transition state proposed for the reaction of siloxanes with $AlCl_3$[2] and the reaction of $(Ph_3Sn)_2O$ with HgX_2[3], and does not seem very unlikely in view of the known donor property of the stannoxanes, discussed in chapter-I. Normally, such an intermediate [II] should undergo instantaneous electron shifts as shown below, leading to the organotin carboxylates.



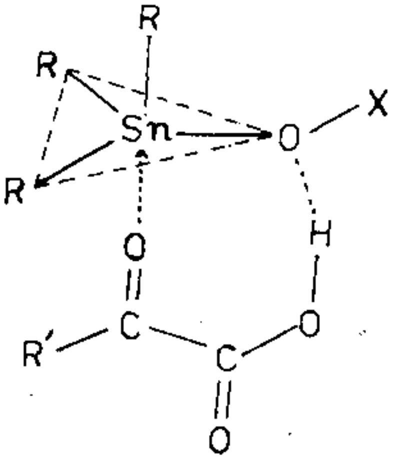
Obviously, the stabilisation of the intermediate II, if at all formed, will depend not only upon the donor-acceptor property of the oxo-organotin compounds, but also upon the presence of other potential donor sites in the $R'COO^-$ moiety, electronegativity and steric factors.

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 ($pK_a < 3.0$) 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



IIIA

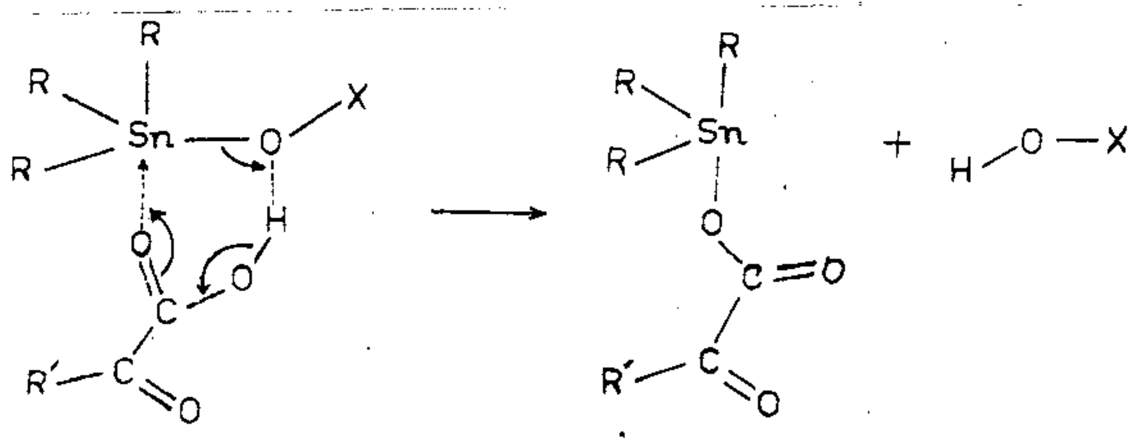


IIIB

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°C (d).

Analysis :	% Sn	% C	% H
Found :	25.86	56.5	4.5
Calculated for $Ph_3SnOH.PvH$:	25.99	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, $146^{\circ}C$(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, $146^{\circ}C$(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, $72-74^{\circ}C$
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 $5^{\circ}C$. Product washed with cold pet.ether.	5 min.	$Bu_3Sn.PPvH$	60, $88^{\circ}C$
6.	Ph_3SnOH + BFH (1:1)	Stirred in cold ether with slight excess acid. Product washed with cold ether.	30 min.	Ph_3SnBF	95, $149^{\circ}C$

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' R (Taft's const.)	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

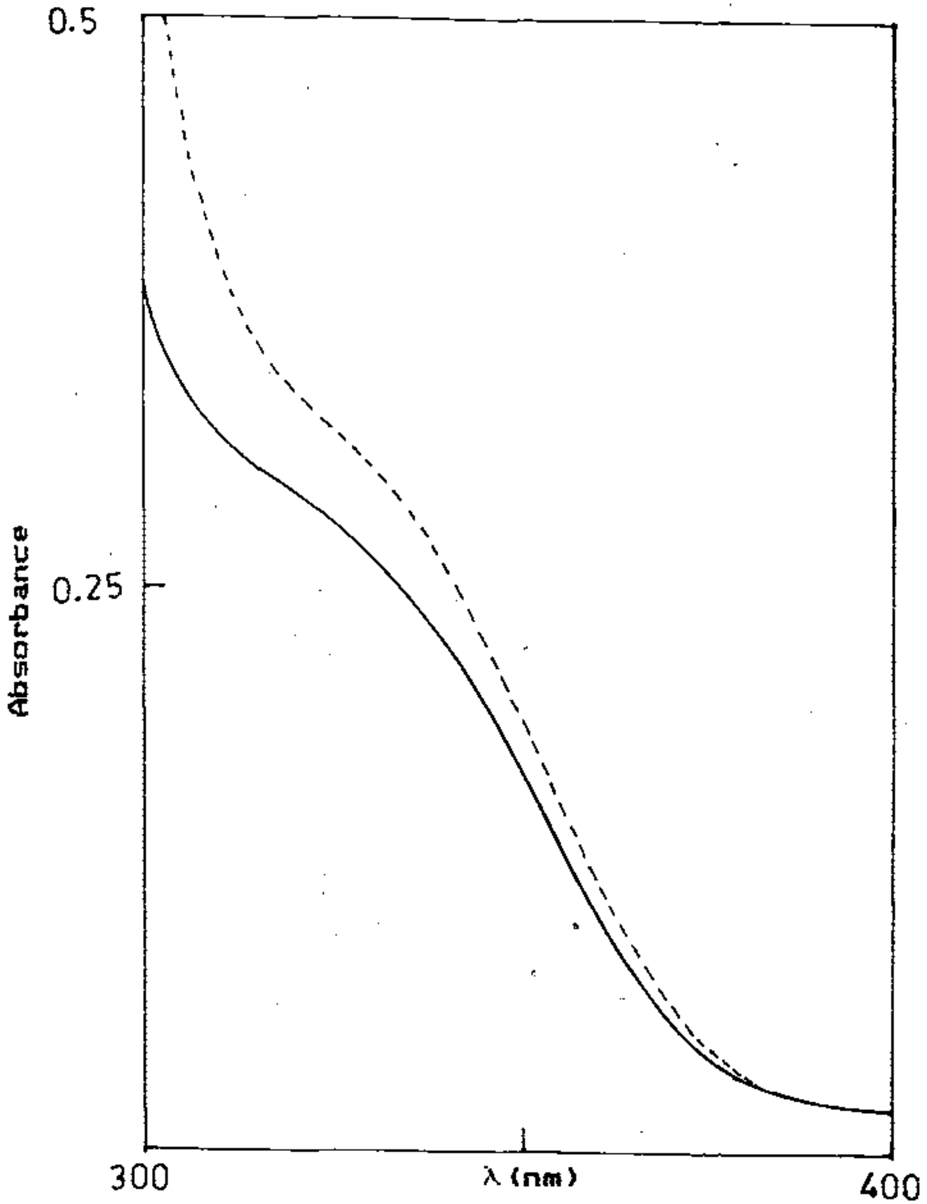


Fig.IV.1. Electronic spectrum of NaPv (in water) from neutralisation of PvH (-------) and decomposition of $Ph_3SnOH.PvH$ (———).

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.	$(Bu_3Sn)_2O$ + PvH	0.086803	21.0 cc 1.111525 N/100	0.02054	0.019387
2.	$(Ph_3Sn)_2O$ + PvH	0.101113	21.3 cc 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 PPvH 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 frequencies (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	1688^b	1688^b	1248 1195	695	-			
8.	$Bu_3SnOH.PPvH$	3425	1620	1725	1402	680 635	-			

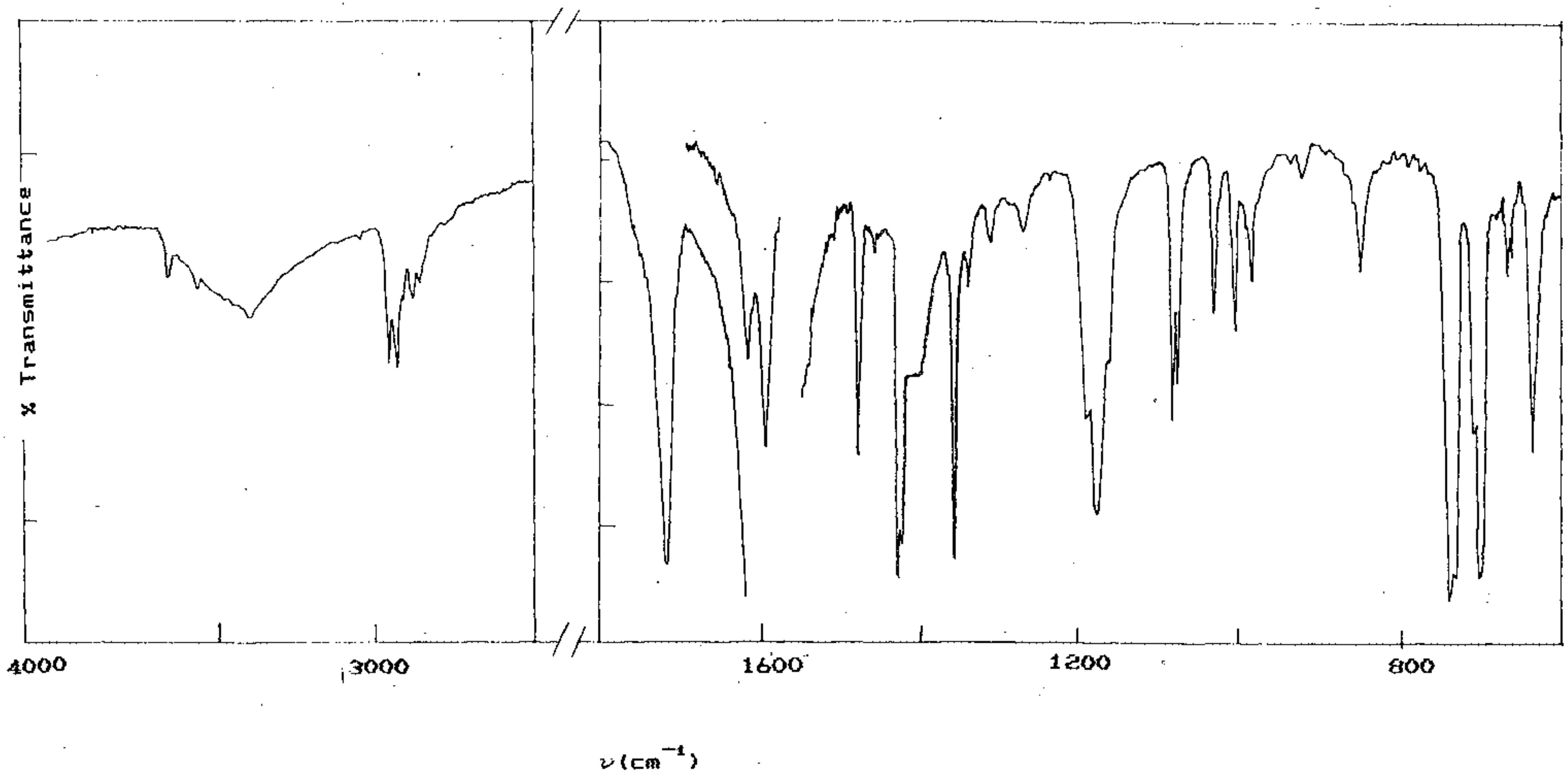


Fig.IV.2. IR Spectrum of $Ph_3SnOH.PvH$ in KBr.

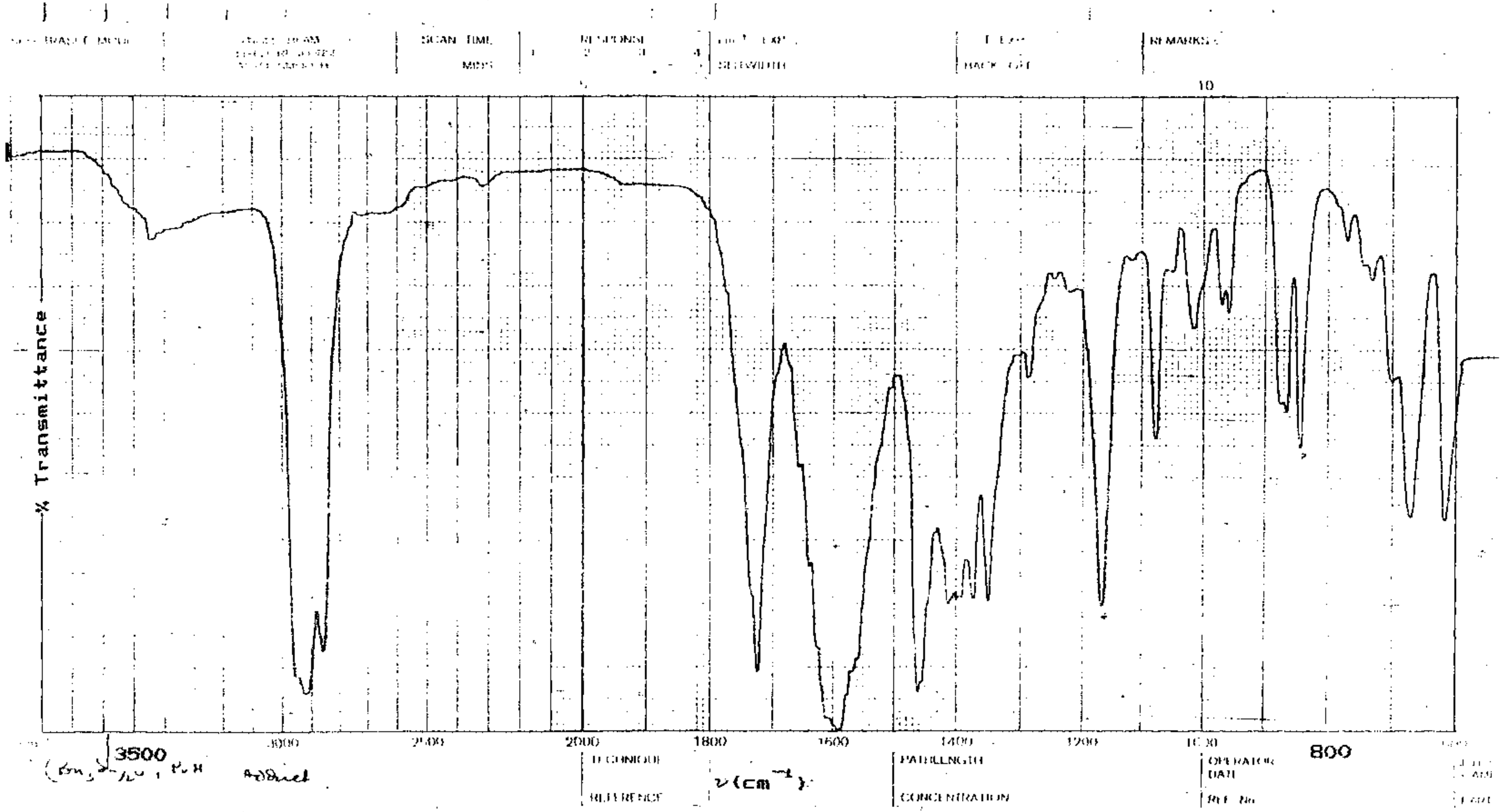


Fig.IV.3. IR Spectrum of Bu$_3$SnOH.PvH in Nujol.

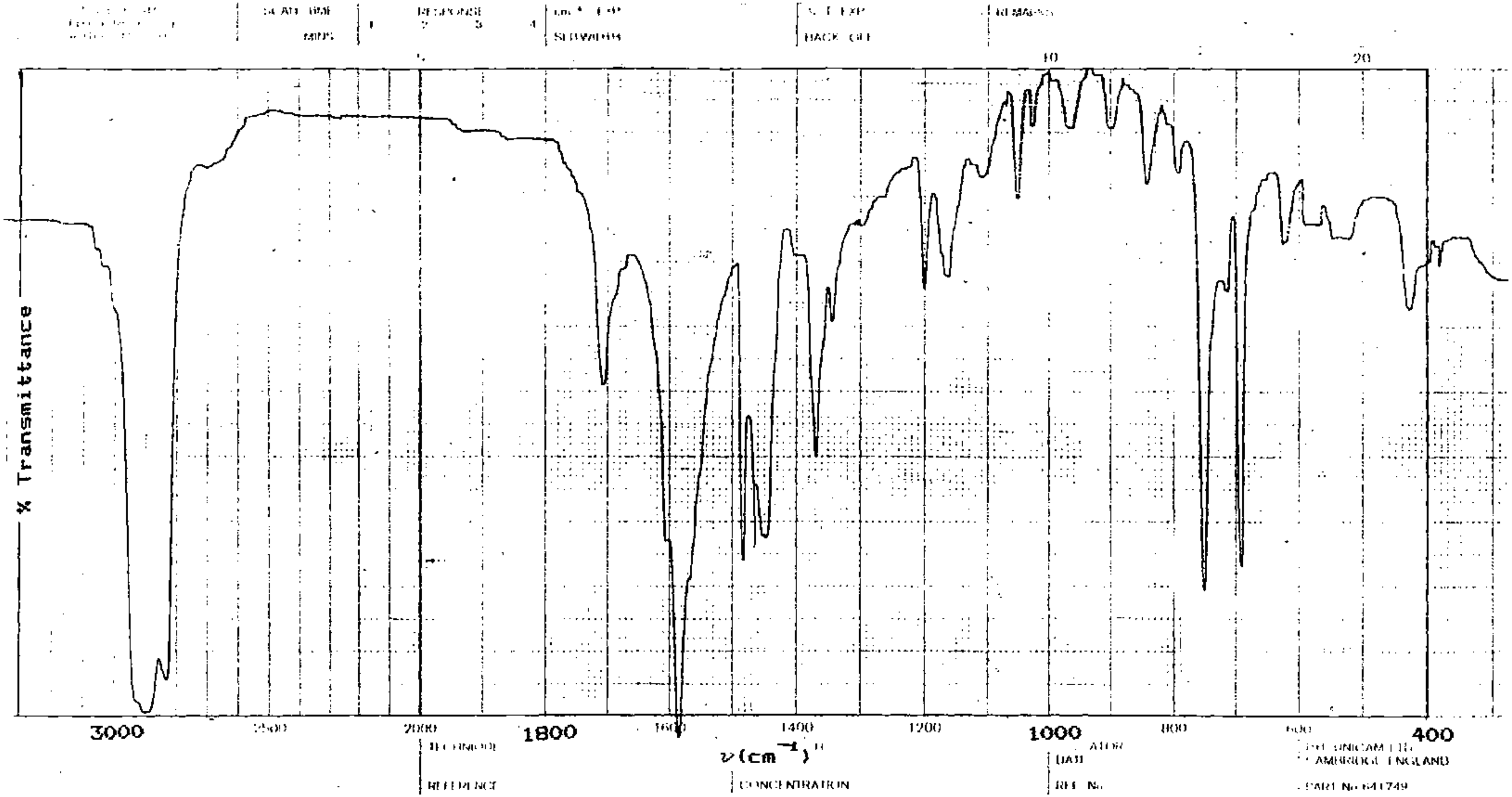


Fig.IV.4. IR Spectrum of Bz_3SnOH.PvH in Nujol.

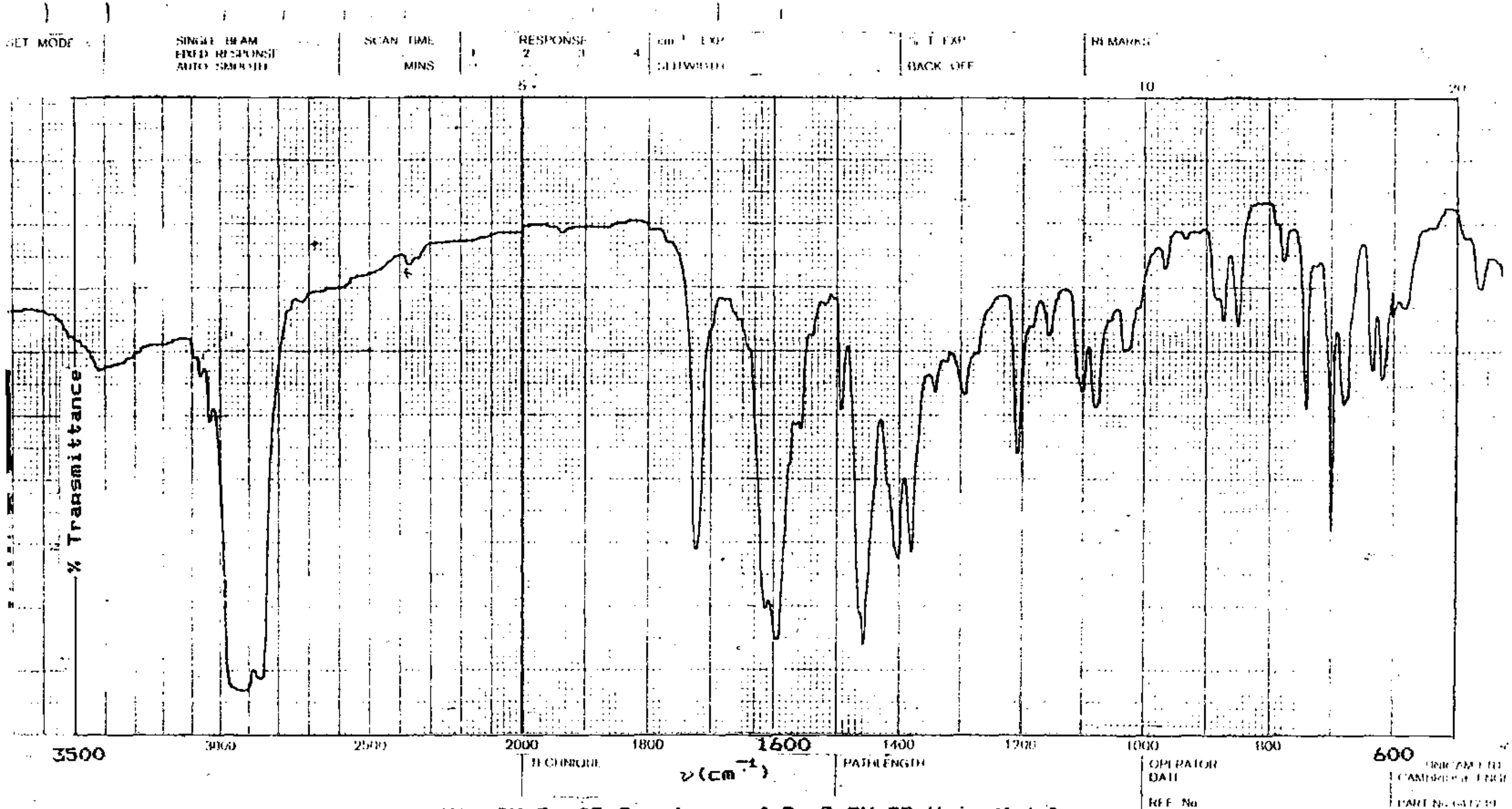


Fig.IV.5. IR Spectrum of Bu$_3$SnOH.PPvH in Nujol.

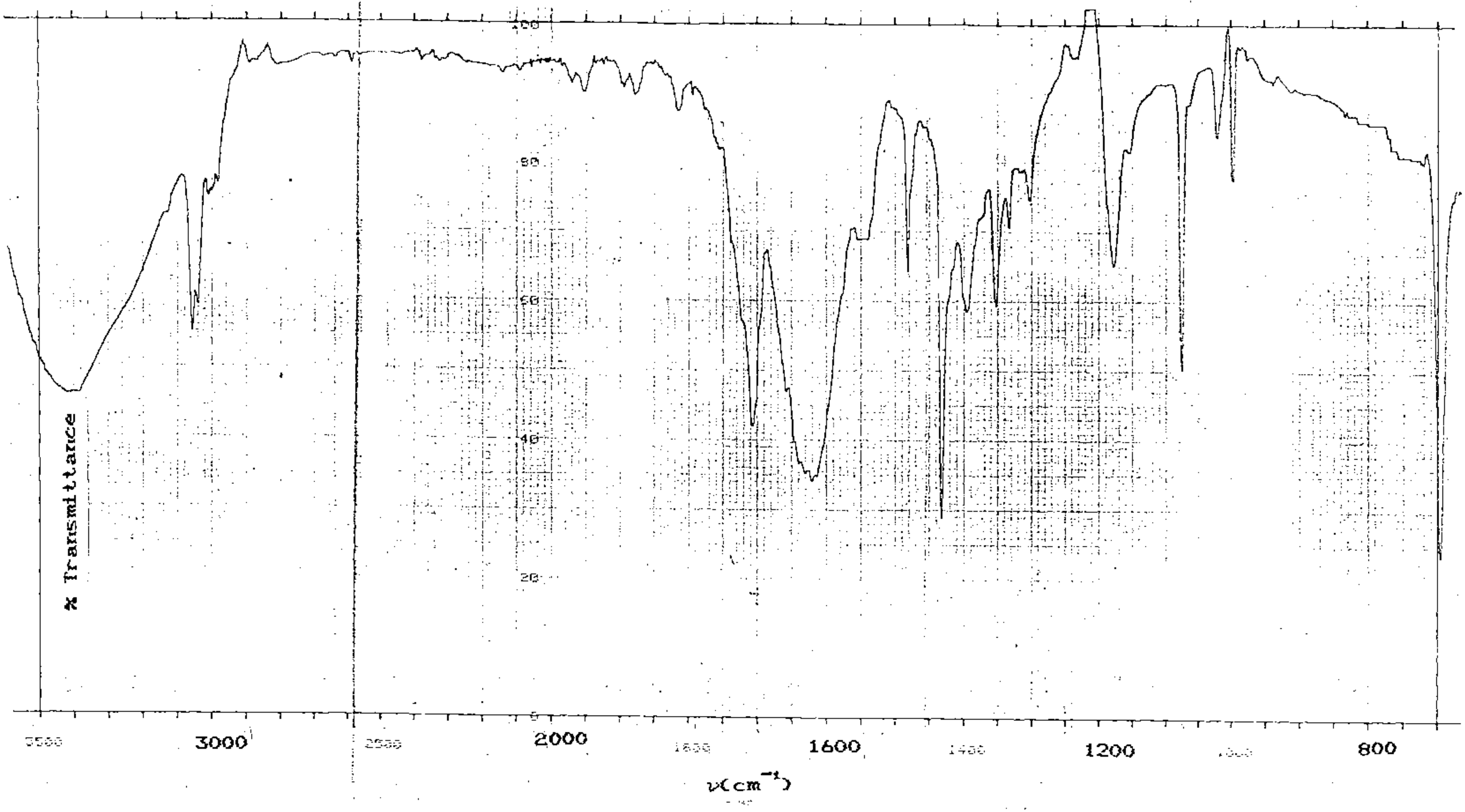


Fig.IV.6. IR Spectrum of Ph_3SnOH PvH in CCl_4.

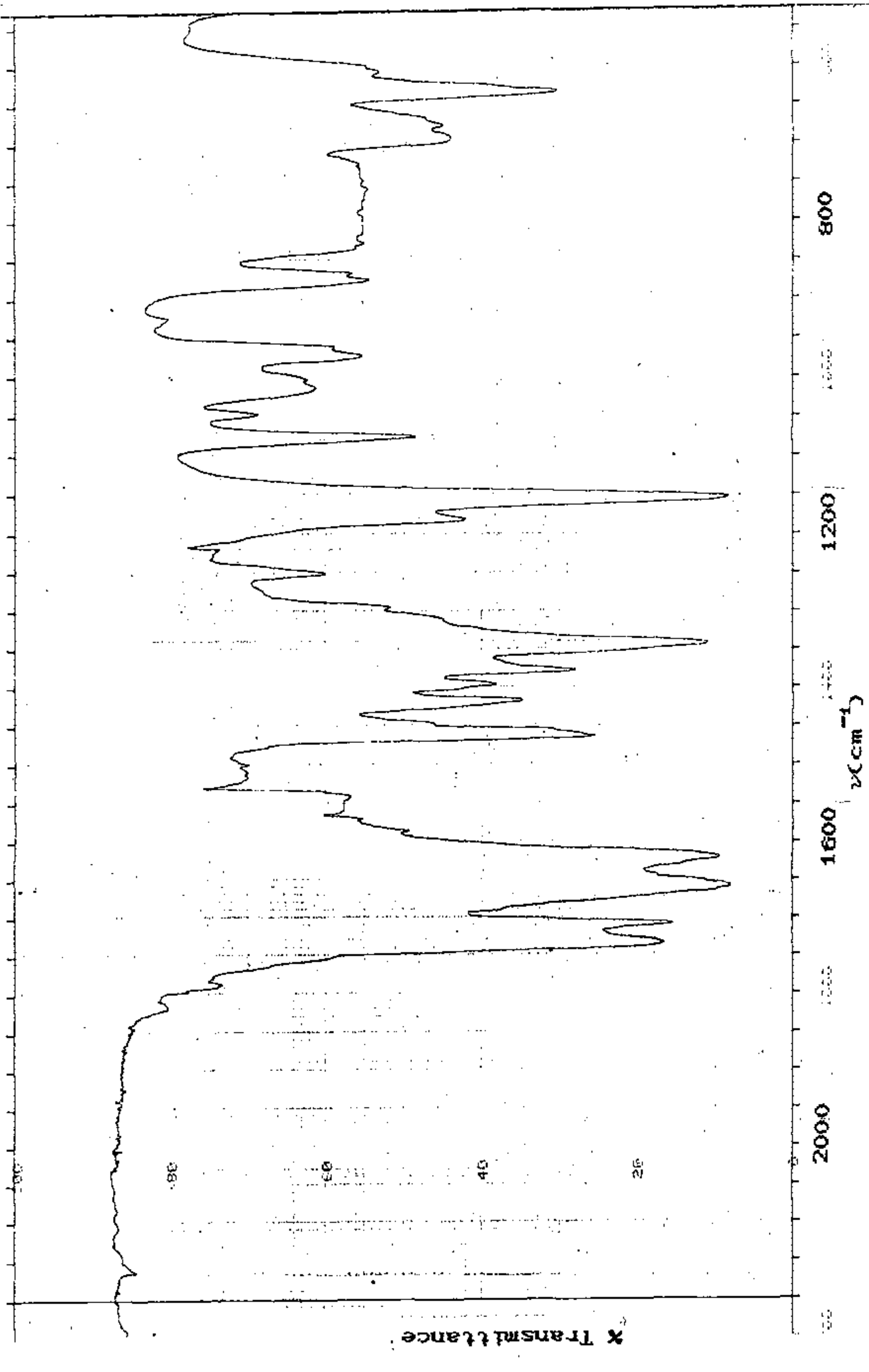


Fig.IV.7. IR Spectrum of $Bu_3SnOH.PvH$ in CCl_4.

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 760 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-π^* 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-π^* 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

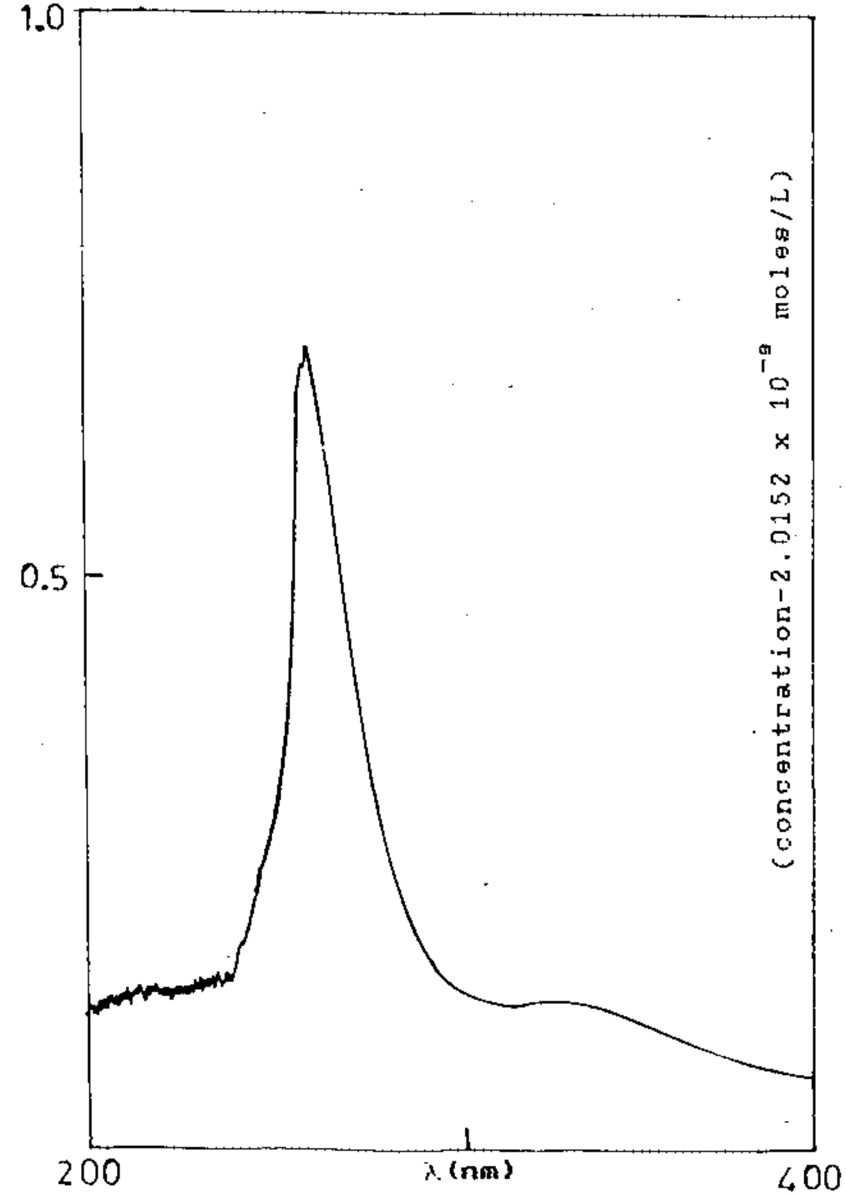


Fig.IV.9. Electronic spectrum of $Bu_3SnOH.PvH$ in CCl_4.

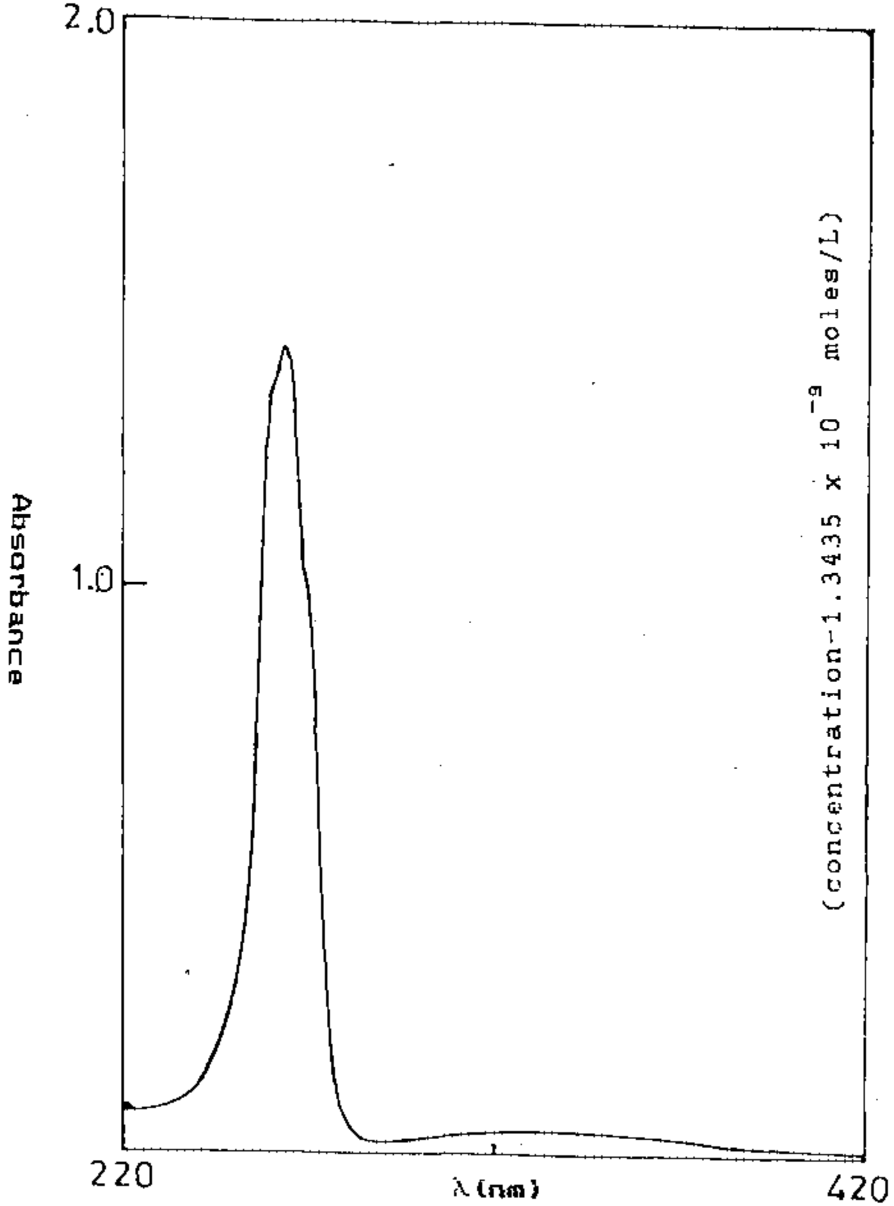


Fig.IV.8. Electronic spectrum of $Ph_3SnOH.PvH$ in CCl_4.

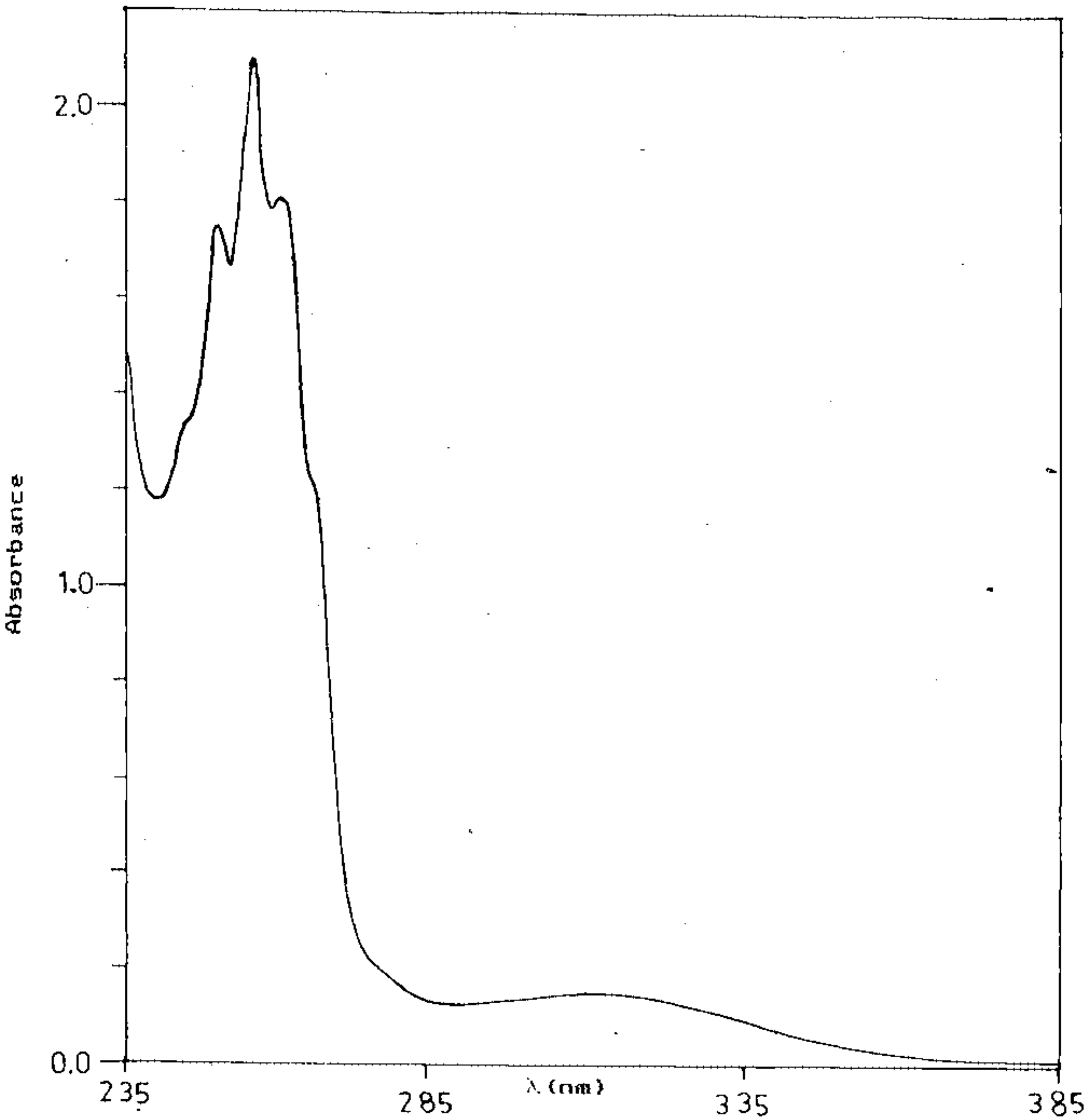


Fig. IV.8a. Electronic spectrum of $Ph_3SnOH.PyH$ in MeOH.

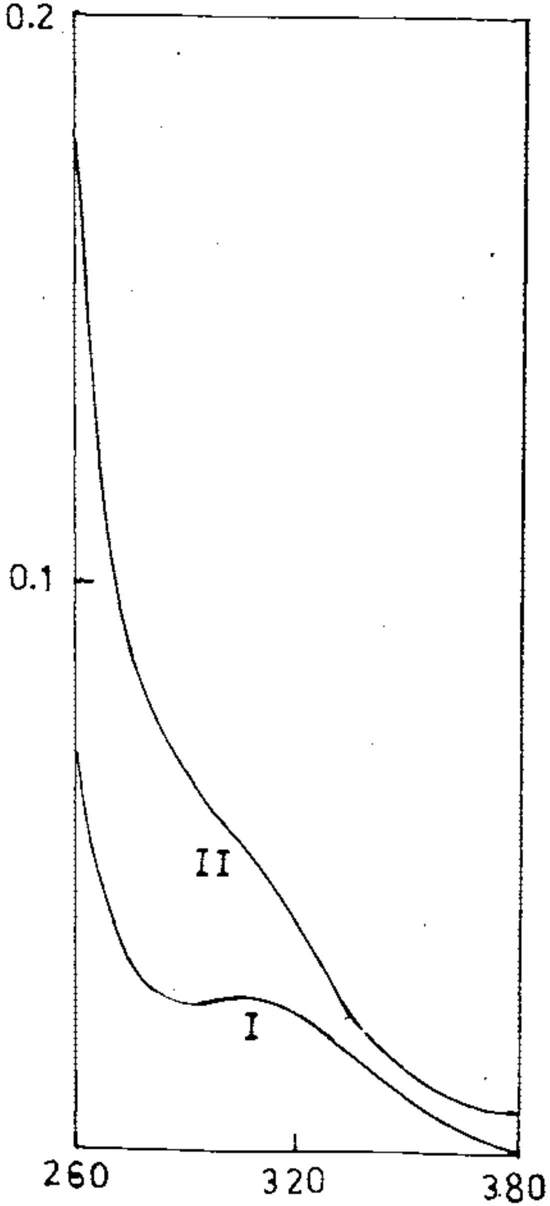


Fig.IV.10. Electronic spectrum of Bu$_3$SnOH.PvH (I) and Bu$_3$SnPv (II) in MeOH.

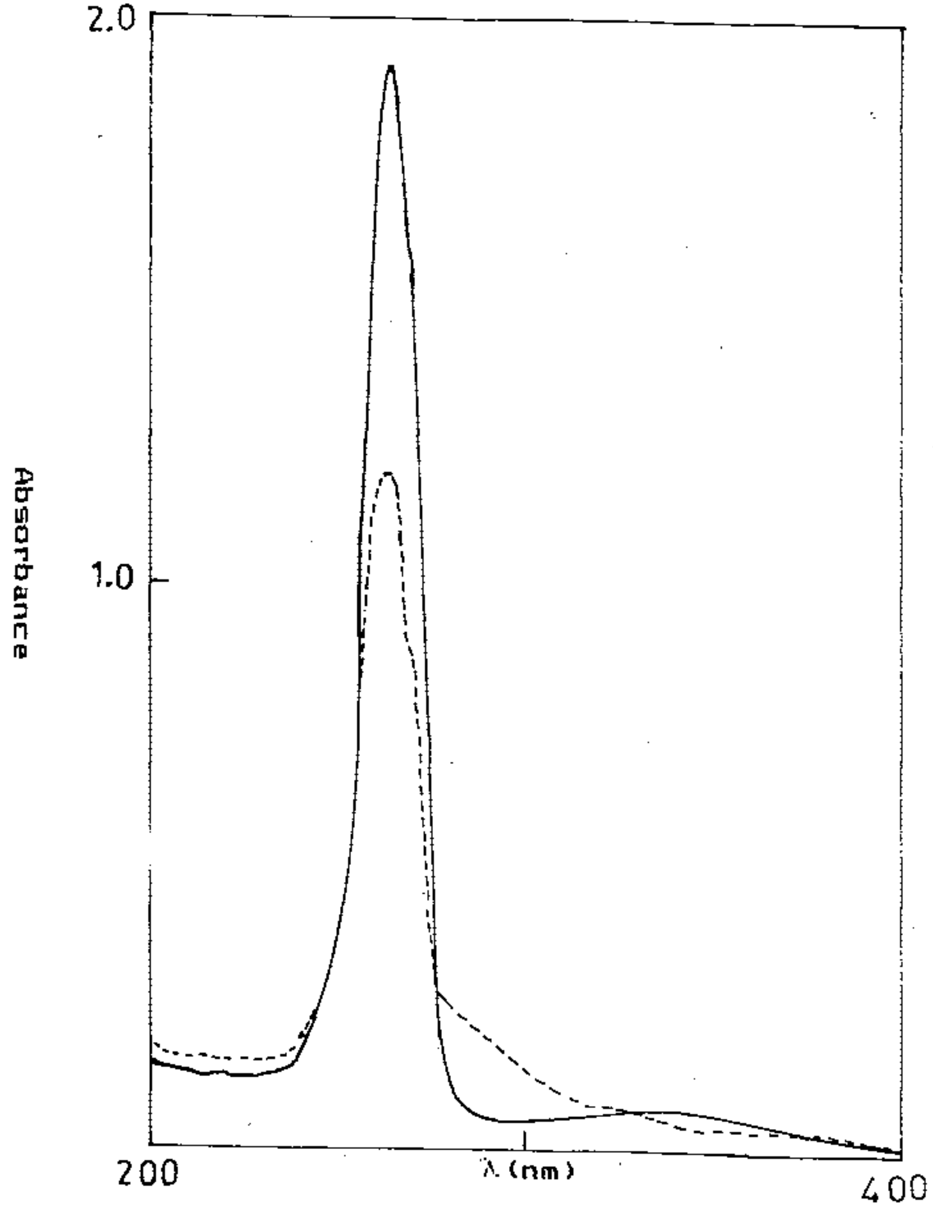


Fig.IV.11. Electronic spectrum of Ph$_3$SnOH.PvH (———) and Ph$_3$SnPv (-------) in CCl$_4$.

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 6.64ppm, 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 $CDCl_3/DMSO-d_6$ 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 $CDCl_3/DMSO-d_6$ 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; 7.2-7.85, 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

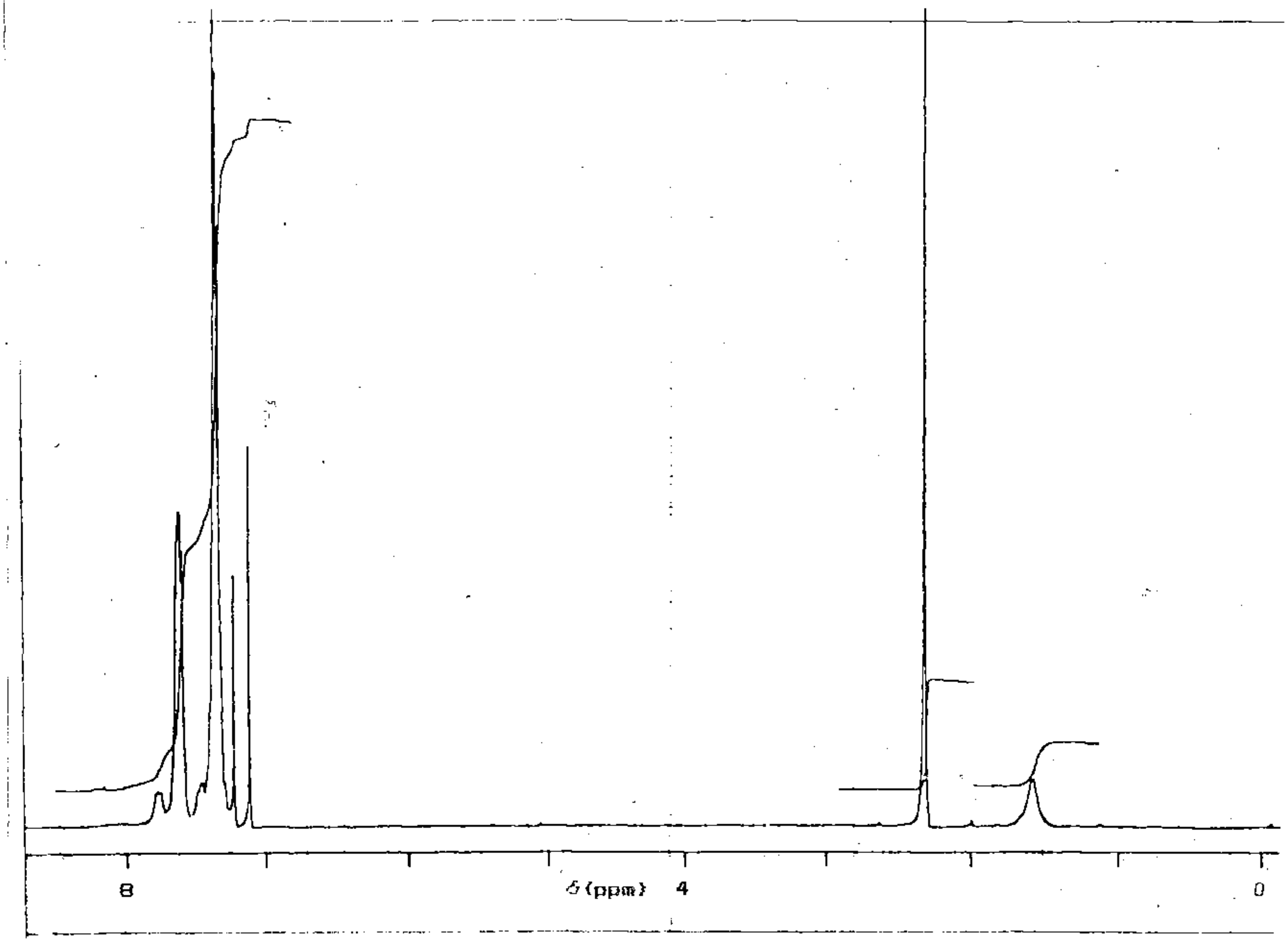


Fig.IV.12. ^{1}H NMR spectrum of $Ph_3SnOH.PvH$ in $CDCl_3$.

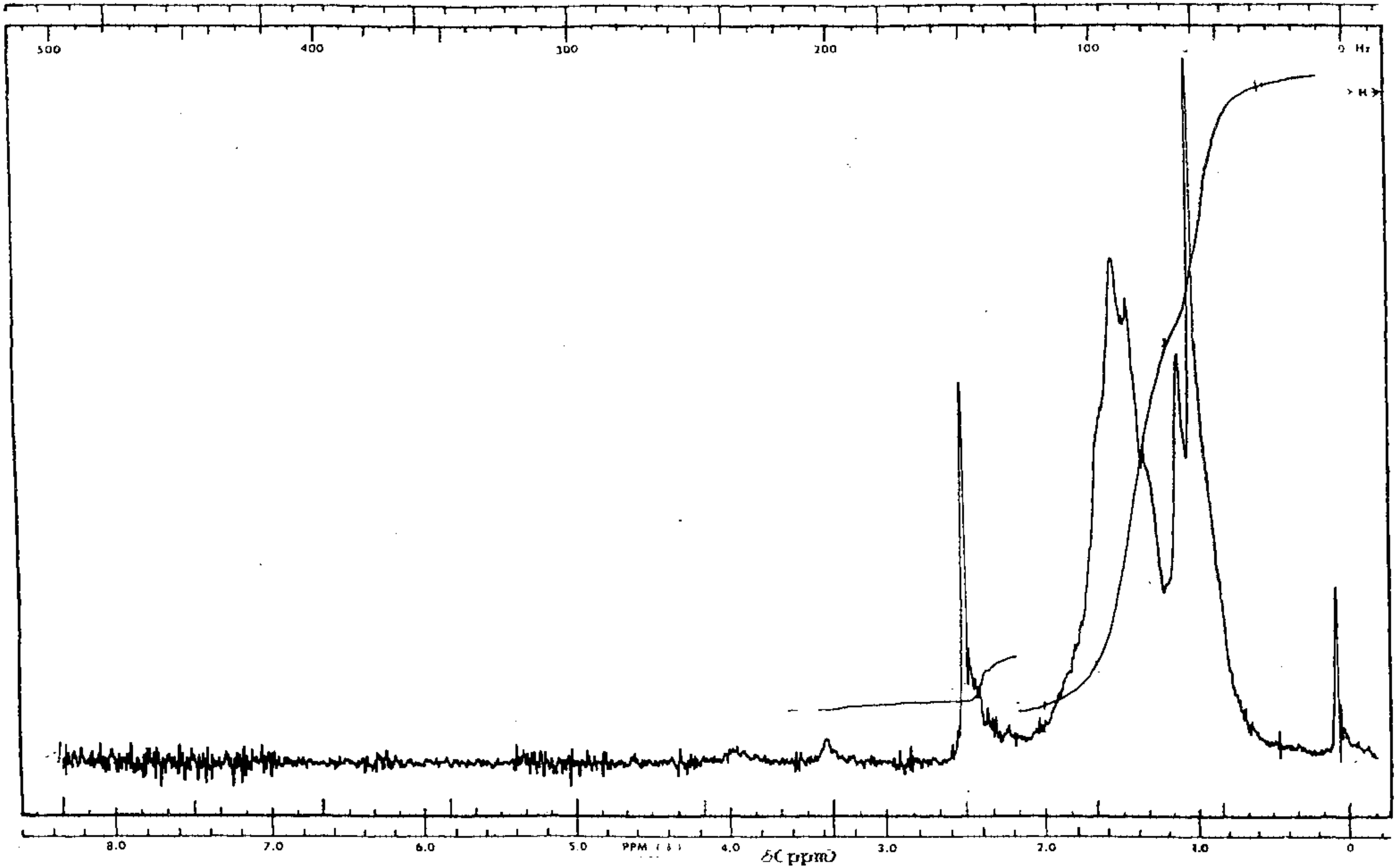
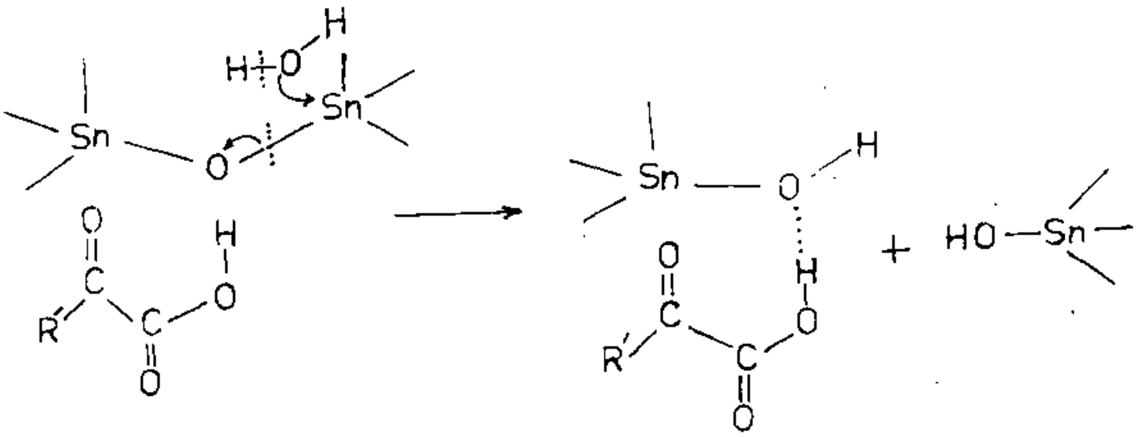


Fig.IV.13. ^1H NMR spectrum of $Bu_3SnOH.PvH$ in $CDCl_3$.

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 :

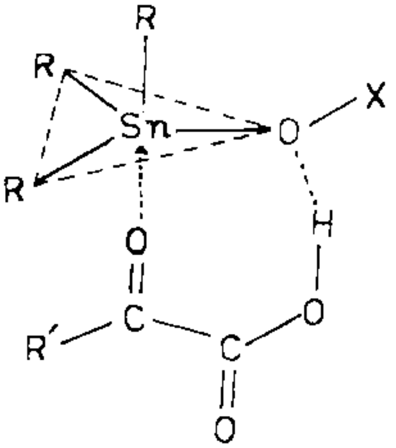
$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH \text{ -------[2]}$$

$$(R_3Sn)_2O + R'COOEt \longrightarrow R_3SnOCOR' + R_3SnOEt \text{ -----[3]}$$

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.



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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.

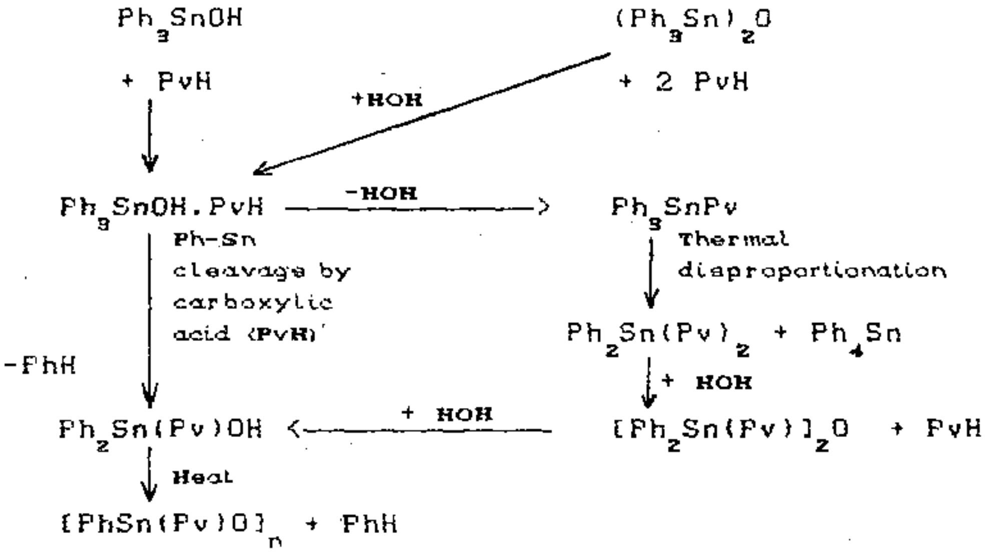
Thus, when the triphenyl tin derivative of PvH was refluxed in dry ether for about an hour, a white solid, which could be formulated as $Ph_2Sn(Pv)OH$ on the basis of elemental analysis and IR spectrum, separated. When the solvent was carefully distilled off, the distillate was found to contain benzene, 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. $115^{\circ}C$)[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.

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