SYNTHETIC AND SPECTROSCOPIC STUDIES OF SOME ORGANOTIN COMPOUNDS

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D E C L A R A T I O N

I hereby declare that this thesis has been composed by myself and that it is a record of my own research work. It has not been accepted in any previous application for a higher degree. All quotations are distinguished by quotation marks and the sources of information are specifically acknowledged by means of references.

JOSIAH JIMOH BONIRE

Date:.....

A B S T R A C T

In this work, hitherto unreported 4-acetylpyridine and 4-benzoylpyridine adducts of Me_3SnCl are synthesized. The adducts are found to be 1:1 Lewis acid: bases,

3-Acetyl-, 3-benzoyl-, 4-acetyl-, and 4-benzoyl pyridine adducts, 1:2 Lewis acid: bases, of Me_2nCl_2, $MeSnCl_3$, $SnCl_4$, $PhSnCl_3$, and Ph_2SnCL_2, are also synthesized.

Infrared spectroscopy shows that only the N binding site of the Lewis bases forms the coordinate bond in adduct formation.

For the 1:1 2-benzoylpyridine adducts of $MeSnCl_3$, $SnCl_4$, and $PhSnCl_3$, i.r. shows that both N and 0 binding sites of the Lewis base coordinate.

I.r. spectroscopy also indicates that for the 1:1 2-pyridine carboxaldehyde adduct of $PhSnCl_3$, both N and 0 binding sites of the Lewis base coordinate. 2-Acetyl-pyridine reacts in a manner different from 2-benzoylpyridine and 2-pyridine carboxaldehyde, with the methyltin, phenyltin, and stannic chlorides. The exact nature of the reactions is yet to be worked out.

Proton magnetic spectra of the pyridine adducts of the methyltin, phenyltin, and stannic chlorides are

presented perhaps for the first time. P.m.r. specra of the new adducts synthesized were also run. P.m.r. chemical shifts of the adducts provide another way of showing Lewis base coordination.

The JSn-C-H values for methyltin chloride adducts of pyridine Lewis bases are found to be almost linearly related to the pV, of the Lewis bases, and could thus be used to correlate the base strength of Lewis bases, especially of a Lewis base and its substituted derivatives, where the substituents do not sterically interfere with the freedom of the Lewis base to bind with a Lewis acid.

Investigation of the substitution reactions of the organotin halide adducts was undertaken. Some methyltin trifluoroacetate adducts were synthesized. $Ph_3SnO.CO.CF_3$ is made by a simpler, more efficient method than previously reported.

By its mode of reaction, $PhSn(O.CO.CF_3)_2$ might serve as a new radical initiator.

Through photolysis or thermal decomposition, diphenyltin bis-trifluoroacetate undergoes an unusual disproportionation reaction, yielding biphenyl and a complex dimer of the phenyltin bis-trifloroacetate radical.

P R E F A C E

This Thesis is a result of an exploration of some branches of the Organotin Chemistry world. The acceptor strength of Sn in organotin chlorides and carboxylates has been critically studied by means of infra red and nuclear magnetic resonance spectroscopy. Quite a number of revelations have been made.

Man takes whatever convinces him to be the truth. It is curiosity then that can drive him near what really is actuality. For those that like questioning before accepting what others call the truth, for those that realise that each new answer raises a new question, and for those that have realised that solving problems is the main occupation and the fuel for the life of Man on earth, this thesis shows that there are still many unanswered questions in Organotin Chemistry.

Dedication:

To the memory of my grandfather, His Highness,

Oba Bonire, the late Oluluke of Iluke.

A C K N O W L E D G E M E N T S

"The room of the life in me I know not,
I think and compute, but how do I think?
To God Almighty the source of all wits,
Designer of brain, be all the glories."

I am immensely grateful to Professor U.D. Gomwalk and Dr. H.T. Bozimo, who supervised this work. Professor Gomwalk has proved his worth as an experienced academician; each of his criticisms was awakening, and he so often put me at ease at difficult times. Dr. Bozimo has supervised this work right from the Masters level. He kept directing and pushing throughout the entire program with a head that seemed impossible to trap; each battle was fought through. I really thank these two experienced teachers, who incidentally have been by me right from my first year in the University.

I thank all member of the Ahmadu Bello University Chemistry Department teaching staff, and the now retired Professor F. Stansfield, for their support in various ways. I thank Mr. A.G. Adeleke, too, for typing the thesis.

I thank my friends for their unceasing prayers for me.

God bless you all!

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I N T R O D U C T I O N

INTERACTION OF CARBONYL - SUBSTITUTED PYRIDINES WITH METHYLTIN, PHENYLTIN, AND STANNIC HALIDES.

Tetravalent tin atom, like other elements in group IV, exhibits sp^3 hybridization. Expansion of its coordination number above four is therefore not possible unless the 5d orbitals are utilized. Tin has been found to differ from the lighter metals of its group by being able to make use of its relatively low-lying 5d orbitals, to expand its coordination number[1,2]. Some tin compounds are capable therefore of coordinating with Lewis bases, and this ability increases with decrease in the electron density around the tin atom in the Lewis acid. The electron density in turn is determined by the substituents attached to the tin: electron-withdrawing substituents render the tin positive and therefore more capable of coordinating with Lewis bases, while electron-donating substituents render the tin negative and therefore less reactive towards Lewis bases. On this basis, while no adduct of tetramethyl tin has yet been reported, adducts of stannic chloride are common. Steric factors would also influence

the Lewis acidity of an organotin compound. The stability of an adduct - hence the probability of its formation - increases with increasing electrophilicity of the Lewis acid, with increasing nucleophilicity of the Lewis base, and with increasing steric freedom around the acceptor atom of the Lewis acid. A Lewis base has to be strong enough to distort and bind with the roughly tetrahedrally substituted tetravalent tin atom to form any stable adduct.

The presence of electron-donating organic groups on tetravalent tin atom (classed as a hard acid) confers on it some measure of softness on the basis of Hard and Soft Acids and Bases Principle[3,4,5]. Thus, most organotin halides bind well with pyridine which is classed as a borderline base under the same principle[5]. Pyridine forms 1:2 adducts with methyltin trihalides and with dimethyltin dihalides; and 1:1 with trimethyltin monohalides.

$$\underset{\text{I}}{MeSnX_3} + \underset{\text{II}}{2Py} \rightarrow \underset{\text{III}}{MeSnX_3.2Py} \quad \ldots\ldots\ldots\ldots \text{(i)}$$

$$\underset{\text{IV}}{Me_2SnX_2} + 2Py \rightarrow \underset{\text{V}}{Me_2SnX_2.2Py} \quad \ldots\ldots\ldots\ldots \text{(ii)}$$

$$Me_3SnX + Py \rightarrow Me_3SnX.Py \quad \ldots\ldots\ldots \quad (iii)$$

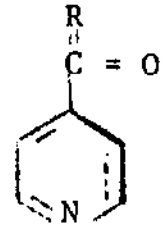
VI **VII**

where X = Cl, Br, or I.

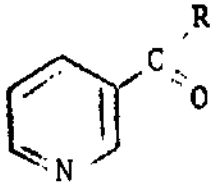
Pyridine adducts of diphenyltin dihalides and phenyltin-trichlorides are known to be unstable[6].

Spectroscopy offers a lot in the study of the nature and stereochemistry of pyridine adducts of organotin and stannic halides[7,8,9,10,11,12,13,14]. Coordination through pyridine nitrogen is indicated by a positive shift of the pyridine breathing motion which absorbs at 995cm^{-1} in the free, and at 1010 - 1030 cm^{-1} in the complexed ligand[14]. Metal-nitrogen coordination is also indicated by U.V. spectroscopy[14]. JSn-C-H values for methyltin halides are found to increase generally on complexation with Lewis bases[13]. Mass spectrometry, Mossbauer and Raman spectroscopy all give useful information for the study of organotin complexes[7].

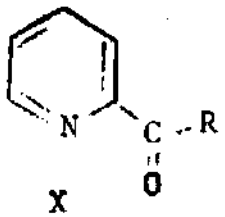
Carbonyl - substituted pyridines are ligands with two binding sites, N and O.



VIII



IX

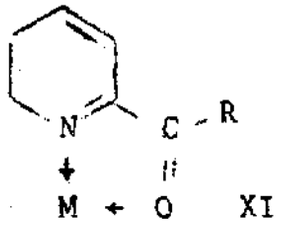


X

where R = H, CH_3,...-.....C_6H_5, ...e.t.c.

Both sites have electron pairs, and therefore, presumably, could bind datively on an organotin Lewis acid.

The presence of a bulky substituent at the 2-position on the pyridine ring would, presumably, cause some hinderance in the coordination of the molecule on a Lewis acid. With the α-substituted carbonyl pyridine which has its oxygen stereochemically suitably placed to chelate along with the nitrogen on some Lewis acid, the effect of steric hinderance is nullified or, at least, reduced.

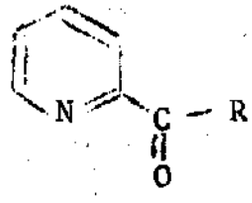


XI

where R = H, CH_3, C_6H_5, e.t.c.

The donor strength of the O might or might not be high enough, however, to enable the O to effectively bind along with N on M to give any stable isolable product. The interaction of 2-acetylpyridine with the first-row transition metals has recently been studied by Plytzanopoulos et al[15]. They found that both the N and O

coordinate on the metals in complex formation. In another study[16], Plytzanopoulos et al reported the interaction of the first row transition metals with 2-benzoylpyridine, concluding from their experiments that 2-benzoylpyridine acts either as mono- or as a bidentate agent, depending on such factors as the halide used (Cl^- or Br^-), the solvent, and the presence of further complexation between the adduct and HCl or HBr. Similar results were obtained when the study was extended[14] to other ligands of formula;

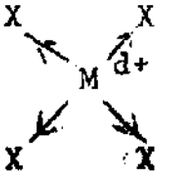


X where R = H, CH_3,.....C_6H_5,..... e.t.c

Similarly, Jain has reported[17] that 2-acetylpyridine reacts with $TiCl_4$ and $SnCl_4$, giving 1:1 adducts with both N and O chelating on the metal. Plytzanopoulos et al[16], in their study of the interaction of 2-benzoyl-pyridine with the first-row transition metals, have said that the carbonyl stretch in the i.r. shifts to lower frequencies when the oxygen is coordinated to the metal

and slightly higher frequencies in the case of N - only coordination.

Coordination of Lewis bases on transition metal halides would be easy, because partially filled d-orbitals which could accommodate electrons from Lewis bases are present in the valence shell. The halogens on the metal are electron - withdrawing, thereby rendering the metal amenable to attack by Lewis bases.



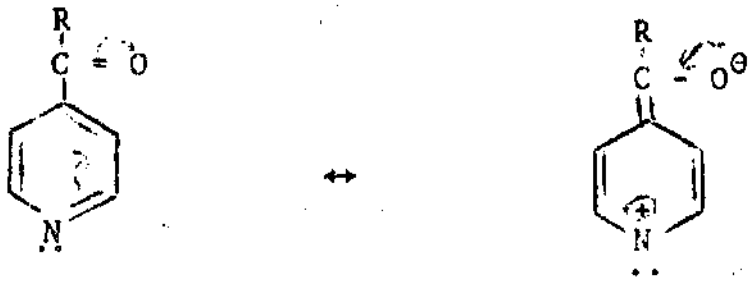
XII

where X = halogen,

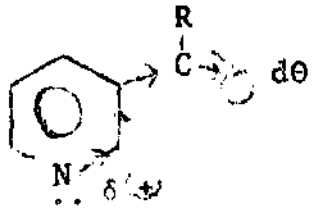
M = transition metal

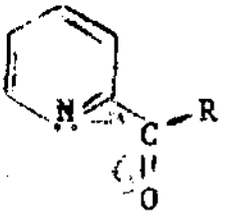
Where organic groups with positive inductive effect are attached to the metal, the latter is less affinitive for electron - donating Lewis bases; and where vacant d-orbitals are not available in the valence shell, as in many main group metals, coordination could be

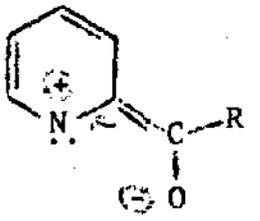
difficult. Sn is especially known for its ability to utilise its d-orbitals next to the valence shell in forming coordination compounds. But organotin halides might or might not be as strong as the transition metal halides in coordinating with carbonyl substituted pyridines. This depends very strongly on steric factors since organic groups on organotins are bulky compared with the halogens on transition metals. Also carbonyl bearing groups substituted on the pyridine ring would have an overall electron withdrawing effect on the N of the ring, thereby reducing the coordinating ability of the Lewis bases, especially, compared with unsubstituted pyridine.



VIII







Different types of electron - withdrawing processes on the pyridine ring in a substituted pyridine would make the donor strength of its N vary. Also, the adduct formation tendency of an organotin halide would be decided by the steric freedom around, and the resultant electrophilicity of, its central Sn atom. It has been of interest therefore to examine the interaction of carbonyl substituted pyridines with organotin halides, by means of spectroscopy.

BINDING STRENGTH OF THE LIGANDS.

The strength of a metal ligand bond in an adduct, would depend directly on the degree of interaction of the accepting orbitals of the metal atom with the donor orbitals of the electron - pair - bearing atom of the ligand. Where the metal atom is highly electron affinitive, the degree of interaction and therefore strength of the metal-ligand bond would be a direct function of the 'nucleophilicity' of the ligand, which in this case is the availability

of the lone pair of electrons on the donor atom. Where the ligand bears electron-withdrawing groups, the availability of the electron pair for dative bonding decreases. Infering from literature[17,18], n.m.r. spectroscopy might offer much in studying the binding strength of the carbonyl substited pyridines with the JSn-C-H of the corresponding adducts.

Three naturally occuring tin nuclides have magnetic moments: ^{115}Sn, ^{117}Sn, and ^{119}Sn, all of them with nuclear spin $I = \frac{1}{2}$. Because of their higher relative abundance, ^{117}Sn and ^{119}Sn are the most important (^{115}Sn, 0.34%; ^{117}Sn, 7.54%; ^{119}Sn, 8.62%)[17]. The magnitudes of the indirect tin-proton coupling constants, $J^{117}Sn\text{-}C\text{-}H$ and $J^{119}Sn\text{-}C\text{-}H$, are often informative in structural studies of organotin compounds, most especially organotin halides and their adducts, and are found to be dependent on the solvent used and the number and type of halogens attached to the tin, i.e. the electron density on the tin atom[17]. It has been generally accepted[18] that the Fermi contact term is the main contribution to $J^{119}Sn\text{-}C\text{-}H$ constants, and therefore that these are proportional to the s-electron densities on the nuclei

coupled. From the n.m.r. spectra of Me_3SnHal. dissolved in different bases, the studies of the limiting values of $J^{119}Sn\text{-}C\text{-}H$ for Me_3SnHal. have led Drago et al to suggest[12] that the magnitude of $J^{119}Sn\text{-}C\text{-}H$ depends on the 'nature' of the base. They have also attempted to establish a relationship between the J Sn-C-H values for Me_3Sn Hal. in various donor solvents with the heats of formation of the Me_3Sn Hal. adduct of each of the donor solvent.

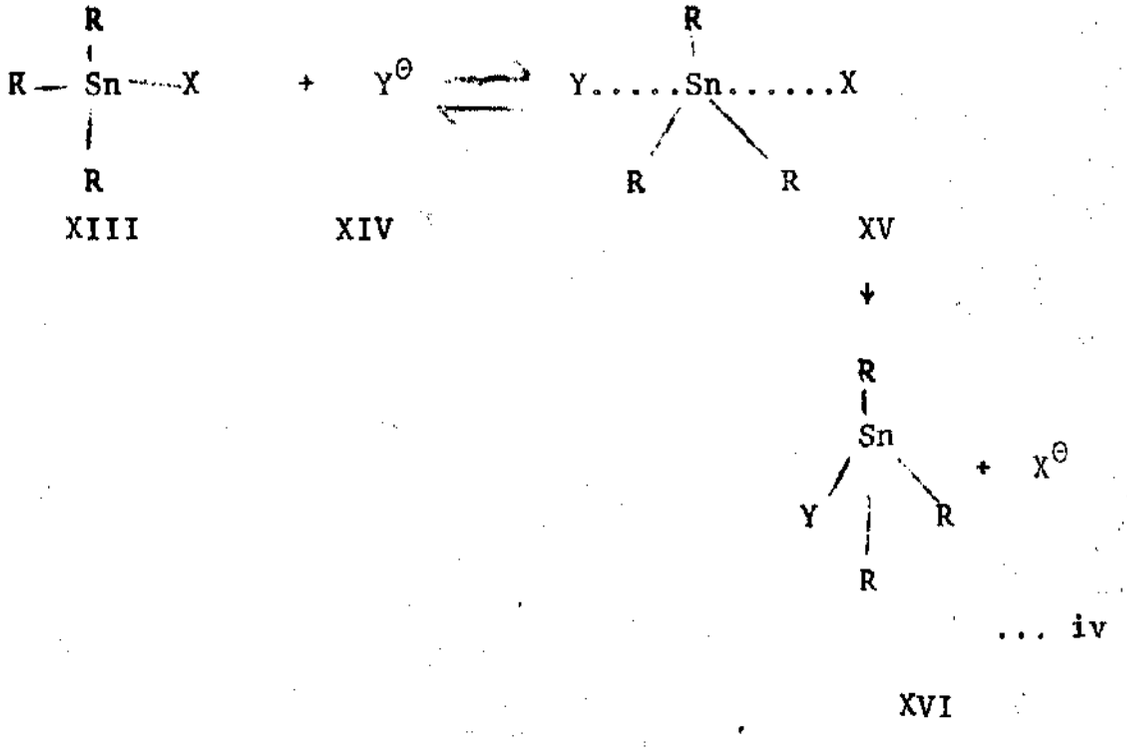
From the study of the variation of J Sn-C-H values with varying Donor/Acceptor ratio in dichloromethane of Me_3Sn Cl and a number of donor solvents, Petrosyan et al[18] have concluded that J Sn-C-H values increase with increasing donor - acceptor bond strength, and this, they suggested, represented the solvating abilities of the solvents. They further postulated that the complexation of methyltin haldies with electron donor solvents is followed by an increase of the relative content of S - electrons in the Sn-C-H site. This arises from the assumption that the complexation is essentially a p - d donor - acceptor interaction and is thus not affected by the S - electron density on the metal.

To be able to make a meaningful correlation of the variation of J Sn-C-H for a methyltin halide in its complexes with a set of bases of varying donor strengths, stoichiometric amounts of the Lewis acid and base, as would be found in the isolated complex, are measured into a common inert solvent. Alternatively, the adduct could be first prepared and then measured out into the solvent. The J Sn-C-H value of the methyltin halide is then measured. An independent method also has to be available to determine the strength of each of the bases. No report has been found of this type of study, as many adducts of methyltin halides had been found to be insoluble in common inert solvents. Of pyridine adducts especially, only Me_3Sn Hal. Py have been found to be sufficiently soluble[13,18] for quantitative study of the J Sn-C-H.

It has been of interest therefore to study the relationship between the J Sn-C-H of some methyltin halide pyridine complexes, and the strength of the Lewis base of each complex.

SUBSTITUTION REACTIONS OF ORGANOTIN CHLORIDE ADDUCTS.

Poller[19] has stressed the ease with which the halogens of organotin halides can be replaced by a variety of nucleophiles. The halogens, due to their relatively high electronegativities, render the tin of organotin halides positive and therefore more susceptible to nucleophilic attack. Because of their small size compared with, say, a carboxyl group, the halogens on organotin halides would not give much steric hinderance to an attacking nucleophile as the latter attacks in an SN_2 fashion.



For these reasons, organotin halides have been found to be good starting materials in the preparation of other organotin compounds[20]. Anderson et al[20] have drawn up a "conversion series" for the interconversion of triethyltin compounds:

$(Et_3Sn)_2S \rightarrow Et_3SnI \rightarrow Et_3\ SnBr \rightarrow Et_3SnCH \rightarrow Et_3Sn\ NCS \rightarrow$
$Et_3SnCl \rightarrow (Et_3Sn)_2O \rightarrow Et_3Sn(NCO) \rightarrow Et_3SnO.CO.CH_3 \rightarrow Et_3SnF.$

Anderson found[20] that using the appropriate nucleophilic reagent, any of the compounds in the series could be converted to any other one to its right, but none to the left.

A similar series has been drawn by Eaborn[21] for some triorganosilicon compounds:

$R_3SiI \rightarrow (R_3Si)_2S \rightarrow R_3SiBr \rightarrow R3SiNC \rightarrow R_3SiCl \rightarrow R_3SiNCS \rightarrow R_3SiNCO$

Eaborn has pointed out, in drawing up his "conversion series" for organosilicon compounds, that the formation of an organosilicon halide or psuedohalide in preference to another is dependent on the relative affinity of the halogen or pseudohalogen for the silicon. Thus Si-Cl bond in R_3SiCl is stronger than Si-Br bond in R_3SiBr. The former would therefore not be converted to the latter. Using a

similar argument for organotin compounds, a reaction of the type

$$R_nSnX_{4-n} + 4-nY^{\Theta} \rightarrow Rn\ Sn\ Y_{4-n} + 4-nX^{\Theta} \ldots\ldots\ v$$

would occur if Y^{Θ} has a higher affinity for Sn than X^{Θ}. This has been proved experimentally by Anderson[20] in his conversion series for some organotin compounds.

In interconverting organotin halides and pseudohalides, silver salts are most often used. If could be inferred from Eaborn's explanation of his interconversion reactions of organosilicon halides and pseudohalides that the rate-determining step in the interaction of a tin compound ≡SnX, with a metal salt, MY, is the nucleophilic attack of the Y^{Θ} ion on the tin atom. However, the fact that silver salts are outstandingly effective suggests that the metal ions play some significant part in the reactions, possibly assisting the removal of anion from ≡SnX.

If nucleophilic substitution reactions of organotin halides and pseudohalides actually go by the SN_2 mechanism, then adducts of organotin halides cannot be reactive, because of steric difficulties due to over-crowding in the intermediates. By the stepwise process of the SN1 mechanism however, substitution reactions might be easier.

Although many adducts of organotin halides are known[7], no report has as yet been made of any investigation of the reactions of organotin adducts. The hexacoordination of the tin atom in many of these compounds would make them resistant to nucleophilic attacks, and, many of them are insoluble in common organic solvents and would only slowly hydrolyse in aqueous media. Interest therefore developed in carrying out a study of substitution reactions of organotin halide adducts.

Presumably replacement of the halogen in an organotin halide with another substituent would be more feasible if the halogen could be forced off the organotin halide to form a more stable compound. This is one of the reasons for the suitability of silver, salts, since silver forms stable halides which are soluble only in amine solvents. This advantage has been exploited in preparing many organotin compounds[22].

$$R_{4-n}SnCl_n + nAgY \rightarrow R_{4-n}SnY_n + {}_nAgCl \quad \text{.....vi}$$

where Y could be PO_4, AsO_4, SO_4, AsF_6, ClO_4, CO_3, $O_3SC_6H_4Me - p$

Only one report has so far been made[25] of the use of this method to prepare an organotin ester.

$$Ph_2SnCl_2 \quad + \quad AgO.CO.CH_3 \xrightarrow[\text{room temp.}]{\text{ether}} Ph_2Sn(O.CO.CH_3)_2$$

XVII XVIII XIX

$$+ \ 2AgCl \quad \ldots\ldots\ldots \quad vii$$

XX

Organotin esters have however been prepared in various other ways[26].

$$Ph_3SnOH \quad + \quad CF_3COOH \longrightarrow Ph_3SnO.CO.CF_3$$

XXI XXII XXIII

$$+ \ H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad Viii$$

$$Me_2Sn(CH{:}CH_2)_2 \quad + \ CF_3.CO.OH \longrightarrow Me_2Sn(O.CO.CF_3)_2$$

XXIV XXV

$$+ \ 2CH_2.CH_2 \quad \ldots\ldots\ldots \quad ix$$

$$Et_4Sn \quad + \ 2CF_3CO_2Ag \longrightarrow Et_2Sn(O.CO.CF_3)_2 \quad \ldots\ldots\ldots\ldots \quad x$$

XXVI XXVII XXVIII

Silver trifluoroacetate dissolves easily in many organic solvents. Its reactions with some of the new adducts prepared in this work have therefore been studied. In the process, diphenyltindichloride bis-4-acetylpyridine was found to react with silver trifluoroacetate in acetone to give a product in which tin was absent. This led to the investigation to the

reaction of silver trifluoroacetate with phenyltin chlorides, a study which had hitherto not been reported.

The work now being reported therefore was aimed at studying

(i) the interaction of carbonyl substituted pyridines with methyltin, phenyltin, and stannic chlorides;

(ii) the variation of $J^{119}Sn\text{-}C\text{-}H$ in complexes of substituted pyridines with methyltin chlorides, with the base strength of the ligands.

(iii) the substitution reactions of pyridine adducts of methyltin, and phenyltin chlorides with various nucleophiles.

(iv) the reactions of phenyltin chlorides with silver trifluoroacetate.

DISCUSSION

SECTION A

Synthesis, Physical and Spectral Properties of the Acetyl and Benzoyl pyridine complexes of Methyltin, Phenyltin, and Stannic Chlorides.

(a) Synthesis of the complexes

i. 3 - and 4 - Acetyl and Benzoyl pyridine adducts of methyltin, Phenyltin, and Stannic chlorides.

Organotin halide adducts are usually prepared by mixing solutions of the organotin halide and the Lewis base in an inert solvent. Beattie et al[9] have prepared the pyridine adduct of dimethyltin dichloride in benzene, and of trimethyltin chloride in light petroleum. Carbon tetrachloride, carbon disulphide and chloroform have also been used in preparing $MeSnCl_3.2Py$, $MeSnCl_3.Phen.$, and $Me_2SnCl_2.2PyHCl$ respectively[9]. In preparing an organotin halide adduct, a solvent has to be chosen such that it is inert, fairly volatile, anhydrous, and capable of dissolving the reactants very well but yielding the adduct as a precipitate or preferably, crystals. Pyridine adducts of many organotin halides are known to precipitate as soon as the reactants are mixed[9]. Although the yield in such preparations are usually high, the

synthesis of a compound via precipitation most often yields an impure product.

Except in a few cases where carbon tetrachloride was used, dichloromethane was chosen as the medium of reaction in the preparation of the following acetyl and benzoyl-pyridine adducts of methyltin, phenyltin, and stannic chlorides now being reported. Dichloromethane has proved to be superior to most other inert solvents used in preparing adducts, for its volatility and high ability of solubilizing the reactants and yielding the products in most cases as crystals. Even pyridine adducts came out of dichloromethane media as purer powders, as the reactants are extremely soluble in the solvent.

Unlike pyridine adducts of organotin halides that are obtained as powders or at best small crystals when prepared in dichloromethane, acetyl and benzoylpyridine adducts of methyltin and phenyltin chlorides, in most cases, are obtained as crystals. In many cases, clear solutions are obtained when the reagents are mixed; crystals separate out only on standing or cooling. Many of these adducts could be recrystallised from suitable solvents thereby enhancing high purity, unlike pyridine adducts that

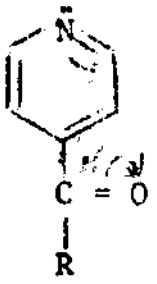
precipitate and are not soluble in most solvents.

The precipitation of pyridine adducts could be due to the high rate of reaction between the organotin halide and pyridine, since free pyridine bears no electron withdrawing substituents making its lone pair of electrons highly available for coordination. Its small size, compared with that of the bulkier substituted pyridines, would also make coordination very effective.



Phridine

II



Substituted Pyridine

VIII

$R = CH_3$, C_6H_5.

In making a solution of an adduct in a solvent, high temperature breaks the lattice energy of the crystal, then the solvent molecules compete with the ligand molecules for coordination on the Lewis acid. The adduct is solubilized where this state can be achieved. But where the adduct ligand molecules are much stronger Lewis base than the

solvent molecules, competition for coordination is greatly reduced; the adduct molecules soon associate, and the adduct is seen as only feebly soluble in the solvent. Since pyridine would form stronger dative bonds with Lewis acids than would acetyl and benzoyl-pyridines, it is not surprising that pyridine adducts of organotin chlorides most often precipitate while the acetyl and benzyol pyridine analogues slowly crystallize out.

Table 1 below shows the adducts, the form of the products, and the solvent used for their preparation.

TABLE 1

The 3- and 4- acetyl and benzoyl pyridine adducts of methyltin, phenyltin, and stannic chlorides prepared.

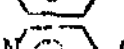
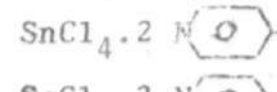
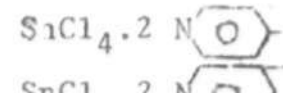
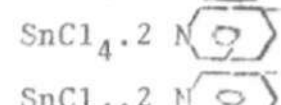
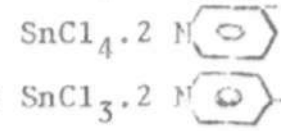
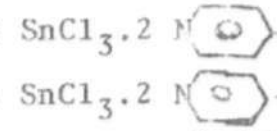
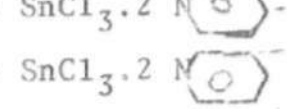
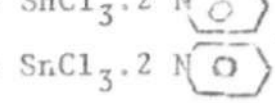
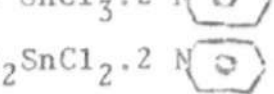
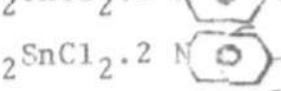
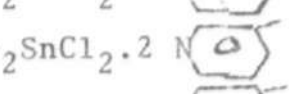
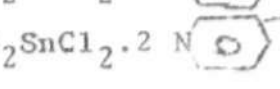
Adduct	Form	Solvent
$Me_3SnCl.$ 	Crystals	CCl_4
$Me_3SnCl.$ 	"	CCl_4
$Me_2SnCl_2.2$ 	"	CH_2Cl_2
$Me_2SnCl_2.2$ 	"	CH_2Cl_2
$Me_2SnCl_2.2$ 	"	CH_2Cl_2
$Me_2SnCl_2.2$ 	"	CH_2Cl_2
$Me\ SnCl_3.2$	"	CH_2Cl_2

Table 1 (CONTD')

Adduct	Form	Solvent
Me $SnCl_3$.2 	Crystals	CH_2Cl_2
$SnCl_4$.2 	"	CH_2Cl_2
$SnCl_4$.2 	"	CH_2Cl_2
$SnCl_4$.2 	"	CH_2Cl_2
$SnCl_4$.2 	"	CH_2Cl_2
Ph $SnCl_3$.2 	"	CCl_4
Ph $SnCl_3$.2 	"	CH_2Cl_2
Ph $SnCl_3$.2 	"	CCl_4
Ph $SnCl_3$.2 	"	CH_2Cl_2
Ph_2SnCl_2.2 	"	CH_2Cl_2
Ph_2SnCl_2.2 	"	CH_2Cl_2
Ph_2SnCl_2.2 	"	CH_2Cl_2
Ph_2SnCl_2.2	"	CH_2Cl_2

ii. 2-Acetylpyridine, 2-benzoylpyridine, and 2-pyridine carboxaldehyde complexes of methyltin, phenyltin, and stannic chlorides.

As with the synthesis of 3- & 4- acetyl and benzoyl pyridine adducts of the methyltin, phenyltin, and stannic chlorides, the reactions of the 2-carbonyl pyridines with the organotin Lewis acids were tried in the inert, non-polar medium of dichloromethane, at room temperature. But, unlike the speed and pattern of reaction of the 3- & 4-carbonyl pyridines, the reaction of the 2-carbonylpyridines with the methyltin, phenyltin, and stannic chlorides occurred much more slowly, and in many cases, oily products were first obtained. Some of these crystallised on cooling. All products of reaction of stannic chloride with the three 2-carbonyl-pyridines rapidly formed yellow crystals, unlike the products of reaction with methyltin and phenyltin chlorides. 2-Benzoylpyridine did not react with phenyltin or methyltin trichloride until the reaction mixture was warmed. Yellowish crystals separated out however as the warm mixtures cooled. No reaction was observed between 2-benzoylpyridine and dimethyltin or diphenyltin dichlorides, or trimethyltin and triphenyltin chlorides.

2 - Acetylpyridine reacted with phenyltin and methyltin trichlorides to give oily products. Solidification of the oils was effected by first warming the mixtures to boiling, and then leaving them to stand for several hours. Near white crystals separated out. With dimethyltin dichloride, 2-acetylpyridine slowly reacted to yield light yellowish crystals, but with diphenyltin dichloride, a thick brown oil was produced after several hours. Heating was only a little effective in promoting the speed of the reactions. In carbon tetrachloride however, diphenyltin dichloride gave a yellow solid with 2-acetylpyridine. No reaction was observed between trimethyltin or triphenyltin chloride and 2-acetylpyridine.

2-Pyridine carboxaldehyde reacted with stannic chloride, methyltin and phenyltin trichlorides, and also with dimethyltin and diphenyltin dichlorides, but most of the products of reaction were unstable. The products of reaction of the ligand with stannic chloride, methyltin and phenyltin trichlorides were solids, but thick non-isolable oils were obtained as the products of the ligand with dimethyltin and diphenyltin dichlorides.

It was possible to purify the products of reaction of the 2-acetylpyridine with dimethyltin and diphenyltin dichlorides by recrystallization, but the products of the other 2-carbonylpyridines with methyltin and phenyltin trichlorides, and stannic chlorides could only be purified by washing and drying

(b) State, Purity, and Stability of Products.

Pyridine adducts of methyltin, phenyltin, and stannic chlorides have been known[9,10] to be white, mostly amorphous solids, purified only by washing with the blank solvent used for their preparation, and then by drying. A lot of excess pyridine is usually removed during the drying.

All 3- and 4- acetyl and benzoyl-pyridine adducts of methyltin, phenyltin and stannic chlorides have been found to be light yellowish crystalline solids. The adducts of trimethyltin, dimethyltin, and diphenyltin chlorides are purified by recrystallisation from light, polar non-hydroxylic solvents like acetone. The sharpness of their melting points shows them to be of high purity. The methyltin, phenyltin, and stannic chlorides' adducts were obtained in pure form by using large quantities of the solvent - in most cases

dichloromethane - for the preparation and washing. In all cases, the products separated out slowly as crystals, thereby further enhancing the purity. All products were stable at room temperature.

The isolable complexes of 2-acetyl and 2-benzoylpyridines with stannic chloride, phenyltin and methyltin chlorides, were light yellowish crystalline solids. Products obtained with 2-pyridine carboxaldehyde were mostly brownish amorphous solids. The 2-acetyl - and 2-benzoyl-pyridine complexes were all stable at room temperature. Those of 2-pyridine carboxaldehyde did not appear to be quite as stable - most of them kept changing colour, on storage at room temperature.

c. Melting and decomposition temperatures.

With the exception of the 4-acetyl - and 4 - benzoyl - pyridine adducts of trimethyltin chloride which have higher melting points than their pyridine analogues, all 3 - and 4 - acetyl - and benzoyl - pyridine adducts of methyltin, phenyltin, and stannic chlorides have been found to have lower melting or decomposition temperatures than their pyridine analogues. The fact that the 4-acetyl - and 4- benzoyl - pyridine adducts of trimethyltin chloride are

higher melting than the pyridine adduct of trimethyltin chloride seems to suggest that the latter decomposes rather than melt at 40°, Possibly, as soon as there is enough thermal energy to vapourise the pyridine, only a little more energy would be needed to dissociate the weak Sn - Py bond. The solid therefore collapses and melts easily. On the other hand, 4-acetylpyridine and 4-benzoylpyridine, although seemingly weaker donors than pyridines (see Discussion, section B) are much heavier than pyridine and therefore would not vaporise easily. It is possible therefore that their weights keep them on the Me_3SnCl, and the adducts stay solid until their melting or decomposition temperatures.

Unlike some pyridine adducts, e.g. $Ph_2SnCl_2.2Py$, that are known to be unstable[2], all the 3 - and 4 - acetyl - and benzoyl - pyridine adducts of methyltin, phenyltin, and stannic chlorides are stable at room temperature, but all melt or decompose below 360°, unlike some pyridine adducts of organotin chloride Lewis acids that are known[27] to be so thermally stable as not to fuse below 360°. The melting or decomposition temperatures increase generally from the adducts of trimethyltin and diphenyltin chlorides across their respective series to those of stannic chloride.

Although a complex's Lewis acid-Lewis base bond strength alone might not be enough to predict the melting points of a series of complexes, this observation appears to be in line with the common observation that the Lewis acid-Lewis base bond strength in organotin halide adducts increases from the adducts of the trialkyltin or triaryltin halide across to the adducts of stannic chloride[2], i.e. the Lewis acid - Lewis base bond strengths follow the order

$$R_3XSn - L < R_2X_2Sn - L < RX_3SnL < X_4Sn - L$$

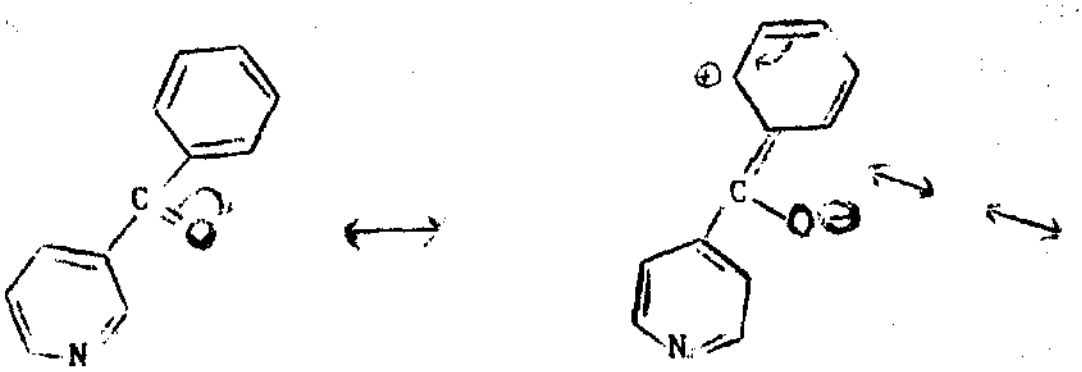
where R = alkyl or aryl,
X = halogen,
L = Lewis base.

This trend is explained by the fact that the electrophilicity of the Sn increases with increase in the number of electron withdrawing - halogen substituents on it.

In addition, to a good degree, the melting points appear to reflect the comparative binding strength of the Lewis bases. The unsubstituted pyridine adducts are generally higher melting than those of the substituted pyridines. The para-substituted pyridine adducts in turn are mostly higher melting than their meta-substituted pyridine adducts, because

the substituents of the former would not interfere sterically with the Lewis acid as the substituents of the latter probably might. The para-benzoyl pyridine adducts are higher melting than the para-acetylpyridine adducts, which seems to suggest that 4-benzoylpyridine might be a stronger Lewis base than 4-acetylpyridine (See Discussion, Section B).

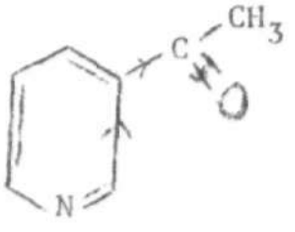
The melting points of the 3-benzoylpyridine adducts are generally higher than those of the 3-acetylpyridine adduct (see table 2). The reason for this is not clear, but it could be due to the mesomeric effect of the phenyl in 3-benzoylpyridine on the carbonyl of the molecule. The electron withdrawing effect of the C = O is neutralised by the mesomeric influence of the phenyl:



XL1

This effect is not present in 3-acetylpyridine. It is possible then that the electron withdrawing effect of

the carbonyl in 3-acetylpyridine is conducted via the σ - frame of the molecule, and this effect would make its nitrogen a poorer donor, compared with the 3-benzoylpyridine where mesomerism would neutrialize the electron withdrawing effect of the carbonyl, leaving the N virtually unaffected.



The suggestion holds where the S ← N bond strength, to a good degree, determines the melting or decomposition temperatures of the complexes, and it is feasible since most of the 3-ketopyridine adducts, especially of the methyltin and stannic chlorides, decompose rather than melt.

However, the melting points of a few of the complexes have been found to be out of trend (see table 3), for reasons not immediately explicable.

Compared with the 3- and 4- carbonyl pyridine adducts, the 2-acetyl- and 2-benzoyl pyridine complexes were found to be very sharp melting, and all melted with decomposition. The complexes obtained from 2-pyridine carboxaldehyde melted over comparatively larger ranges, which seems to suggest their instability and non-purity.

Table 2

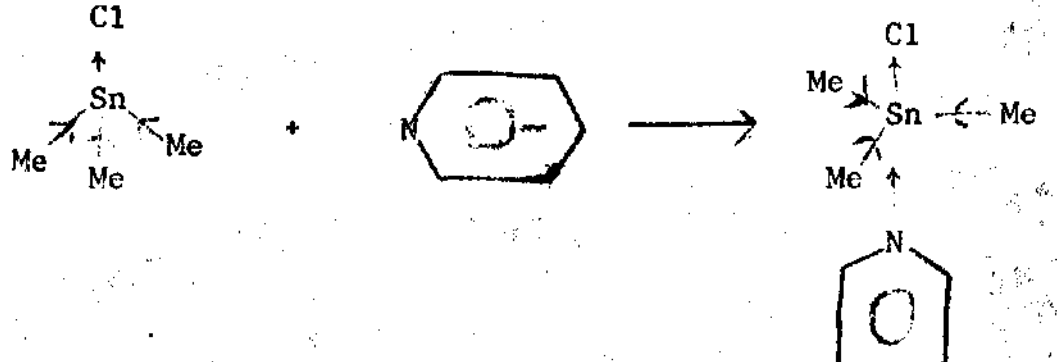
The comparative melting points of the pyridine, acetyl and benzoyl pyridine adducts of the methyltin, phenyltin, and stannic chlorides.

Lewis Acid	Pyridine	4-Acetyl Pyridine	4-Benzoyl Pyridine	3-Acetyl-Pyridine	3-Benzoyl-Pyridine
Me_3SnCl	40-41°C	55-56°C	65-66°C	- °C	-°C
Me_2SnCl_2	163	114-115°	157-159	109-110°	109-111
$MeSnCl_3$	Sublimed 280-290	138-140 decomp.	300-303 decomp.	185-187 decomp.	222-225 decomp.
$SnCl_4$	Sublimed >300°	181-183 decomp.	322-323 decomp.	233-236 decomp.	250-252 decomp.
$Ph\ SnCl_3$	Sublimed 310-315	140-143 decomp.	255-257° decomp.	133-135	95-97
Ph_2SnCl_2	151-152	94-96°	124-126	62-64	119-121

(d) Analyses and Stoichiometry

3- and 4-acetyl- and benzoyl-pyridine adducts of the methyltin, phenyltin, and stannic chlorides.

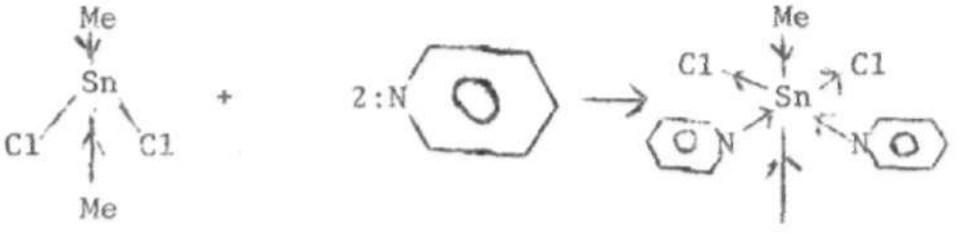
It has long been known[4,9] that triorganotin halides form 1:1 complexes while diorganotin dihalides, monoorganotin trihalides, and stannic halides form 1:2 complexes with monodentate ligands. Triorganotin halides form no more than 1:1 adducts with monodentate ligands, possibly because of steric repulsion which results from crowding around the tin atom. Another possible factor is electron saturation around the tin atom, since the organic substituents have a positive inductive effect.



VI VII

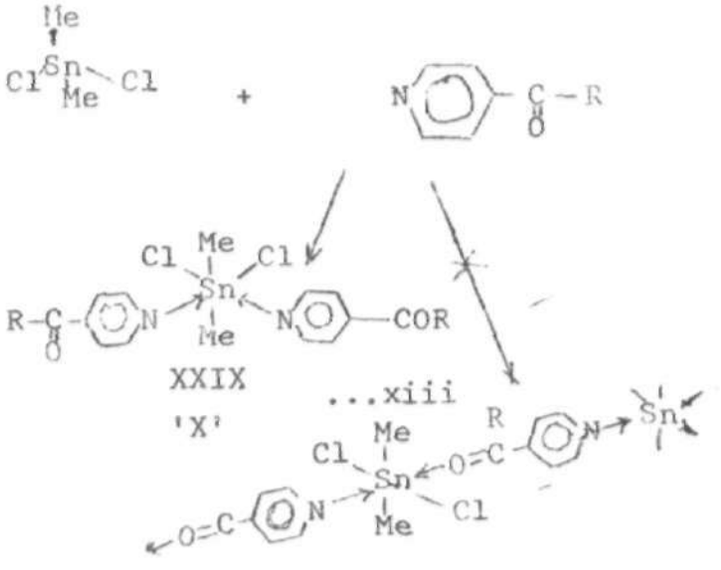
When there are two or more electron withdrawing groups on the tin, the tin atom is now positive enough to bind with two

electron donating sites; its two e.g. d-orbitals are used to accomodate the incoming electrons:



IV V

Acetyl and benzoyl - pyridines have two possible pyridine "N" and carbonyl"O". With Me_2SnCl_2, for example, many types of bonds could be formed:



XXIX

'X'

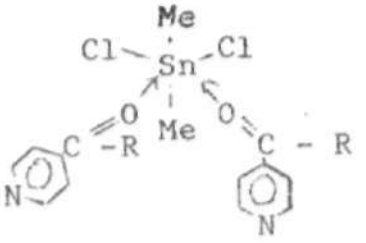
...xiii

...xiv

XXX

'Y'



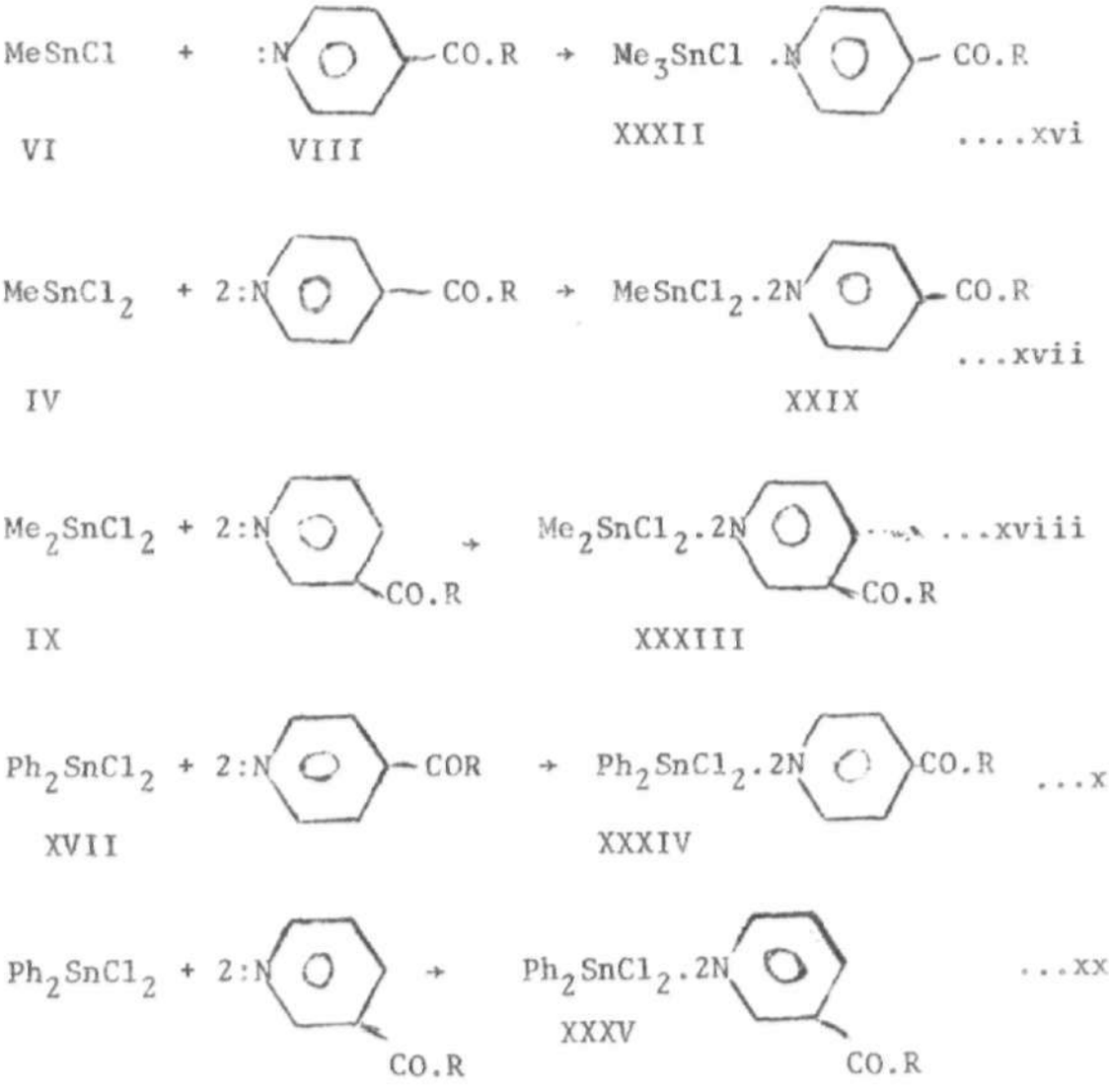


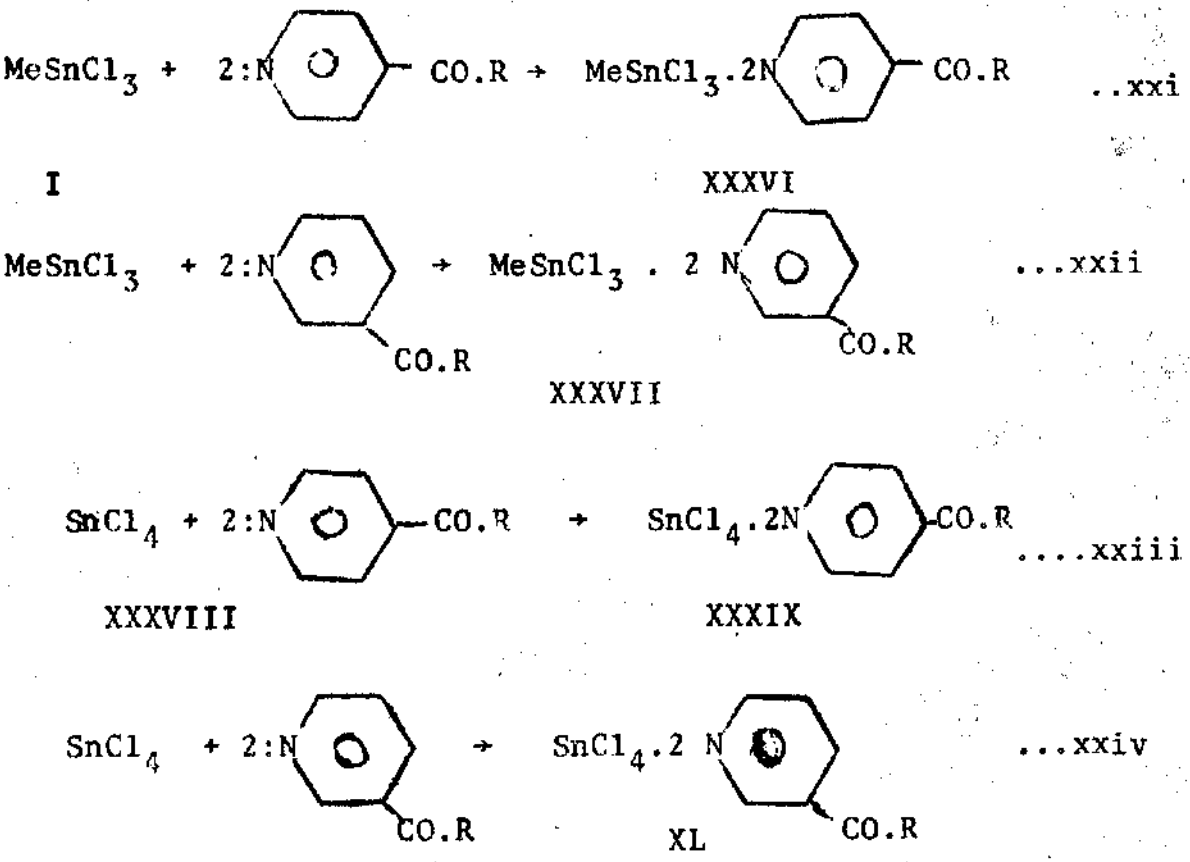
...xv

"Z' XXX1

In 'X', the Lewis base is monodentate and coordinating through N; the resulting adduct is 1:2. In 'Y' the ligand binds with both N and O, and is therefore bidentate, and by its geometry, the product would be polymeric, though fundamentally a 1:1 adduct. In 'Z', only the O is binding; a 1:2 adduct would result. However, since the electron pair on nitrogen would be more available for coordination than a pair on the more electronegative oxygen, and since in terms of steric hindrance, the nitrogen end is free than the oxygen end, in a situation of competition, the binding of the ligand would be through N rather than O. Elemental analysis have confirmed that the triorganotin halide adducts are 1:1 while the diorganotin,

monoorganotin, and stannic chlorides' complexes are 1:2 adducts. Infra red spectroscopy (see later in this section) has shown that only the N binding sites on the ligands are involved in bond formation. Thus:





where R = Me, C_6H_5

Table 3

The melting points of, and the elemental analysis results for, the 3- & 4-acetyl,and 2-,3-and 4-benzoyl pyridine adducts of the methyltin, phenyltin, and stannic chlorides.

	M.O.°C	Calculated, %					Found, %				
		C	H	Cl	N	Sn	C	H	Cl	N	Sn
$Me_3SnCl.4.Ac.Py$	55-56	37.48	4.99		4.37	37.07	37.69	5.00		4.43	37.25
$Me_3SnCl.4-Be.Py$	62-63	47.10	4.71		3.66	31.05	47.34	4.73		3.85	31.50
$Me_2SnCl_2.bis-4-Ac.Py$	117-118	41.60	4.36		6.07	25.70	41.84	4.45		5.76	25.79
$Me_2SnCl_2.bis-4-Be.Py$	157-159	53.27	4.10		4.78	20.26	53.35	4.17		4.75	20.40
$Me_2SnCl_2.bis-3-Ac.Py$	109-110	41.60	4.36		6.07	25.70	41.90	4.41		5.95	25.75
$Me_2SnCl_2.bis-3-Be.Py$	109-111	53.27	4.10		4.78	20.26	53.37	4.14		4.73	20.46
$MeSnCl_3.bis-4-Ac.Py$	138-140	37.33	3.53		5.81	24.61	36.92	3.59		5.65	24.80
$MeSnCl_3.bis-4-Be.Py$	300-303	49.41	3.62		4.61	19.58	49.50	3.65		4.60	19.85
$MeSnCl_3.bis-3-Ac.Py$	185-187	37.33	3.53		5.81	24.61	37.10	3.61		5.70	24.87
$MeSnCl_3.bis-3-Be.Py$	222-225	49.41	3.62		4.61	19.58	49.52	3.66		5.68	19.82
$SnCl_4.bis-4-Ac.Py$	181-183	33.42	2.79	28.25	5.57	23.61	33.12	2.81	28.62	5.45	23.91
$SnCl_4.bis-4-Be.Py$	322-323	45.96	2.87	22.66	4.46	26.75	45.85	2.85	22.81	4.48	26.84
$SnCl_4.bis-3-Ac.Py$	233-236	33.42	2.79	28.25	5.57	23.61	33.02	2.86	28.57	5.43	23.98
$SnCl_4.bis-3-Be.Py$	250-252	45.96	2.87	22.66	4.46	26.75	45.82	2.83	22.85	4.47	26.87
$PhSnCl_3.bis-4-Ac.Py$	140.143	44.10	3.49		5.15	21.81	44.24	3.64		4.89	22.10

TABLE 3 (CONTD)

	M.P. °C	Calculated, %					Found, %				
		C	H	Cl	N	Sn	C	H	Cl	N	Sn
$PhSnCl_3$.bis-4-Be.Py	255-257	53.88	3.44		4.19	17.76	53.95	3.52		4.08	18.10
$PhSnCl_3$.bis-3-Ac.Py	133-135	44.10	3.49		5.15	21.81	44.15	3.55		4.97	22.05
$PhSnCl_3$.bis-3-Be-Py	95-97	53.88	3.44		4.19	17.76	53.96	3.60		4.21	18.05
Ph_2SnCl_2.bis-4-Ac.Py	94-96	53.27	4.10		4.78	20.26	53.01	4.05		4.68	20.48
Ph_2SnCl_2.bis-4-Be.Py	124-126	60.87	3.95		3.95	16.72	60.56	4.04		3.89	16.94
Ph_2SnCl_2.bis-3-Ac.Py	62-64	53.27	4.10		4.78	20.26	52.98	4.14		4.70	20.51
Ph_2SnCl_2.bis-3-Be.Py	119-121	60.87	3.95		3.95	16.72	60.64	3.98		3.90	16.85

11 2-Acetylpyridine, 2-benzoylpyridine, and 2-pyridine carboxaldehyde complexes of methyltin, phenyltin, and stannic chlorides.

It would be expected that a 2-carbonyl pyridine, by its geometry, when it coordinates on a Lewis acid, would act as a simple bidentate ligand to yield a stereochemically stable five membered ring:



...XXV

XI

where M = Lewis acid,

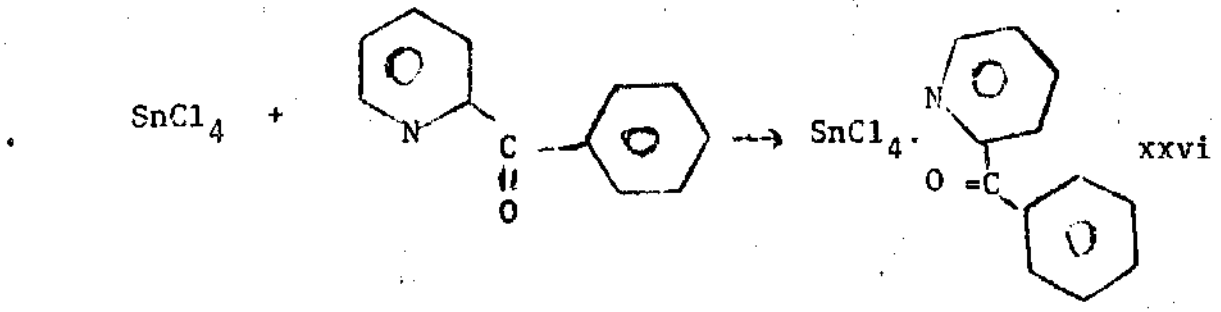
R = H, alkyl, or aryl.

Jain has reportedly[29] obtained a 1:1 complex from stannic chloride and 2-acetylpyridine. He however claimed to have obtained 1:2 complexes for $SnBr_4$ and SnI_4 with 2-acetylpyridine.

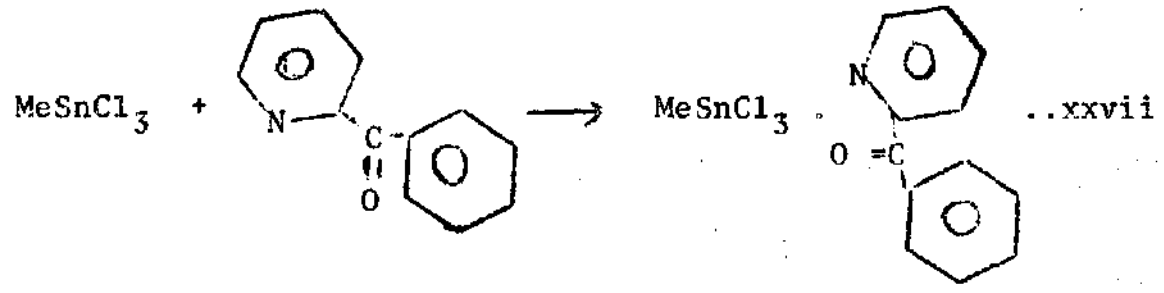
In their study of the interaction of the row transition metals with 2-acetyl- and 2-benzoyl-pyridine, and 2-pyridine carboxaldehyde, Plytzanopoulos et al have reported[14] that both the N and O of the ligands are involved in dative bonding, implying that they act as bidentate ligands and therefore would

be expected to give only 1:1 complexes with organotin halides, since the maximum coordination number of Sn is six[1,2].

It has been found in this work, by elemental analysis and spectroscopy that 2-benzoylpyridine reacts with stannic chloride, methyltin trichloride, and phenyltin trichloride to give 1:1 complexes, in which both N and O are involved in bonding.

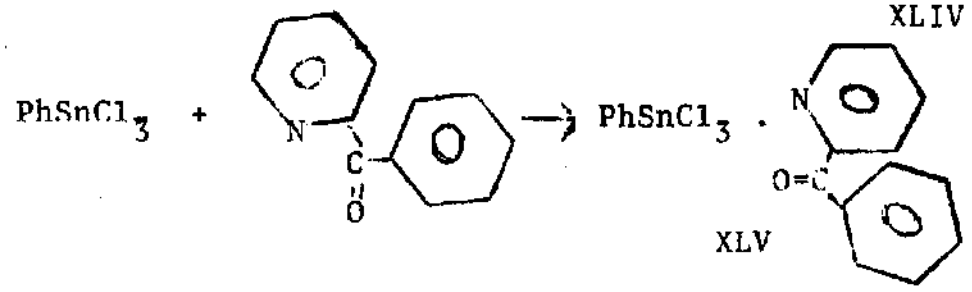


XLII XLIII xxvi



..xxvii

XLIV



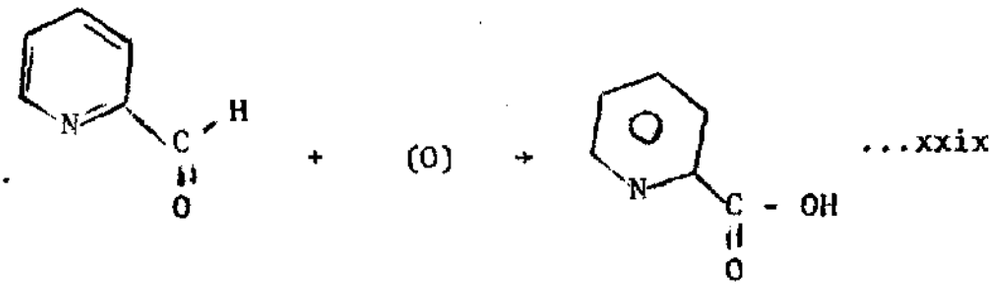
XLV

No product was isolable in the reaction of the diorganotin and triorganotin chlorides with 2-benzoylpyridine, possibly because the products were too unstable due to steric factors arising from over crowding around the tin atom. The phenyl of the benzoyl group would be repelled by the other organic groups on the tin, implying the repulsion of the entire ligand.

It has been found in this work that the reaction of 2-acetylpyridine with stannic chloride and the organotin chlorides is not as simple and straightforward as that of 2-benzoylpyridine. As opposed to the findings of Jain[29], elemental analysis suggests that the complex obtained when stannic chloride reacts with 2-acetylpyridine in dichloromethane contains $SnCl_4$ and 2-acetylpyridine in the ratio of 1:2. Phenyltintrichloride and 2-acetylpyridine also are present in their product in the ratio of 1:2. Diphenyltin dichloride, unlike the case with 2-benzoylpyridine, also gave a product in which Ph_2SnCl_2 and 2-Acetylpyridine seem to be present in the ratio 1:2. 2-Acetyl pyridine did not give any observable reaction with triphenyltin chloride.

With the methyltin chlorides, 2-Acetyl pyridine reacted to give products for which neither elemental analysis nor the available spectroscopic methods could provide any meaningful structural or even stoichiometric interpretation. Trimethyltin chloride however has not given any observable reaction with 2-acetylpyridine.

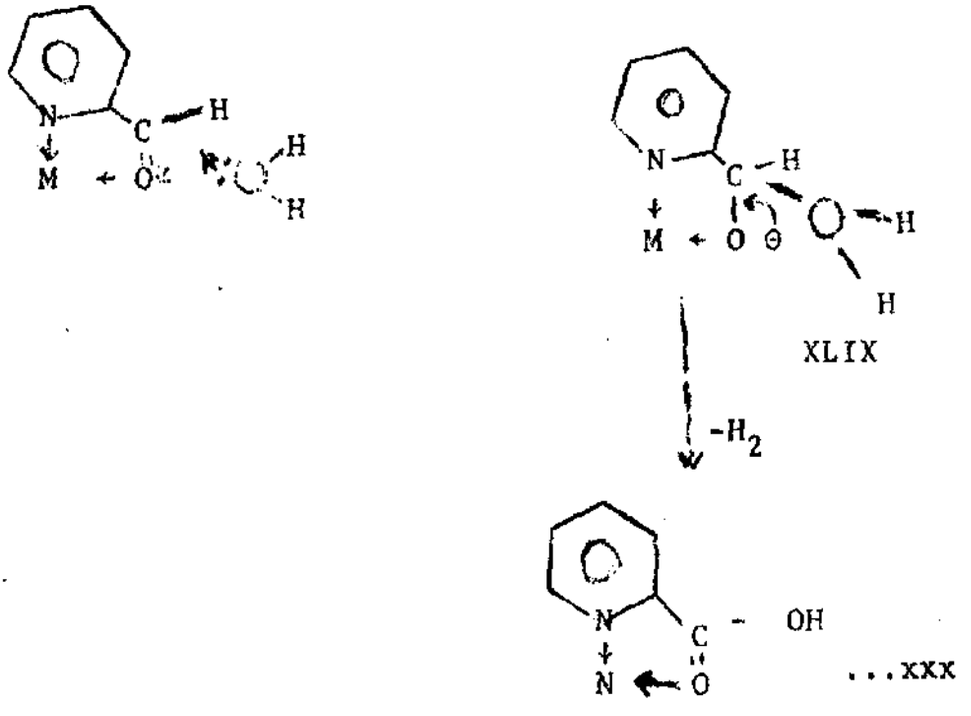
2-Pyridine carboxaldehyde has not appeared to be a good Lewis base, as most of the products with stannic chloride and the organotin chlorides were unstable. Of all the Lewis acids tried, only phenyltin trichloride gave a product of meaningful stoichiometry (1:1) with the ligand. With stannic chloride, it gave a dirty white unstable solid; with methyltin trichlordie, it gave a brown unstable solid; with dimethyltin and diphenyltin dichlorides, it gave thick oils that could not be purified. No reaction was observed between the ligand and the triorganotin chlorides. The instability of the products a reaction of 2-pyridine carboxaldehyde with stannic chloride and the organotin chlorides could be due to the easy oxidation of 2-pyridine carboxaldehyde to 2-pyridine carboxylic acid.



...xxix

XLVI XLVII

Coordination of the oxygen of the carboxaldehyde to some Lewis acid would make oxidation of the carboxaldehyde easy, as its C is made more +ve and therefore more susceptible to attack by water:



XLIX

...xxx

I

where M = Lewis acid

This suggestion seems to be substantiated by the presence of an absorption at ≈ 3500cm^{-1} (OH) in the i.r. spectrum of the product of reaction of stannic chloride and 2-pyridine carboxaldehyde.

Table 4

The melting points and the elemental analysis results for the complexes of 2-acetyl and 2-benzoyl-pyridine with methyltin and phenyltin trichlorides, and stannic chloride

Compound	M.P. °C	Calculated %					Found %				
		C	H	Cl	N	Sn	C	H	Cl	N	Sn
$SnCl_4$.2-Be.Py	271-273 dec.	32.46	2.03		3.16	26.75	32.57	2.10		3.06	26.80
$MeSnCl_3$.2-Be.Py	182-183	36.86	2.84	25.17	3.31	28.01	36.85	2.88	25.23	3.27	28.35
$PhSnCl_3$.2-Be.Py	209-211	44.52	2.89	21.95	2.89	24.46	44.29	2.97		2.83	24.78
$SnCl_4$.bis-2-Ac.Py?	253-255	33.42	2.79	28.25	5.57	23.61	32.91	2.87		5.36	23.90
$PhSnCl_3$.bis-2-Ac.Py?	189-191	44.10	3.49	19.57	5.15	21.81	43.72	3.63		5.09	22.05

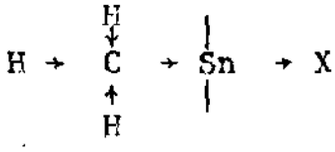
(e) Spectral Properties of the Complexes: Nuclear Magnetic Resonance.

A lot has been reported[7,17,30] on the proton magnetic resonance spectroscopy of methyltin halides. Generally, it has been found that the chemical shift of the methyl protons of methyltin halides increases with decrease in the electron density on the tin atom. The chemical shift values, δ, for methyltin halides follow the order

$$MeSnX_3 > Me_2SnX_2 > Me_3SnX$$

where X = halogen.

Thus, with increasing number of the comparatively electronegative halogen atoms on the tin atom, the deshielding experienced by the methyl protons increases.



LI

Any process that makes the Sn more positive, like the ionisation or partial ionisation of the organotin halide, would enhance the electron drift from methyl to tin, thereby further deshielding the protons. The reverse would be felt, with increase of the electron density on Sn.

Many other factors which might influence the values of the chemical shift of the methyl protons of methyl tin halides have been intensively studied[17]. These factors include the polarity and polarizability of the solvent used. The methyltin chloride tends to ionize in polar media[17] solvation of the positive Sn might influence its electron density, which in turn determines the degree of deshilding of the methyl protons.

N.M.R. investigation of pyridine complexes of methyltin chlorides was successful only for $Me_3SnCl.Py$, which alone was soluble enough for N.M.R. study[13,31]. Detailed studies of the pyridine adducts of the methyltin chlorides had therefore been possible for only $Me_3SnCl.Py$; other adducts, $Me_2SnCl_2 \cdot 2Py$ and $MeSnCl_3.2Py$, were found to precipitate in the solvents tried [13,18]. Use of other physical methods such as I.R. and Raman, Nuclear Quadrupole Resonance, Mossbauer spectroscopy e.t.c. had to be resorted to for even qualitative studies.

The difficulty in making use of N.M.R. spectroscopy in the study of the pyridine adducts of methyltin and even stannic chlorides has been overcome in this work.

Deuterodimethyl sulphoxide has been found capable of dissolving the pyridine adducts well enough for spectroscopic study.

Unlike the pyridine adducts, many of the substituted pyridine adducts of the methyltin chlorides have been found soluble enough in common organic solvents for meaningful studies by NMR spectroscopy. The 4-acetyl and 4-benzoyl pyridine adducts of trimethyltin chloride are soluble in carbon tetrachloride; while the analogous adducts as well as those of 3-acetyl and 3-benzoyl-pyridine of dimethyltin dichloride are soluble enough in deuteroacetone. The corresponding adducts of methyltin trichloride and stannic chloride, however, were soluble only in deuterodimethyl sulphoxide. This has been a fortunate breakthrough, for NMR can now be used vis-a-vis other spectroscopic methods and elemental analysis, for the qualitative identification, especially in terms of mole proportion of the ligand in the complex.

Van der Berghe et al have reported[30] the chemical shifts of methyltin halides. They found, among other things, that the chemical shift, δ, increased with increasing

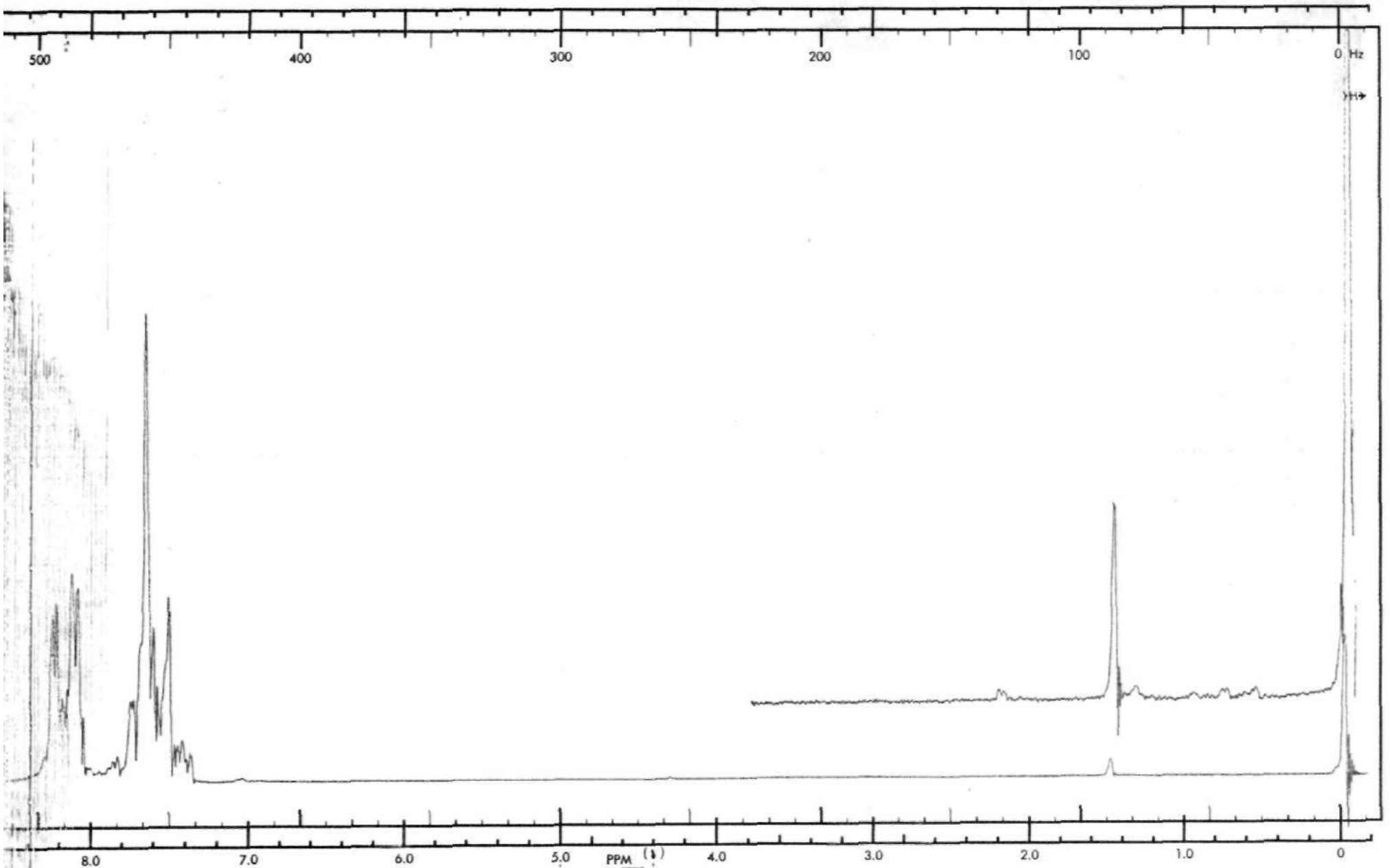
number of halogen substituents on Sn. i.e.

$$\delta\ MeSnX_3 > \delta\ Me_2SnX_2 > \delta\ Me_3SnX.$$

This implies that δ increases with decrease of the electron density on Sn. It would be expected therefore, that complex formation of a methyltin halide with a Lewis base would increase the electron density on Sn, and thus reduce the deshielding effect of Sn on the methyl protons. Moreover, it would also be expected that the degree of reduction of the deshielding effect of the Sn on the methyl protons should increase with increasing donor strength of the Lewis base.

i. The Pyridine adducts of Methyltin, phenyltin, and stannic chlorides.

Since no spectrum of the methyltin chloride adducts of pyridine other than that of $Me_3SnCl.Py$[13] had been previously reported, little had been known of the n.m.r. spectra of pyridine adducts of methyltin halides. Contrary to expectation, it has been found that the chemical shift of the methyltin protons increases as the methyltin chloride adds to pyridine. Thus the δCH_3 values are lower for the methyltin chloride pyridine adducts (see table 5). The reason



MANUAL AUTO ☐

SWEEP OFFSET (Hz): /

SPECTRUM AMPLITUDE: 10

INTEGRAL AMPLITUDE: /

SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 250

SWEEP WIDTH (Hz): 25 50 100 250 500

FILTER: Y 2 3 4 5 6 7 8

RF POWER LEVEL: 0.1

(250)
(500)
(2)
(.05)

SAMPLE: $Me_2SnCl_2 \cdot 2NO$

REMARKS:

SOLVENT: Nitrobenzene

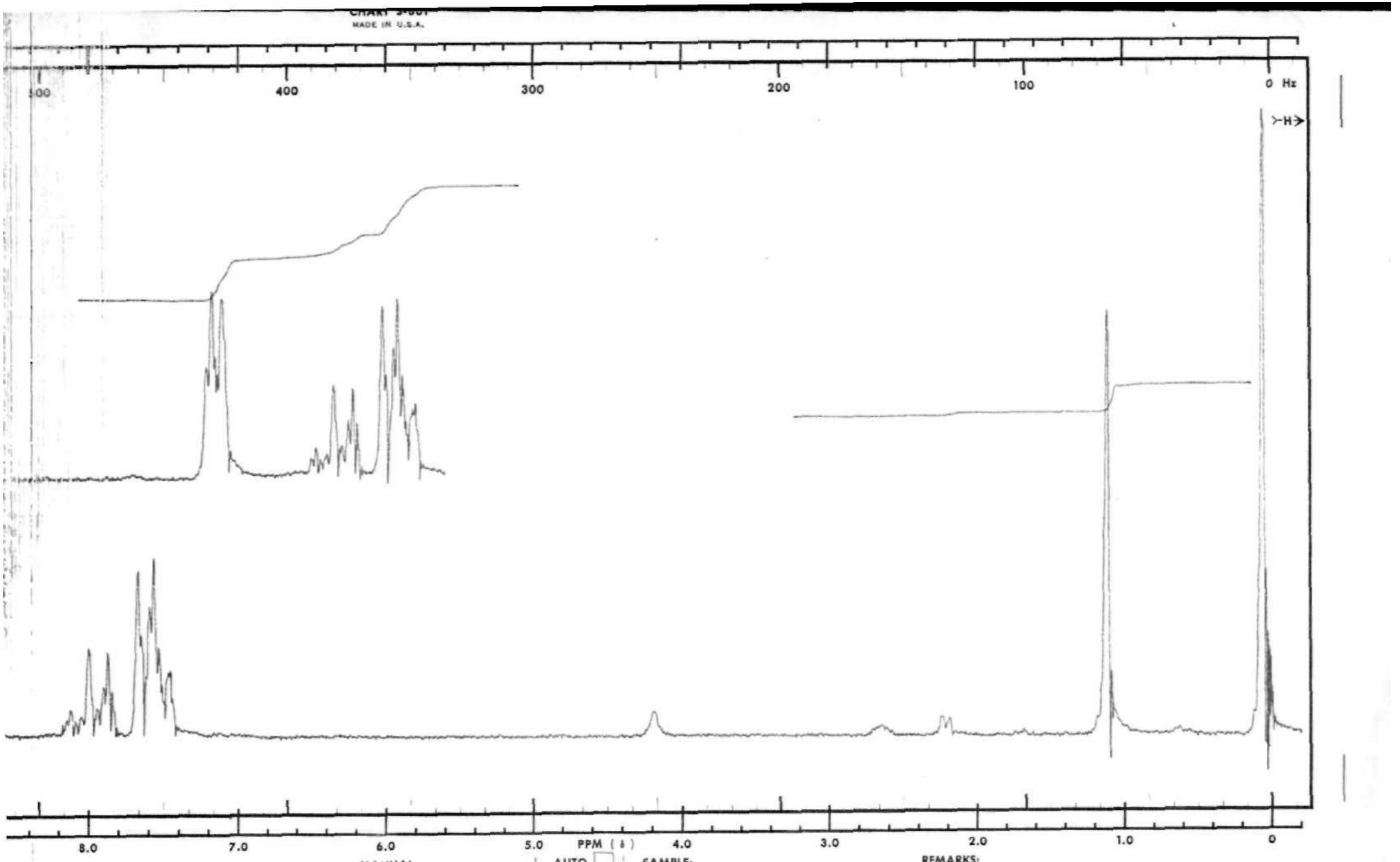
STOHLER ISOTOPE CHEMICALS
49 JONES RD., WALTHAM, MASS. 02154, U.S.A.
IM BAUMGARTEN CH 3044 INNERBERG, SWITZELAND
P.O. BOX 1134, MONTREAL 101, CANADA

PRINTED IN U.S.A.

DATE: 22/8/80

OPERATOR: Bonine

60 MHz NMR
SPECTRUM NO.



MANUAL AUTO ☐

WEEP OFFSET (Hz): 100
PECTRUM AMPLITUDE: 10
NTEGRAL AMPLITUDE: 3
PINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 0.1

(250)
(500)
(2)
(.05)

SAMPLE: $MeSnCl_3 \cdot 2Py$

SOLVENT: d-DMSO

REMARKS:

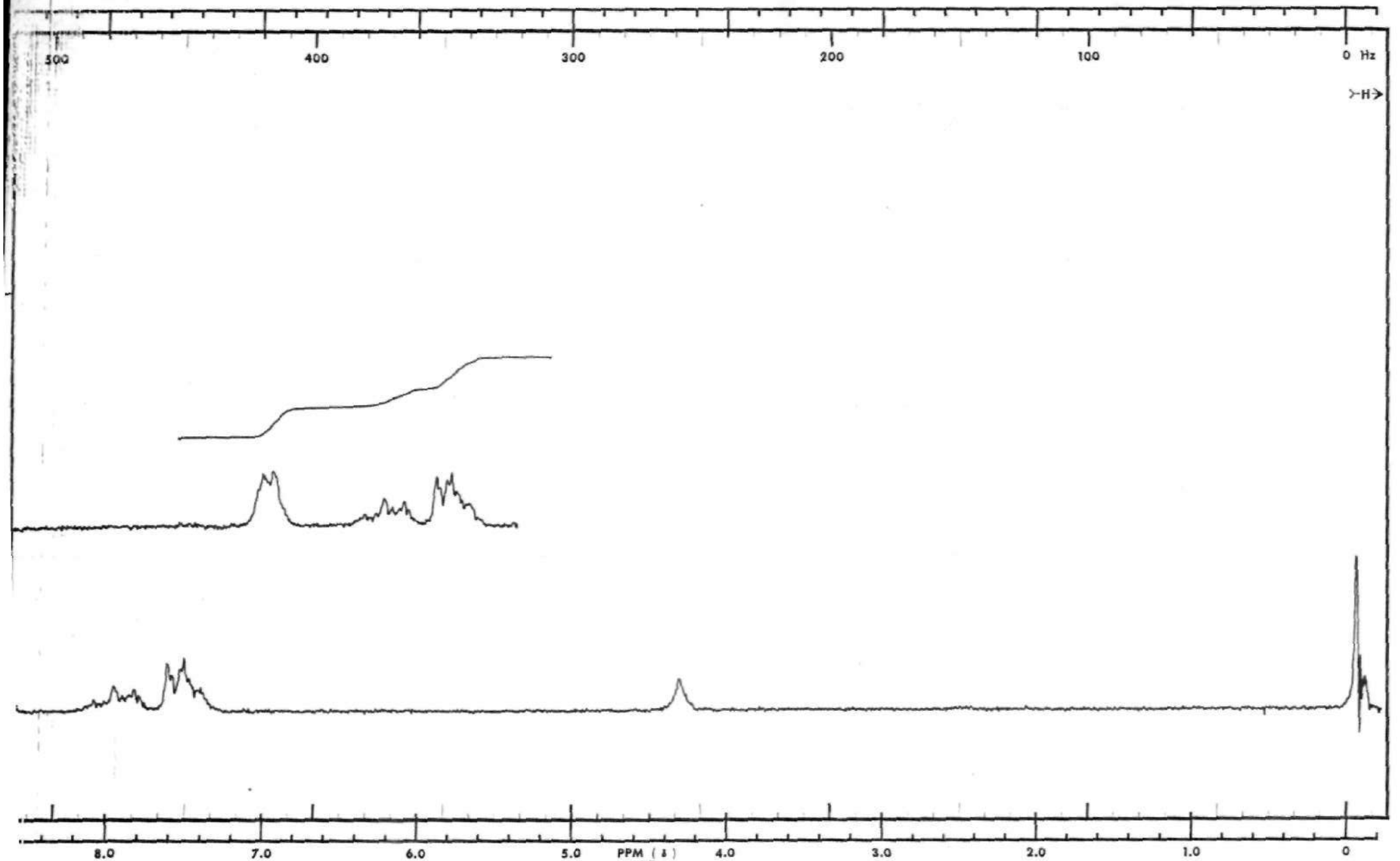
varian
analytical instrument division

DATE: 28/11/80

OPERATOR: Bonine

60 MHz NMR
SPECTRUM NO.

CHART S-60T
MADE IN U.S.A.



MANUAL | AUTO ☐ | SAMPLE: | REMARKS:

WEEP OFFSET (Hz): 100
ECTRUM AMPLITUDE: 1.0
ITEGRAL AMPLITUDE: 5
INNING RATE (RPS): 40

SWEEP TIME (SEC): 50 250 — (250)
SWEEP WIDTH (Hz): 25 50 100 250 500 — (500)
FILTER: 1 2 3 4 5 6 7 8 — (2)
RF POWER LEVEL: 0 — (.05)

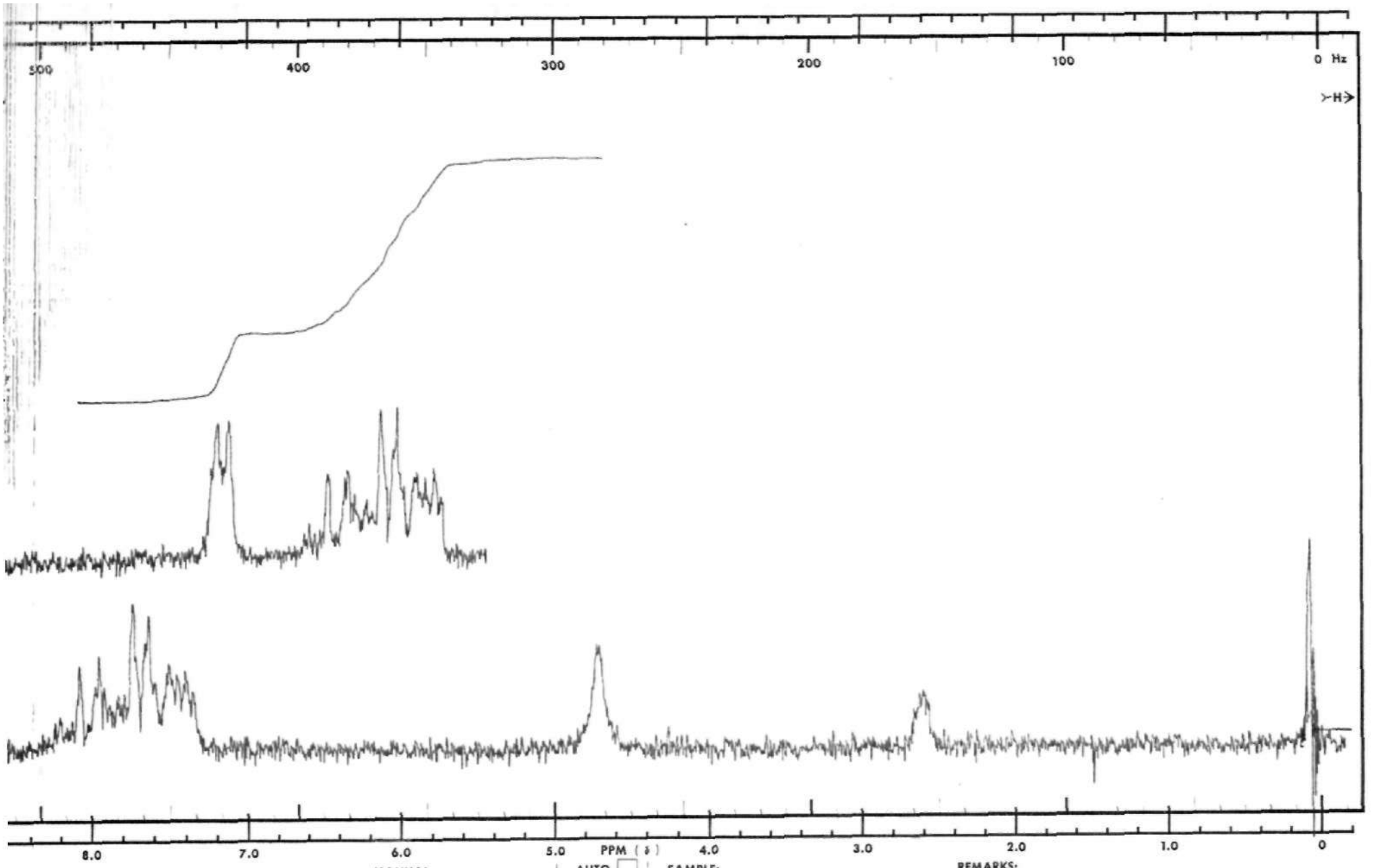
SOLVENT: d-DMSO

varian
analytical instrument division

DATE: 11/4/81

OPERATOR: Bonin

60 MHz NMR
SPECTRUM NO.



MANUAL AUTO ☐

SAMPLE: $Ph_3SnCl_3 \cdot 2H_2O$

REMARKS:

SWEEP OFFSET (Hz): 100

SPECTRUM AMPLITUDE: 40

INTEGRAL AMPLITUDE: 6

SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 250 (250)

SWEEP WIDTH (Hz): 25 50 100 250 500 (500)

FILTER: 1 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: 0.1 (.05)

SOLVENT: d-DMSO

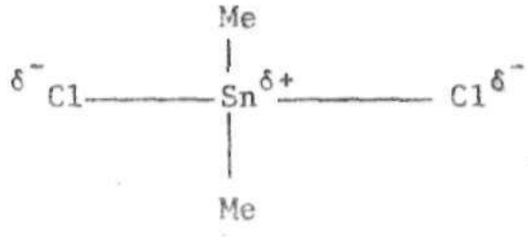
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analytical instrument division

DATE: 1/12/80

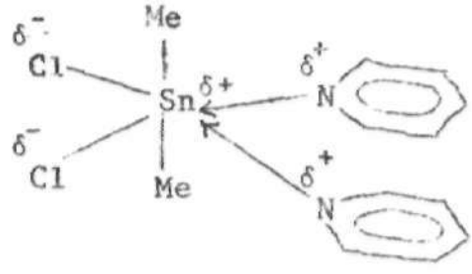
OPERATOR: Bowers

60 MHz NMR
SPECTRUM NO.

for this behaviour is not very clear, but it is possible that anisotropic effects of the pyridine ring might enhance the deshielding of the methyl protons, as the pyridine binds to the methyltin chloride. Also, since the Sn-Cl bond is polar, the tendency for the methyltin chloride to ionize would be enhanced in solvents of high dielectric constants, like dimethyl sulphoxide. viz.



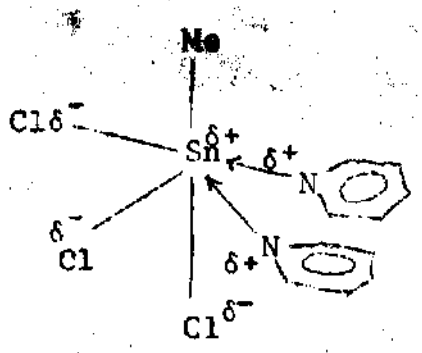
If there are conditions that would stabilize the ions when formed or near completely formed, then the methyltin chloride would assume the ionic state, otherwise electrostatic attraction might tend to inhibit total ionization of the Sn - Cl moieties. Now, as the methyltin chloride complexes with the pyridine, it is possible that the ionic state would be stabilized:



Since pyridine, originally a neutral molecule, binds datively to the Sn in forming a complex, its N becomes positively charged as soon as it binds to the Lewis acid. The positive charge on the Lewis acid and the induced positive charge on the Lewis base would repel, making the Lewis acid - Lewis base interaction a not very strong one. The intense positive charge creacted on the Sn by the presumably almost complete ionization of the halogens then causes a general contraction of the Sn orbitals. The effective nuclear charge at the outer shell increases and the methyl protons are more deshielded by inductive mechanism therefore.

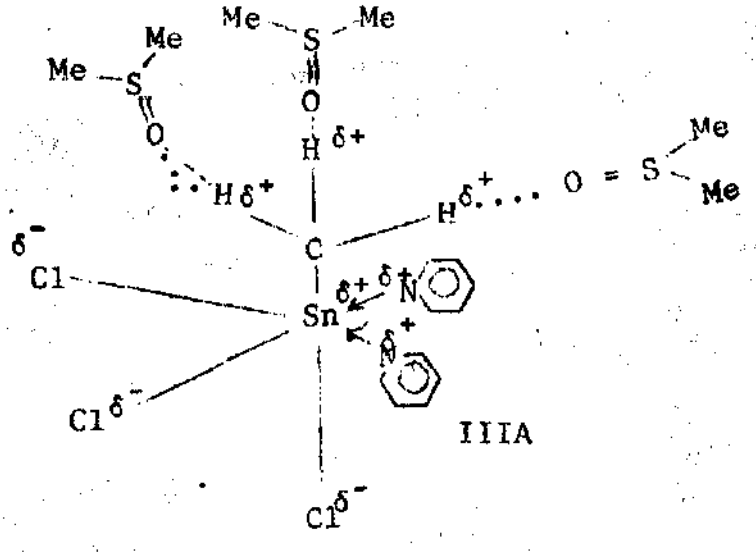
It has also been observed that, contrary to expectation, the chemical shift values for methyltin trichloride and its pyridine adduct are lower than those for dimethyltin dichloride and its pyridine adduct (see table 5). The reason for this, too, is not very clear, but in our opinion, the degree of solvation, considering steric factors, by the solvent molecules on the Sn would be more in methyltin trichloride than in dimethyltindichloride. Sn in $MeSnCl_3$ and its pyridine adduct is sterically freer for solvation by electron donating solvent molecules than Sn in Me_2SnCl_2

and its pyridine adduct. The induced positive charge on Sn in the former, hence its power to attract electron donating solvent molecules, is higher than that on Sn in the latter



III

And dimethyl sulphoxide is known[32] for its strong solvating ability. It is also possible that the induced positive charge on the Sn - Me hydrogens by the positive Sn is high enough to make 'hydrogen bonding' possible between the Sn - Me hydrogens and the solvent donor molecules.



IIIA

This would mean an overall increased shielding of the Sn-Me protons, and hence lower δ values. If this explanation is correct, then the δ values for the Sn - Me protons in δ-DMSO, a strongly solvating medium, would be generally lower than the δ values for the Sn - Me protons in less strongly solvating media. This has been found to be the case; the δ Sn - CH_3 values are higher in acetone than in dimethylsulphoxide (see table 5).

It has been possible, for the first time, to obtain the n.m.r. of phenyltin trichloride and stannic chloride pyridine adducts, which had been deemed too insoluble to study[17]. Apart from their use for qualitative identification however, the spectra have not, as of now, been of much further use as the Lewis base proton signals interfered with the Lewis acid proton signals.

ii. 3- and 4- acetyl and benzoyl pyridine adducts of methyltin, phenyltin, and stannic chlorides.

As with the pyridine adducts, the chemical shift values in DMSO for the methyltin protons in the 3- and 4- acetyl and benzoyl - pyridine adducts of methyltin chloride have been found to be slightly higher than the shift values for the parent methyltin chloride. The shift values are generally

lower than for the corresponding pyridine adducts, however, suggesting that the acylpyridines are weaker ligands than pyridine (see table 5).

The n.m.r. spectra of the hitherto unreported 3- and 4-acetyl and benzoyl - pyridine adducts of the phenyltin and stannic chlorides have also been run; the Ph_2SnCl_2 adducts mostly in deuteroacetone, and $PhSnCl_3$ and $SnCl_4$ adducts mostly in δ-DMSO. The spectra go further to enhance the ease of identification of the adducts.

It is noteworthy that the protons of the Sn-phenyl are divided into two multiplets; the meta- and para-protons, being more shielded than the ortho-protons, give a

TABLE 5

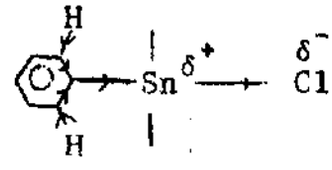
Chemical Shifts of H_3C - Sn ~ protons.

Compound	Chemical Shift, δ, (ppm) in		
	d-DMSO	D-Acetone	CCl_4
Me_3SnCl	0.58		0.67
$Me_3SnCl.Py$	0.60		0.62
$Me_3SnCl.4\text{-}Ac.Py$	0.60	0.68	0.62
$Me_3SnCl.4\text{-}Be.Py$	0.60	0.68	0.62
Me_2SnCl_2	1.02	1.23	1.10

TABLE 5 (CONTD.)

Compound	Chemical Shift, δ, (ppm) in		
	d-DMSO	d-Acetone	CCl_4
$Me_2SnCl_2.2Py$	1.15	1.22	
$Me_2SnCl_2.bis$-4-Ac.Py	1.14	1.21	
$Me_2SnCl_2.bis$-4-Be.Py	1.15	1.20	
$Me_2SnCl_2.bis$-3-Ac.Py	1.13	1.21	
$Me_2SnCl_2.bis$-3-Be.Py	1.14	1.24	
$MeSnCl_3$	0.98		
$MeSnCl_3.2Py$	1.03		
$MeSnCl_3.bis$-4-Ac.Py	1.02		
$MeSnCl_3.bis$-4-Be.Py	1.02		
$MeSnCl_3.bis$-3-Ac.Py	1.02		
$MeSnCl_3.bis$-3-Be.Py	1.01		

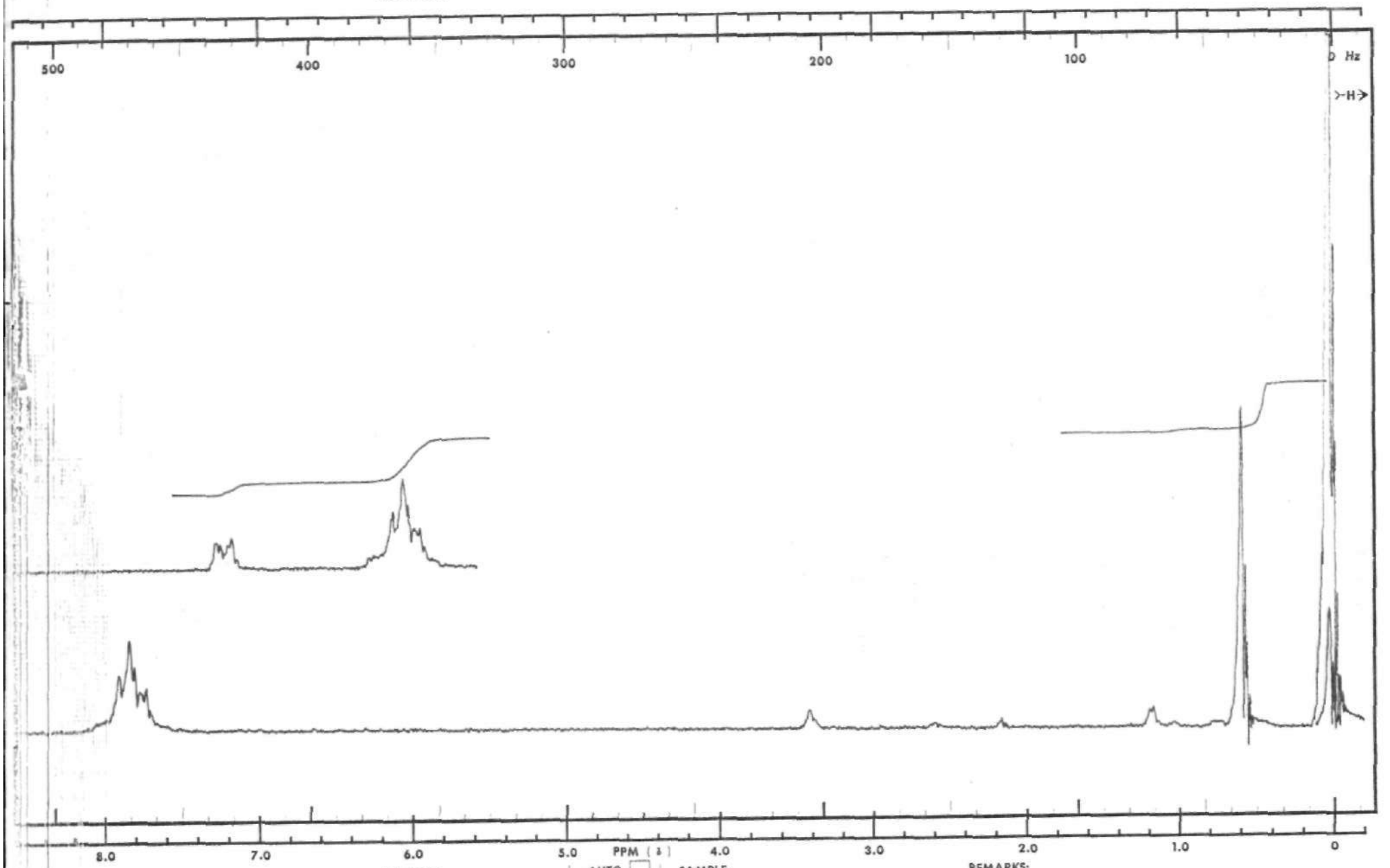
multiplet signal at a higher field than the ortho - protons



LII

Due to the interference of the Lewis base proton signals, it has not been possible to say how complexation of the pyridines affect the chemical shifts of the Sn-phenyl protons of the phenyltin chlorides. A solution to this problem would be to use totally deuterated ligands.

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MANUAL | AUTO ☐

SWEEP OFFSET (Hz): 107
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: 5
SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 250 ✓ (250)
SWEEP WIDTH (Hz): 25 50 100 250 500 ✓ (500)
FILTER: 1 2 3 4 5 6 7 8 ✓ (2)
RF POWER LEVEL: 0.1 (.05)

SAMPLE: 11'-2,5-N(1-NO)-CO-(C)

SOLVENT: d-DMSO

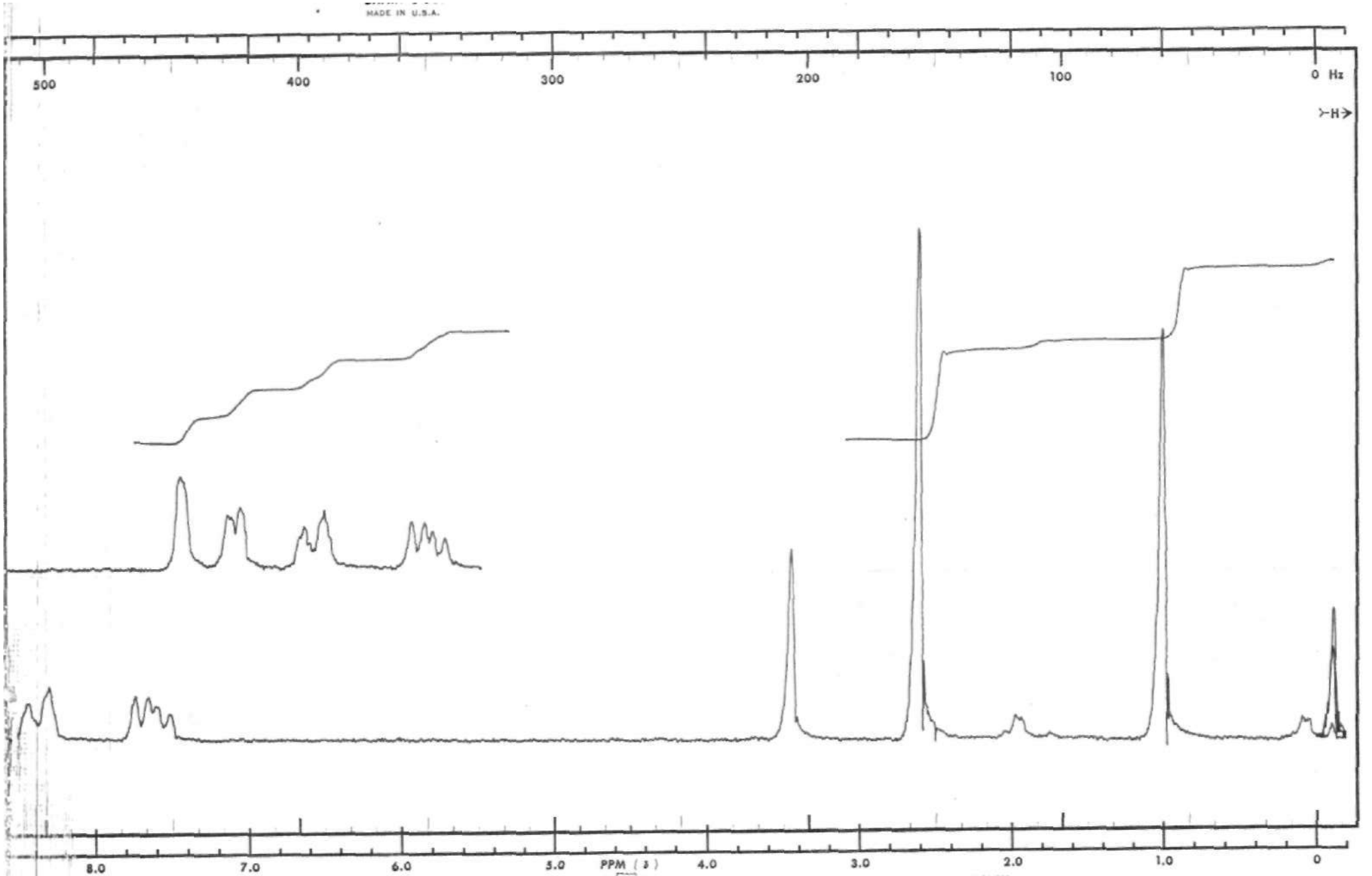
REMARKS:

varian
analytical instrument division

DATE: 8-4-81

OPERATOR: Bonine

60 MHz NMR
SPECTRUM NO.



MANUAL AUTO ☐ SAMPLE: REMARKS:

SWEEP OFFSET (Hz): 1202

SPECTRUM AMPLITUDE: 8.0

INTEGRAL AMPLITUDE: 5.0

SPINNING RATE (RPS): 46

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FILTER: 1 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: 8.1 (.05)

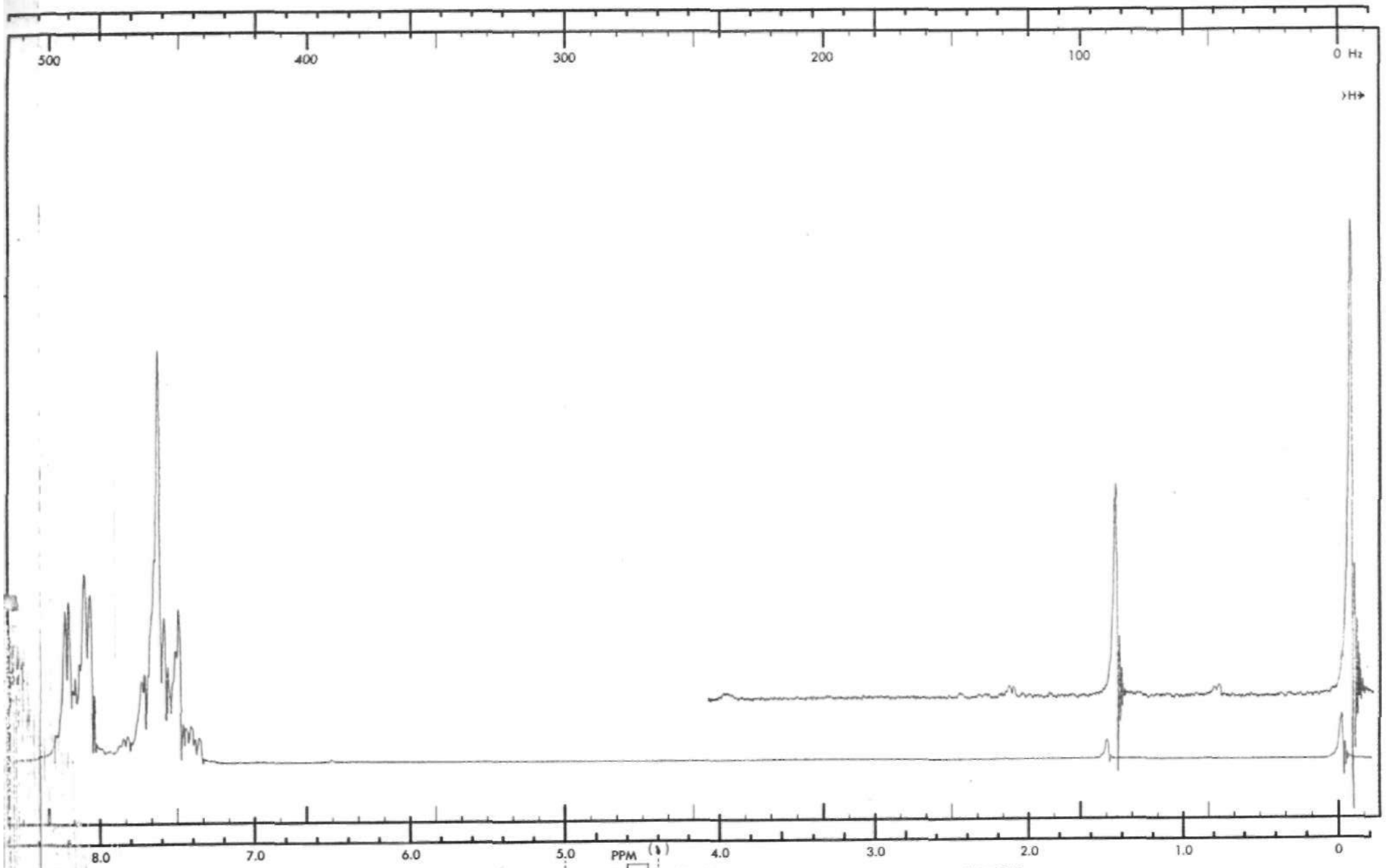
SOLVENT: d-DMSO

varian
analytical instrument division

DATE: 8/14/81

OPERATOR: Bosire

60 MHz NMR
SPECTRUM NO.



SWEEP OFFSET (Hz): /
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: /
SPINNING RATE (RPS): 40

MANUAL / AUTO ☐

SWEEP TIME (SEC): 50 | 250 — (250)
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500 — (500)
FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 — (2)
RF POWER LEVEL: 0.1 — (.05)

SAMPLE: $Me_2SnCl_2 \cdot 2$ 

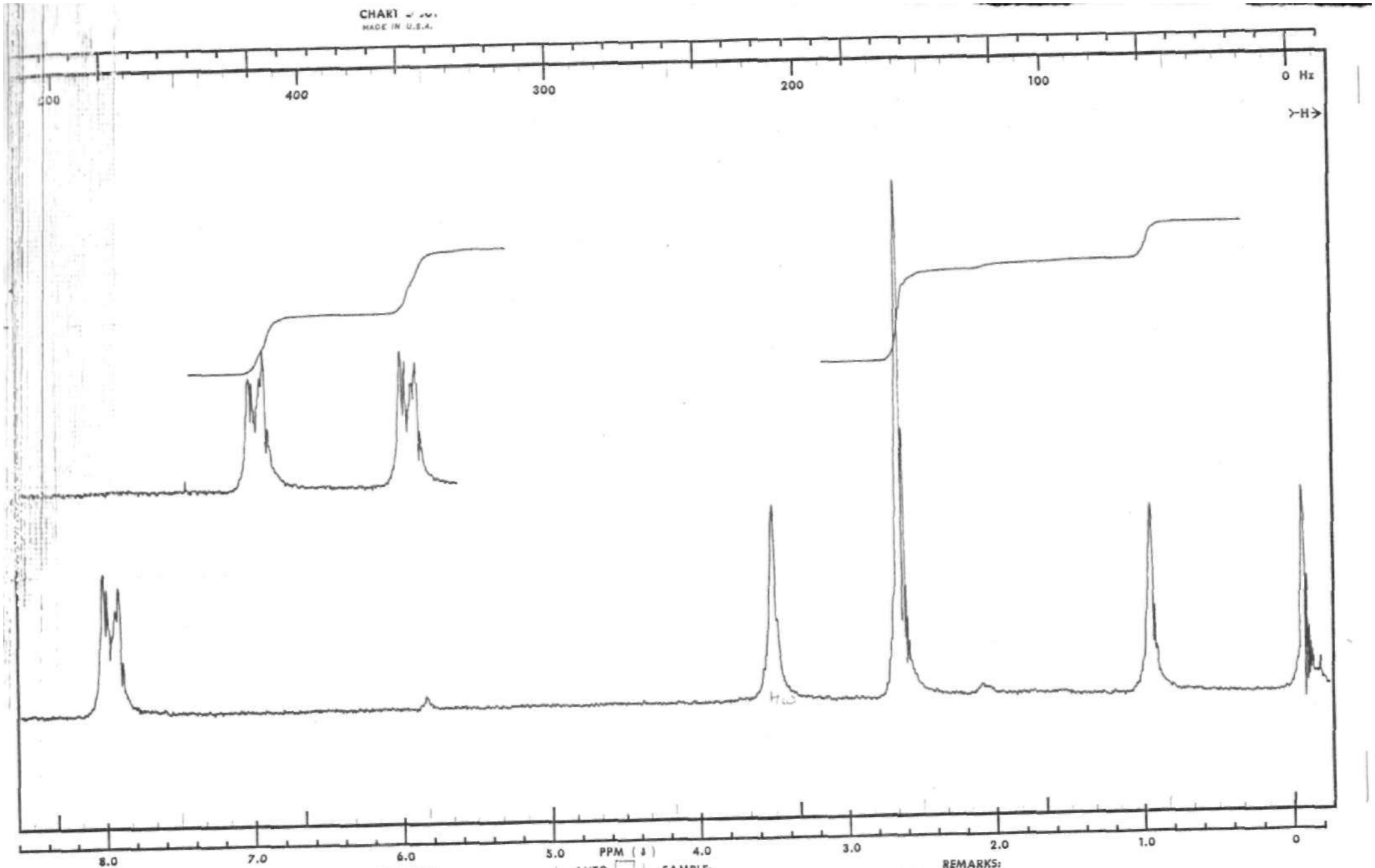
REMARKS:

SOLVENT: Nitrobenzene

STOHLER ISOTOPE CHEMICALS
49 JONES RD., WALTHAM, MASS. 02154, U.S.A.
IM BAUMGARTEN CH 3044 INNERBERG, SWITZELAND
P.O. BOX 1134, MONTREAL 101, CANADA

DATE: 22/8/80 OPERATOR: benóne

60 MHz NMR
SPECTRUM NO.



SWEEP OFFSET (Hz): 100
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: 5
SPINNING RATE (RPS): ~~40~~

MANUAL
SWEEP TIME (SEC): 50 ~~250~~
SWEEP WIDTH (Hz): 25 50 100 250 ~~500~~
FILTER: ~~0~~ 1 2 3 4 5 6 7 8
RF POWER LEVEL: 1

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: [illegible]

SOLVENT: d-DMSO

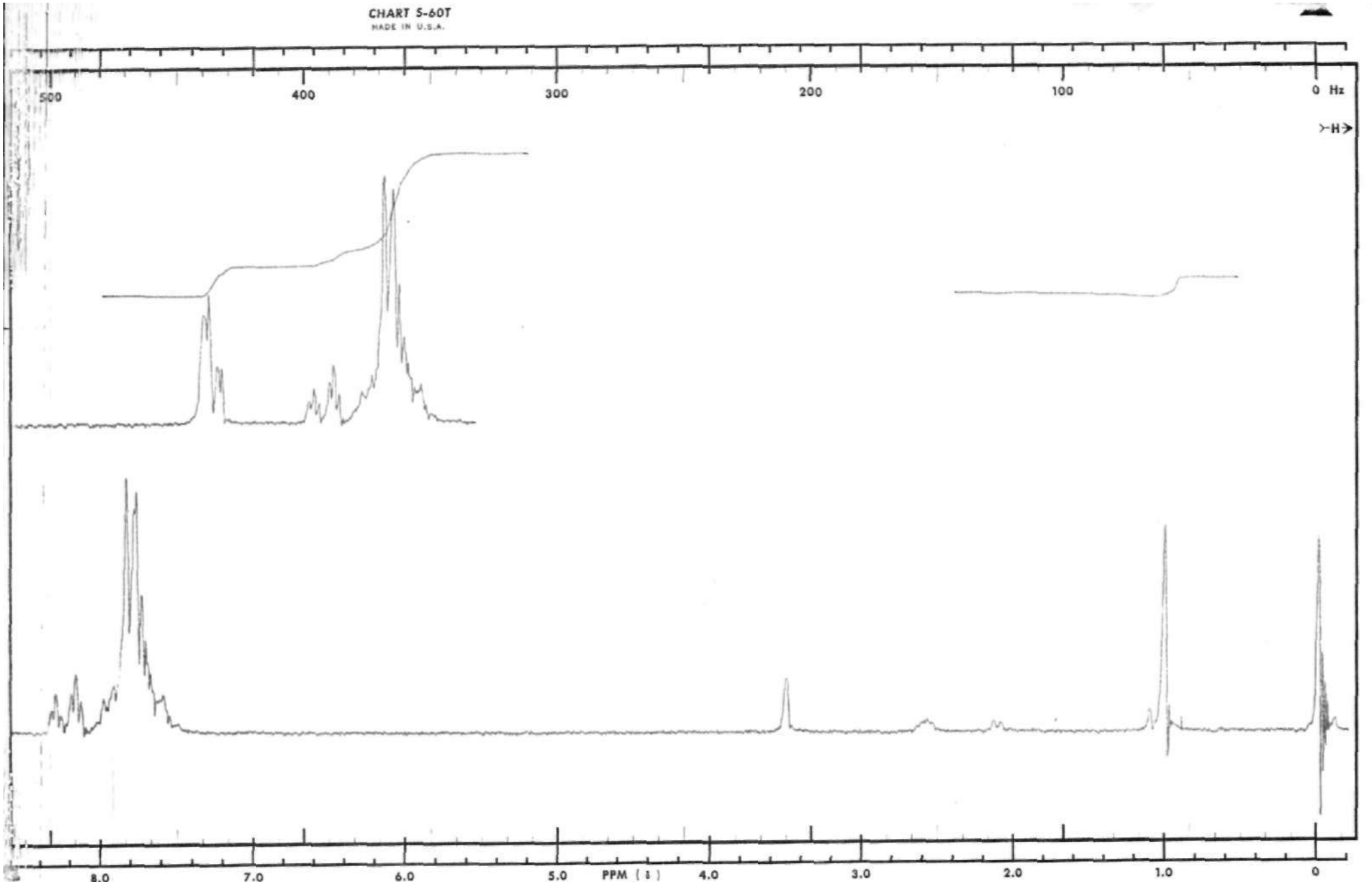
REMARKS:

varian
analytical instrument division

DATE: 8/4/91

OPERATOR: Bowne

60 MHz NMR
SPECTRUM NO.



MANUAL

SWEEP OFFSET (Hz): 100

SPECTRUM AMPLITUDE: 10

INTEGRAL AMPLITUDE: 4

SPINNING RATE (RPS): 40

SWEEP TIME (SEC): 50 250

SWEEP WIDTH (Hz): 25 50 100 250 500

FILTER: 1 2 3 4 5 6 7 8

RF POWER LEVEL: 0.1

AUTO ☐

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(500)

(2)

(.05)

SAMPLE:

Me_2SnCl_2 2M10

SOLVENT: d-DMSO

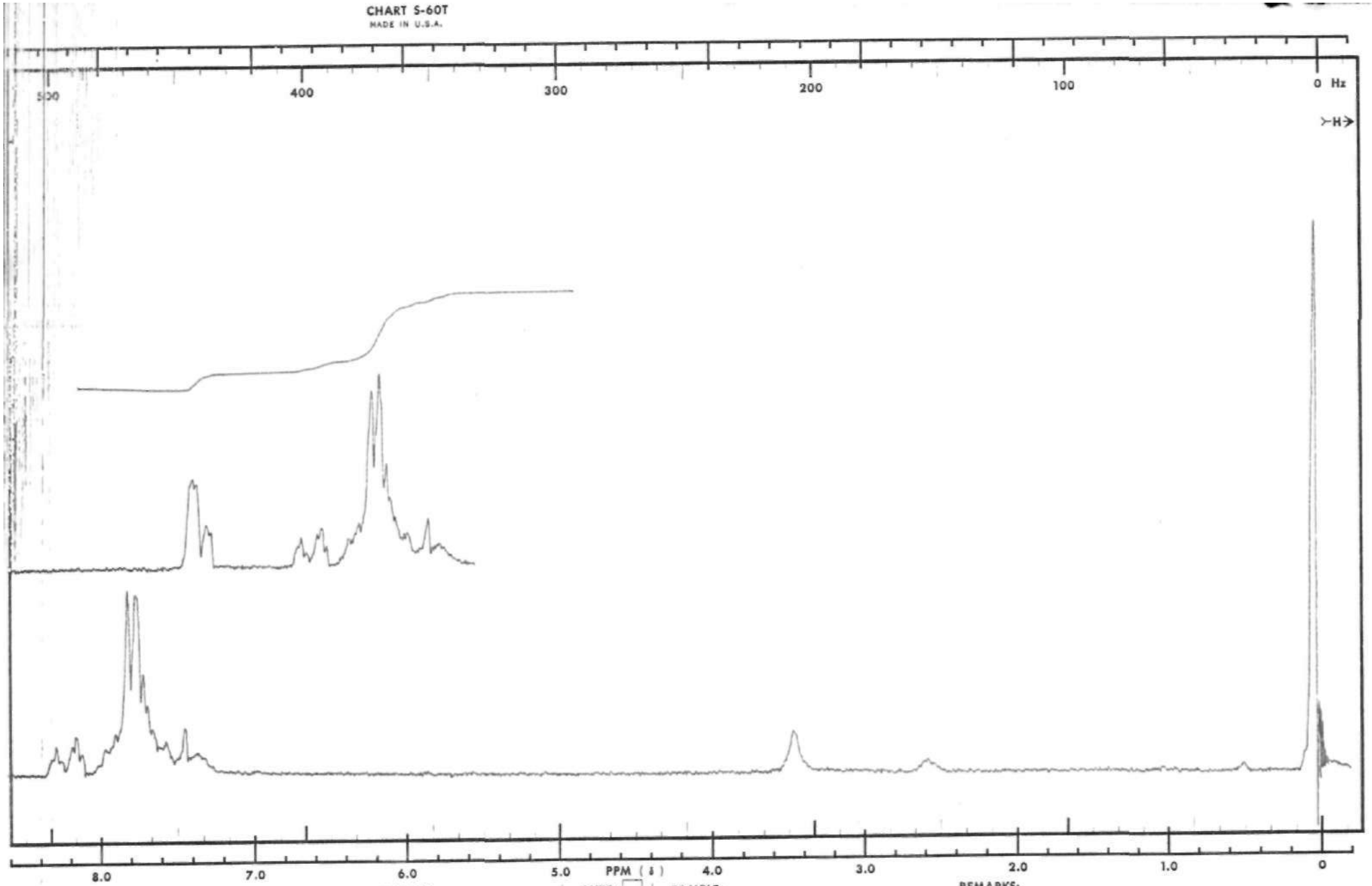
REMARKS:

varian
analytical instrument division

DATE: 27/11/80

OPERATOR: Bonire

60 MHz NMR
SPECTRUM NO.



SWEEP OFFSET (Hz): 100
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: 3
SPINNING RATE (RPS): 40

MANUAL

SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 5.1

AUTO ☐

(250)
(500)
(2)
(.05)

SAMPLE: Ph Sn Cl₃ 40 (S)

SOLVENT: d-DMSO

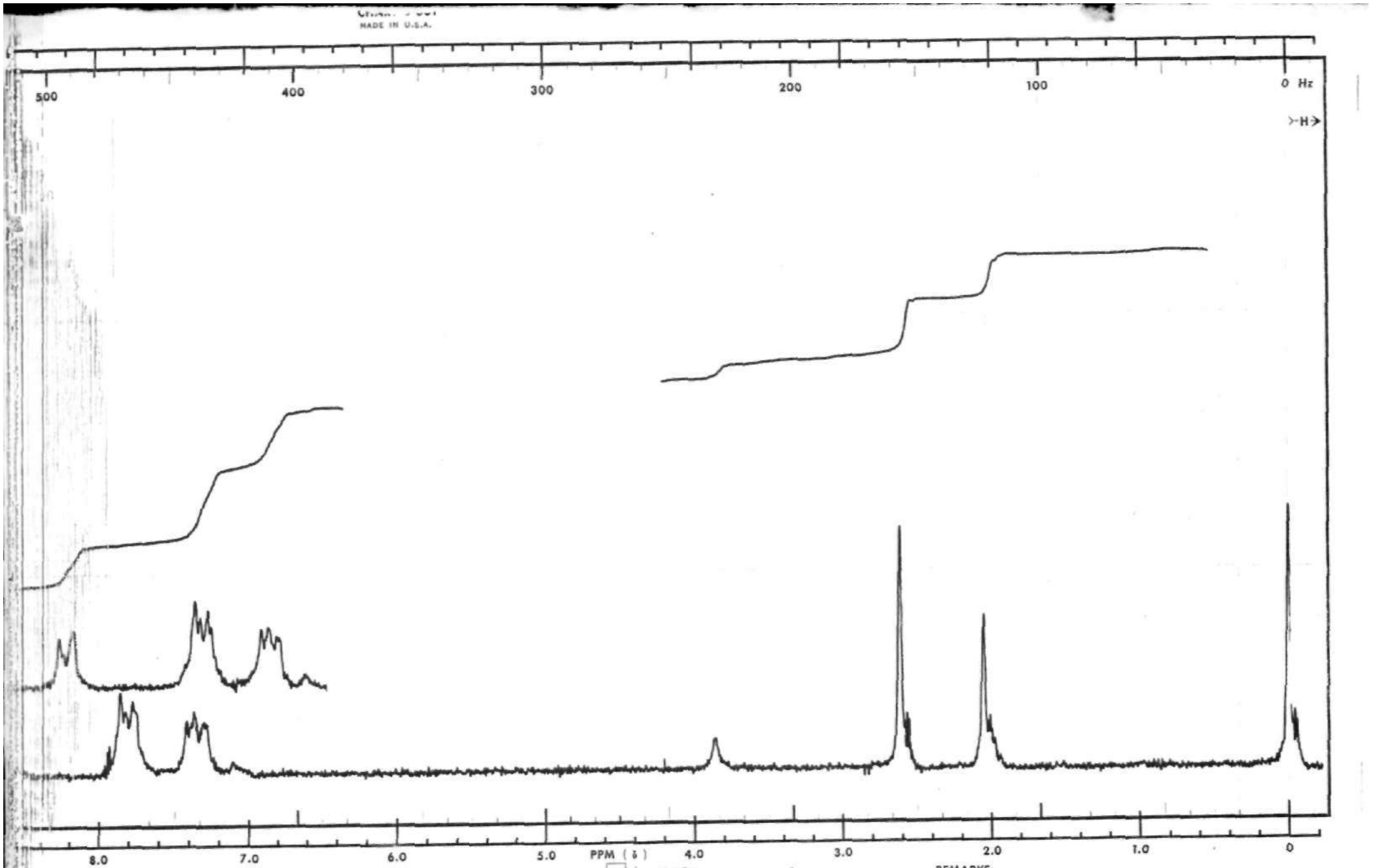
REMARKS:

varian
analytical instrument division

DATE: 28/11/80

OPERATOR: Bonire

60 MHz NMR
SPECTRUM NO.



SWEEP OFFSET (Hz): 30

SPECTRUM AMPLITUDE: 1x2

INTEGRAL AMPLITUDE: 7

SPINNING RATE (RPS): 50

MANUAL

SWEEP TIME (SEC): 50 250

SWEEP WIDTH (Hz): 25 50 100 250 500

FILTER: 1 2 3 4 5 6 7 8

RF POWER LEVEL: 0.05

AUTO ☐

(250)

(500)

(2)

(.05)

SAMPLE: $Ph_2SnCl_2 \cdot (4\text{-Acetylfy})_2$

SOLVENT: D-acetone

REMARKS:

varian
analytical instrument division

DATE: 2/4/76

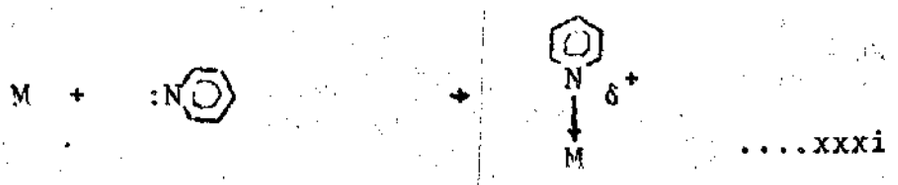
OPERATOR: Roxine

60 MHz NMR

SPECTRUM NO.

iii Effect of complexation on the protons of the Lewis base.

In adduct formation, pyridine binds to a Lewis acid with the lone pair of electrons on the nitrogen. Since this is dative bonding, it would be expected that the N of pyridine would go slightly positively charged, with adduct formation.



....xxxi

LVI

where M = Lewis acid.

The ring would tend to neutralise this small positive charge by effecting an electron drift both from the Π-and σ - system towards the charge. The effect then would deshield the protons of the ring, shifting their signals downfield. With adduct formation therefore, the pyridine proton signals would be shifted downfield.

This expectation is borne out by the n.m.r. spectra of pyridine and acyl-substituted pyridine adducts of stannic and methyltin chlorides, run in a common solvent, deuterodimethyl sulphoxide. The spectra all show slight downfield shieft of the pyridine proton signals in the

adducts, compared with the blank pyridine spectrum in d-DMSO. Due to the multiplet nature of the pyridine signals as well as poor resolution in some cases, it was not easy to get the exact shift values from the spectra. It is however clearly visible that all the pyridine and pyridyl proton signals shift downfield as the pyridine complexes. The shifts are most noticable in the stannic chloride adducts, and are only slight in the trimethyltin chloride adducts (Table 6). This seems to be in agreement with the hypothesis that the Sn ← N coordinate bond is strongest in stannic chloride, and weakest in trialkyltin halides[2].

Previous workers had only studied the J Sn - C - H values of trimethyltin chloride pyridine adduct[13,18], especially since the pyridine adducts of other methyltin halides had been found too insoluble for any meaningful n.m.r. study. From this work therefore, it could be derived that in addition to the other methods known for telling whether there is complexation between pyridine and a Lewis acid, n.m.r. could also be used at least at the qualitative level, as the pyridine proton signals have been observed to shift slightly downfield with complexation.

TABLE 6

N.m.r. Chemical Shift(δ) of some pyridines and their methyltin adducts in d-DMSO

Pyridine Compound	Pyridine H Signals			Shifts, L(δ) ppm		
	Ortho-H	Meta-H	Para.H	Ortho-H	meta-H	para-H
Pyridine	8.70	7.50	7.88			
$SnCl_3$.2Py	8.74	7.58	7.93	0.04	0.04	0.05
$MeSnCl_3$.2Py	8.74	7.56	7.92	0.04	0.02	0.04
Me_2SnCl_2.2Py	8.74	7.58	7.93	0.04	0.04	0.05
Me_3SnCl.Py	8.72	7.52	7.90	0.02	0.02	0.02
4-Benzoyl.Py	8.98					
$SnCl_4$.bis-4-Be.Py	9.02			0.04		
$MeSnCl_3$.bis-4-Be.Py	9.00			0.02		
Me_2SnCl_2.bis-4-Be.Py	9.00			0.02		
Me_3SnCl.4-Be.Py	9.00			0.02		
4-Acetyl.Py	8.97	7.96				
$SnCl_4$.bis-4-Ac.Py	9.00	8.00		0.03	0.04	
$MeSnCl_3$.bis-4-Ac.Py	9.00	8.00		0.03	0.04	
Me_2SnCl_2.bis-4-Ac.Py	8.98	7.98		0.01	0.02	
Me_3SnCl.4-Ac.Py	8.98	7.98		0.01	0.02	

The proton signals of the methyl group on the acyl-substituted pyridines have not been visibly affected by complexation of the parent Lewis base. The acetyl protons on the acetylpyridines

show both in the free and complexed ligand, at δ2.70ppm.

From this work thus, it is now possible to use n.m.r. spectroscopy for qualitative examination of all methyltin phenyltin, and stannic chloride adducts of pyridine, acetyl and benzoyl substituted pyridines.

iv. 2-Acetylpyridine, 2-benzoylpyridine, and 2-pyridine carboxaldehyde complexes of methyltin, phenyltin, and stannic chlorides.

Although the interaction of 2-acylpyridine with some transition metals has been studied to an extent[14,16,34], no mention has been made of the use of n.m.r. spectroscopy as a method of study. Jain has reported[29] his study of the interaction of 2-acetylpyridine with stannic chloride, but no report has been found of the interaction of the 2-acylpyridines with methyl and phenyl tin halides.

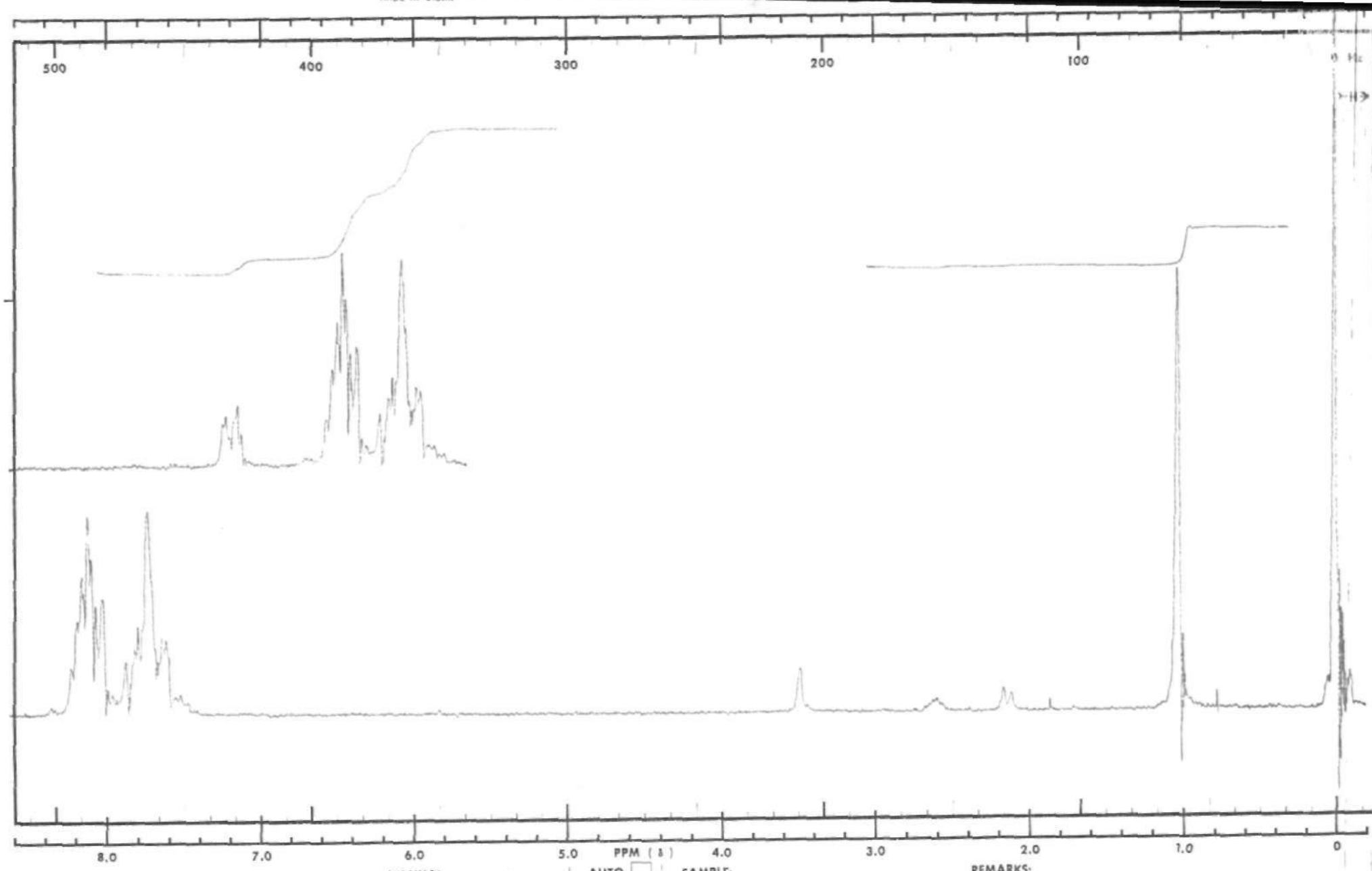
Nuclear magnetic resonance spectroscopy would be another way of examining the products of interaction of the 2-acylpyridines with organotin halides, provided a suitable solvent is found. The organotin halides bear hydrogen atoms that could be monitored along with those of the Lewis base ligands, unlike the complexes of the transition metals that would give just the spectrum of the ligands in their p.m.r. spectra.

Like the adducts of their 3- and 4-acylpyridine analogues of the organotin halides, it has been found that of all solvents suitable for p.m.r. spectral study, deuterodimethyl sulphoxide

appears to be the most suitable. It easily solubilizes all the products.

It has been found in this work that apart from stannic chloride, 2-benzoylpyridine also adds on to methyltin trichloride and phenyltin trichloride. Elemental analysis has shown that 2-benzoylpyridine gives 1:1 adducts with stannic chloride, phenyltin trichloride, and methyltin trichloride. The n.m.r. spectrum of the methyltin trichloride: 2-benzoylpyridine shows a singlet at δ 1.03 ppm for the methyl protons of the methyltin. Compared with the spectrum of the free $MeSnCl_3$ in d-DMSO, the signal has been slightly shifted downfield with complexation. The signals of the complexed ligand appear as multiplets δ7.73 and 8.12, and as a quartet for the pyridine ortho proton at δ 8.85, showing that the proton signals have shifted downfield with complexation. The Sn-phenyl proton signals overlap with those of the Lewis base in phenyltin trichloride. 2-Benzoylpyridine makes the interpretation of the spectrum difficult. However, the distinct quartet shown by the pyridyl-2-proton makes it possible, through analysis of the integral trace, to carry out qualitative identification. A spectrum of the stannic chloride-2-benzoyl pyridine is almost identical with that of the free ligand.

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SWEEP OFFSET (Hz): -122-
SPECTRUM AMPLITUDE: -10-
INTEGRAL AMPLITUDE: -4-
SPINNING RATE (RPS): -40-

MANUAL

SWEEP TIME (SEC): 50 | 250
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500
FILTER: W | 2 | 3 | 4 | 5 | 6 | 7 | 8
RF POWER LEVEL: -2-1-

AUTO ☐

(250)
(500)
(2)
(.05)

SAMPLE: NaBH4 (10) 10-12

SOLVENT: d-DMSO

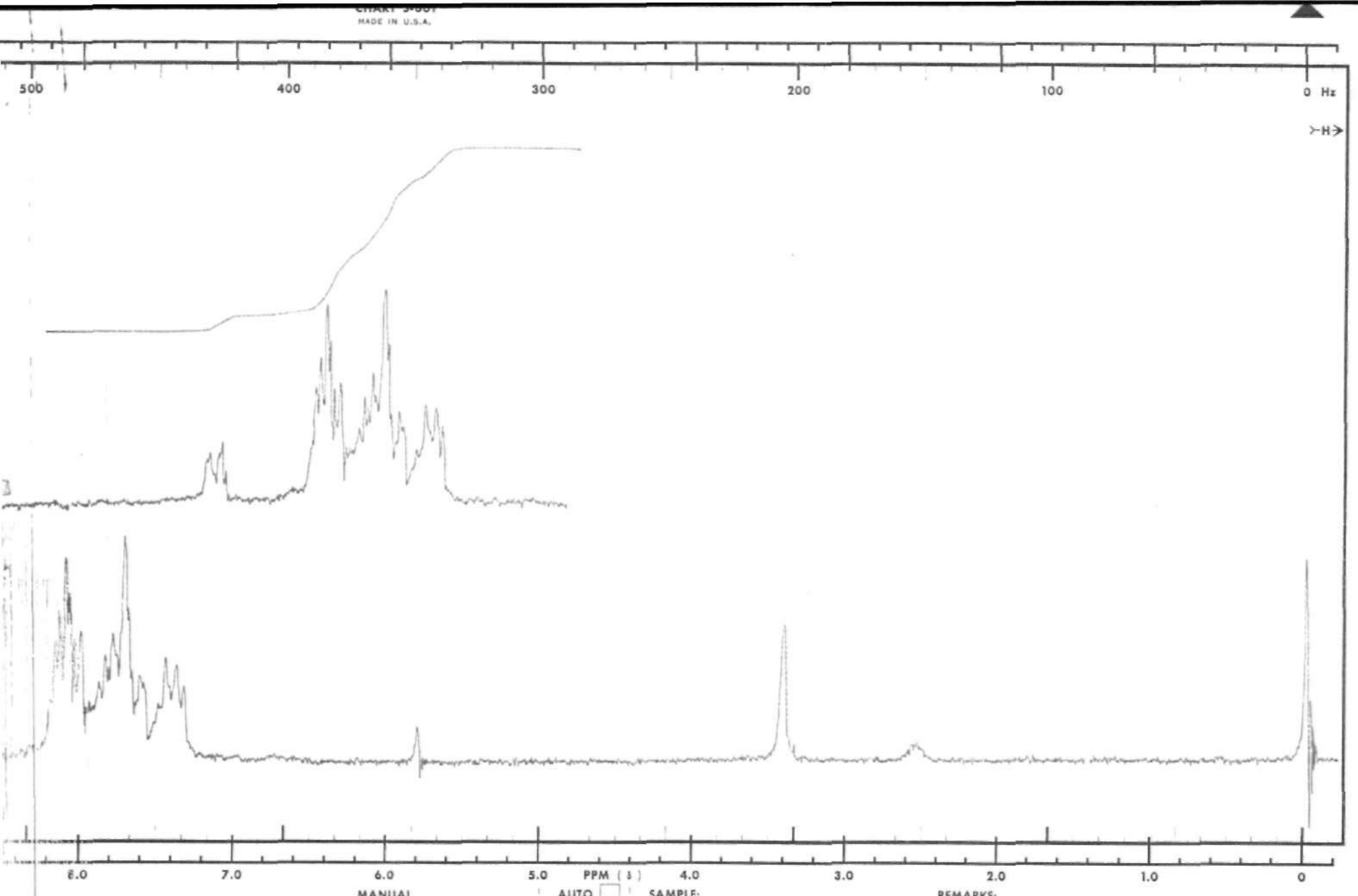
REMARKS:

varian
analytical instrument division

DATE: 27/11/85

OPERATOR: Bruno

60 MHz NMR
SPECTRUM NO.



MANUAL | AUTO ☐ | SAMPLE: | REMARKS:

RF OFFSET (Hz): 100

SPECTRUM AMPLITUDE: 16

INTEGRAL AMPLITUDE: 5

SWEEP RATE (RPS): .10

SWEEP TIME (SEC): 50 250 — (250)

SWEEP WIDTH (Hz): 25 50 100 250 500 — (500)

FILTER: 1 2 3 4 5 6 7 8 — (2)

RF POWER LEVEL: 6 — (.05)

SOLVENT: d-DMSO

varian
analytical instrument division

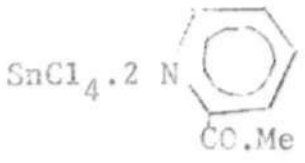
DATE: 6/12/80

OPERATOR: Basil

60 MHz NMR
SPECTRUM NO.

On the whole the n.m.r. spectra of the benzoylpyridine adducts with stannic chloride, phenyltin trichloride and methyltin trichloride simply show the Lewis acid and Lewis base protons, suggesting that they are simple adducts.

Elemental analysis results agree with the formula.



for the product formed from the reaction of stannic chloride with 2-acetylpyridine in dichloromethane. The n.m.r. spectrum of the product, compared with that of the free Lewis base in d-DMSO, shows that the product is not a simple addition product. Contrary to the spectrum expected for a simple adduct, the spectrum of the product shows new singlets at δ1.95, δ2.40, δ3.00, δ5.80, δ7.00 in addition to the δ2.70 singlet for the $-CO.CH_3$. Also, the aromatic signals have fused into a complex multiplet covering a whole region from δ7.00ppm to δ9.50ppm. Even after resorting to IR spectroscopy, it has not been possible as yet to write a reasonable molecular structure for the product.

The n.m.r. spectrum of the product of the reaction of phenyltin trichloride with 2-acetylpyridine, on the other hand, seems to agree with the molecular formula inferred from the elemental analysis of the product. It is a simple spectrum, with a singlet at δ2.70ppm ($-CO.CH_3$), a rather complex multiplet from δ7.30 to δ8.30ppm (the O- and p-pyridyl, and the phenyl protons) and a distinct multiplet at δ8.80 (the pyridyl ortho protons). The integral agrees with the formula inferred from elemental analysis.

$$PhSnCl_3 \cdot 2N\langle\bigcirc\rangle_{CO.CH_3}$$

suggesting the product to be a simple 1:2 adduct.

Elemental analysis suggests the molecular formula of the product of the reaction of Ph_2SnCl_2 with 2-acetylpyridine to be

$$Ph_2SnCl_2 \cdot 2\ N\langle\bigcirc\rangle_{CO.CH_3}$$

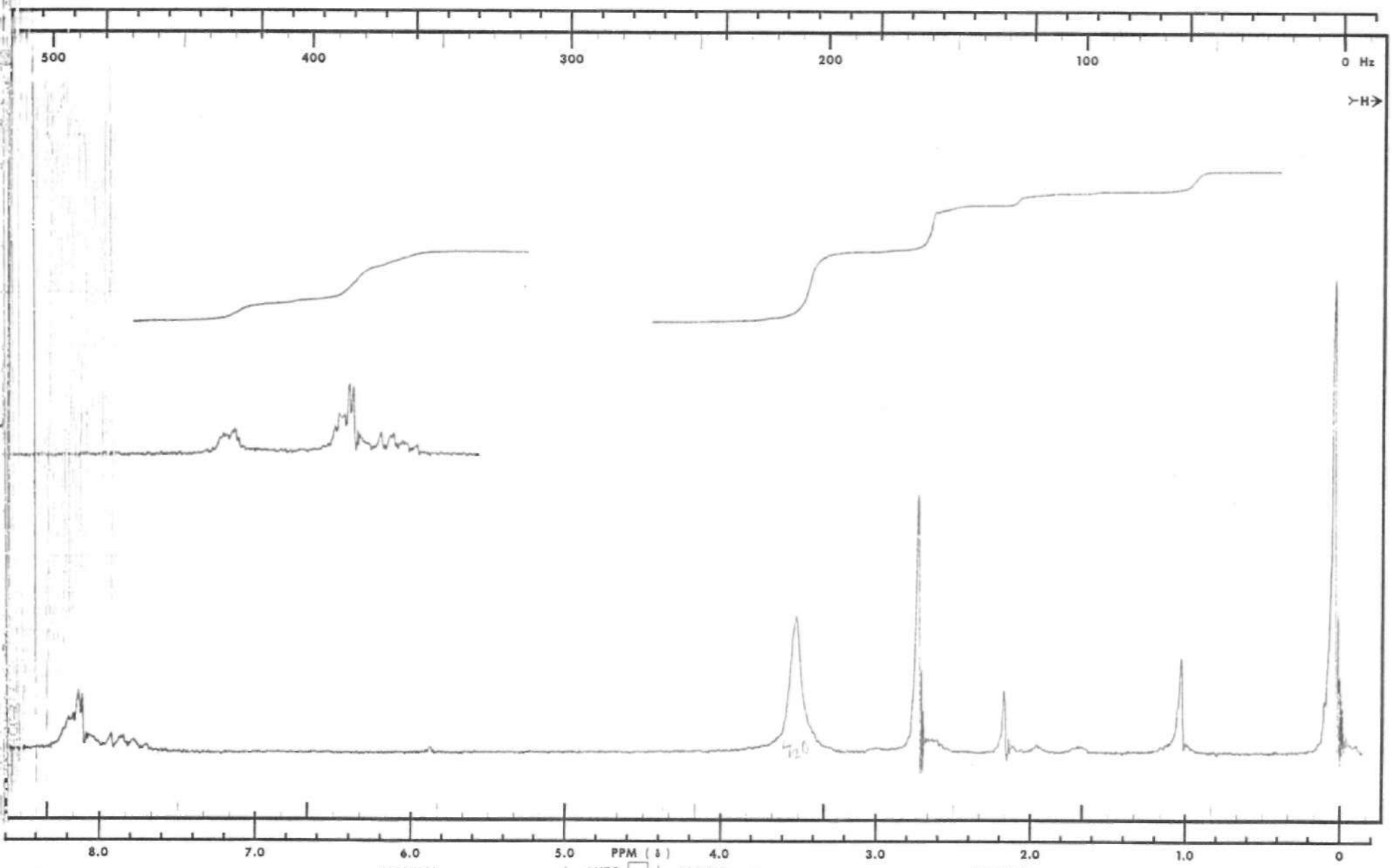
N.m.r. however has shown the $-CO.CH_3$ protons signals to have shifted upfield to δ2.10 ppm; $-CO.CH_3$ signal of the free ligand shows at δ2.70ppm. The reason for this shift is not clear, for the corresponding signal in phenyltin trichloride

bis-2-acetylpyridine shows at δ2.70ppm. The Sn-Phenyl and Lewis base ligands however appear as overlapped signals, mainly at δ7.40 and δ8.00ppm.

2-Acetylpyridine reacts with methyltin trichloride and dimethyltin dichloride, giving products that have so far not been identified. Methyltin trichloride reacts with 2-acetylpyridine, giving a product the elemental analysis results of which are close to those expected for $MeSnCl_3$.bis-2-Ac.Py, but n.m.r. shows a new singlet at δ2.15, in addition to those expected for $MeSnCl_3$.bis-2-Ac.Py. The $Sn-CH_3$ singlet signal however, shows at δ1.00ppm, while another, assignable to $-CO.CH_3$, appears at δ2.70ppm. The pyridyl protons, however, come up clearly as they appear in the spectrum of the uncomplexed ligand.

It has not been possible to interprete the results of the reaction dimethyltin dichloride with 2-acetylpyridine. A new singlet appears, in the n.m.r. spectrum of the sharp-melting product, at δ2.30ppm, in addition to the singlet signal at δ1.05ppm for $Sn-CH_3$. The signal for the $-CO.CH_3$ at δ2.70ppm in the uncomplexed ligand is barely visible. The pyridyl proton signals overlap into a complex pattern.

CHART S-60T
MADE IN U.S.A.



MANUAL ☐ AUTO ☐

SWEEP OFFSET (Hz): 100

SPECTRUM AMPLITUDE: 30

INTEGRAL AMPLITUDE: 6

SPINNING RATE (RPS): 20

SWEEP TIME (SEC): 50 250

SWEEP WIDTH (Hz): 25 50 100 250 500 (250) (500)

FILTER: 1 2 3 4 5 6 7 8 (2) (.05)

RF POWER LEVEL: 2.5

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SOLVENT: d - DMSO

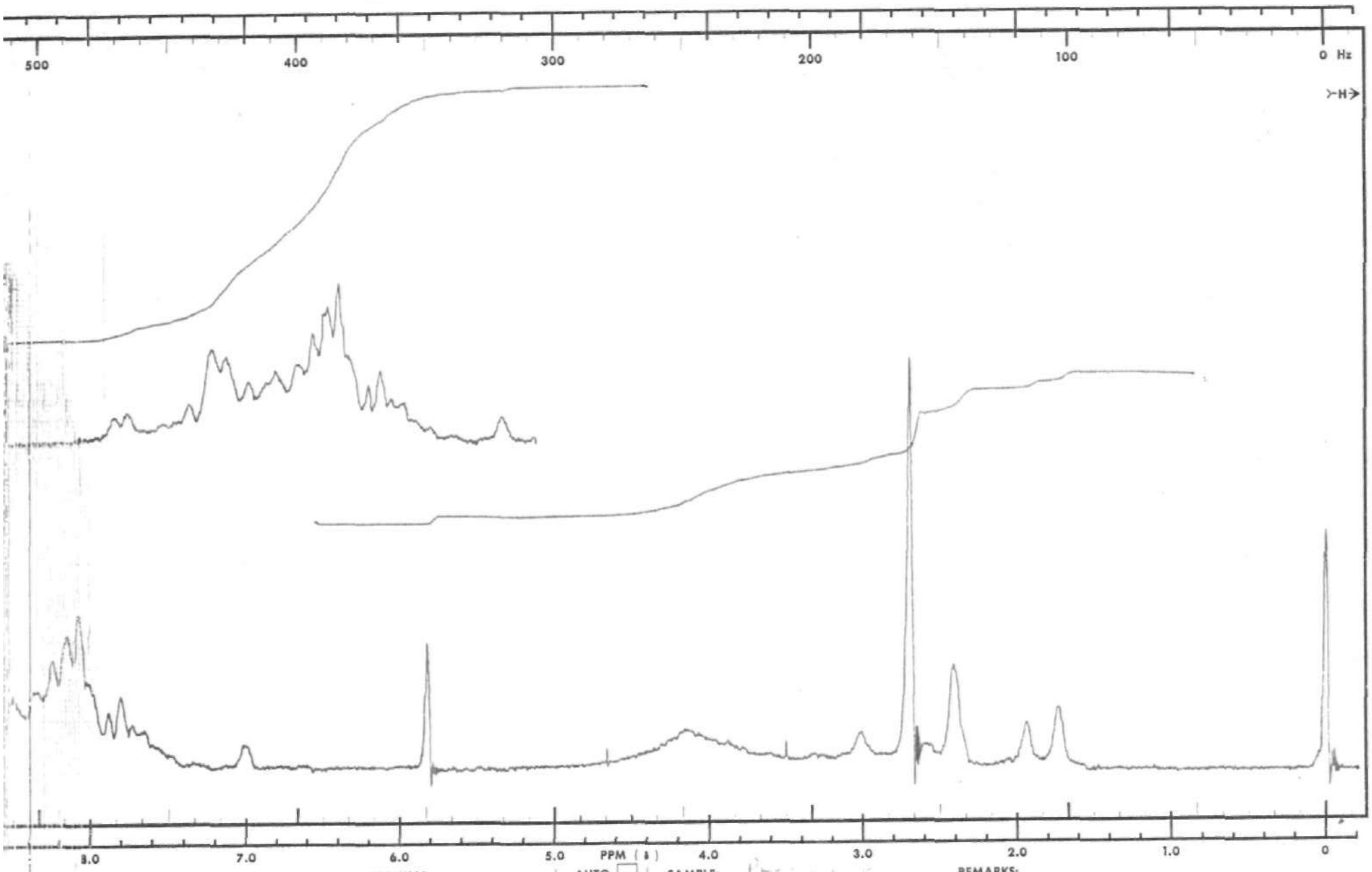
REMARKS:

varian
analytical instrument division

DATE: 12/18/

OPERATOR: Brooks

60 MHz NMR
SPECTRUM NO.



MANUAL AUTO

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SPECTRUM AMPLITUDE:	10	SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500	(500)
INTEGRAL AMPLITUDE:	3	FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8	(2)
SPINNING RATE (RPS):	40	RF POWER LEVEL: 0.15	(.05)

SAMPLE: Product of Sample [illegible]

SOLVENT: d-DMSO

REMARKS:

varian
analytical instrument division

DATE: 2/2/81

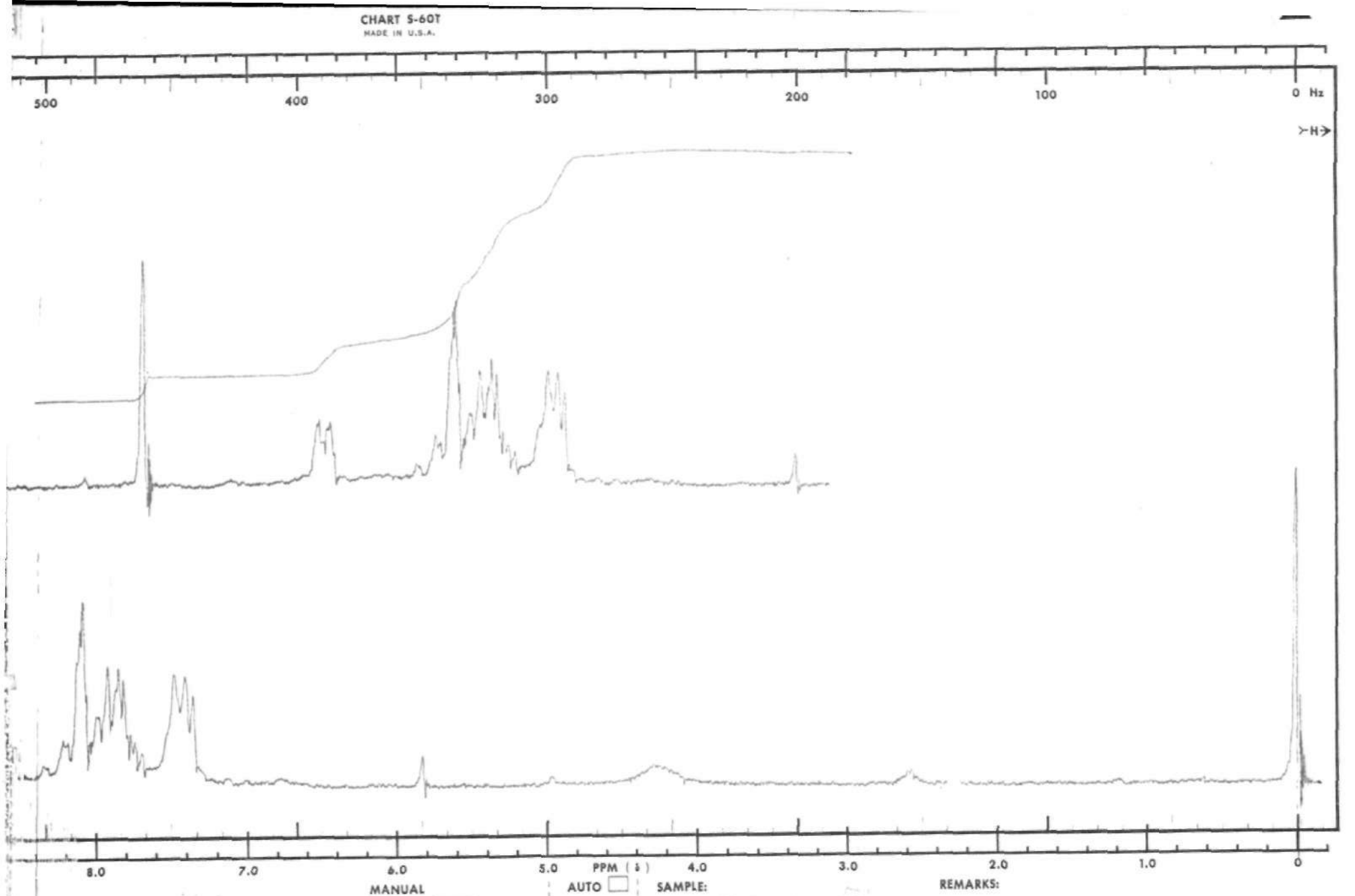
OPERATOR: Bonnie

60 MHz NMR
SPECTRUM NO.

The only identifiable product obtained from the reaction of 2-pyridine carboxaldehyde with stannic, phenyltin and methyltin chlorides was that from the reaction of phenyltin trichloride with the Lewis base. The n.m.r. signals of the product in d-DMSO overlap with those for the pyridyl protons; only the O-pyridyl proton and the carboxaldehyde proton signals appear distinctly as a multiplet at about δ8.90ppm and a singlet at δ9.20ppm respectively. No significant shifts, from the chemical shifts of the free Lewis base, were noticed.

From these results, it is clear that 2-benzoylpyridine would only add to the organotin and stannic chlorides when steric factors are favourable. 2-Acetylpyridine on the other hand seems to undergo some rearrangement when it adds on to the organotins, especially methyltin trichloride and stannic chloride. With dimethyltin dichloride, it seems to react in a less straightforward way than simple addition. This unexplained reaction seems to be much less if not totally absent, when the organic substituent on Sn is aromatic. Also, the reaction seems to be absent altogether when there is no hydrogen α to the carbonyl of the Lewis base; 2-benzoylpyridine gives simple adducts; 2-acetylpyridine gives identifiable adducts with

CHART S-60T
MADE IN U.S.A.



MANUAL | AUTO ☐

SWEEP OFFSET (Hz): _____

SPECTRUM AMPLITUDE: _____

INTEGRAL AMPLITUDE: _____

SPINNING RATE (RPS): _____

SWEEP TIME (SEC): 50 250 — (250)

SWEEP WIDTH (Hz): 25 50 100 250 500 — (500)

FILTER: 1 2 3 4 5 6 7 8 — (2)

RF POWER LEVEL: _____ — (.05)

SAMPLE:

REMARKS:

SOLVENT:

varian
analytical instrument division

DATE: _____

OPERATOR: _____

60 MHz NMR

SPECTRUM NO. _____

phenyltin chlorides, but not with methyltin chlorides.

From the n.m.r. spectrum of the product of the reaction of $SnCl_4$ with 2-acetylpyridine, it is almost certain that Jain[29] obtained not his reportedly simple "1:1 stannic chloride-2-acetylpyridine adduct", but most probably something else.

Perhaps the easy oxidation of 2-pyridine carboxaldehyde to 2-pyridine carboxylic acid (see page 44) makes it a poor Lewis base.

f. Infra red Spectroscopic studies of the pyridine and Acyl pyridine complexes of Methyltin, phenyltin, and stannic chlorides.

Infra red spectroscopy has been used as an aid to preparative organotin chemistry. Important structural information may be obtained by analyzing intensities and frequencies associated with tin-carbon, tin-halogen, and tin-ligand stretching vibrations[13].

Beattie et al have studied[9], the i.r. spectral properties of adducts of germanium tetrachloride and tin tetrachloride with tertiary aromatic bases; and also the addition compounds of some organotin halides with a few Lewis bases[10]. Kriegsmann[35] and Cummins[36] have made a systematic study of the Sn-C absorption bands of a number of tri- and tetra-organotins. Yingst et al[37] have studied the complexes of

of 2-allylpyridine with Cu(I), Ag(I), and Pt(II). Ortego et al[34] have studied the cobalt(II) complexes of di-2-pyridyl ketone. Plytzanopoulos et al[14, 16] have studied the complexes of the first row transition metals with 2-benzoylpyridine, and also with 2-acetylpyridine[15].

The reports of these and many other researchers[9,10,38-40] have shown that there are shifts in some i.r. bands of pyridines as they add on to Lewis acids. Shifts have also been observed in some i.r. bands of the Lewis acid, as it complexes with the Lewis base. Such shifts could be upfield or downfield, depending on the band in question. New vibration modes are created in some complexes, leading to the appearance of new bands in the i.r. spectra. In other cases some modes of vibration in the reactants are not present in the complexes.

A number of factors are thought to be responsible for the shifts, and these include the new geometry assumed by the complex as it is formed, hence i.r. has a lot to offer in the study of the stereochemistry of organotin complexes[9,10]. Also, coordination of a particular atom in a Lewis base on a Lewis acid tends to decrease the electron density on that atom, which seeks stabilization from the neighbouring atoms. This alters the bond strength and hence the vibration

frequency of that bond. Coordination of some groups reduces their degree of freedom hence their modes of vibration; this leads to the disappearance of some bands in the adduct. A number of pyridine adducts of organotin halides and stannic chlorides have been studied[9,10]. Beattie et al[9] noted that the M-Cl vibration frequencies in stannic chloride shifted to longer wavelengths on complexation, as was also found in the pyridine complexes of the methyltin chlorides. In all complexes coordination through pyridine nitrogen is indicated by a positive shift of the pyridine breathing motion which appears at 995cm^{-1} in the free, and at 1010-1030cm^{-1} in the complexed ligand[16]. There is a similar shift of the free ligand band at 1580cm^{-1} to about 1600cm^{-1} with complexation[38,39,40].

Reports of the study of 2-ketopyridine complexes with transition metals[14,15,16] have all shown that the carbonyl stretching frequency shifts towards longer wavelengths with complexation, compared with the stretching frequency of the uncomplexed Lewis base.

On the basis of the above, a qualitative infra-red examination of the ketopyridine adducts of methyltin, phenyltin and stannic chlorides - most of which have hitherto not been reported - could be made. I.r. spectroscopy provides a

range of information on organotin adducts, but attention was initially paid to the shifts in the M-Cl, C=O, and C=C (ligand) vibration frequencies, in an effort to establish the sites of coordination and the mole ratio of the adducts.

1. Effect of complexation on the Sn-X stretching frequencies.

Considering a diatomic molecule A-X, with f_{A-X} as the force constant of its bond, the wave number value of the A-X stretching vibration is given by the Hooke's law expression[41].

$$\nu_{A-X} = \frac{1}{2\Pi C} \left(\frac{f_{A-X}}{\mu_{A-X}} \right)^{\frac{1}{2}}$$

where

$$\nu_{A-X} = \frac{M_A M_X}{M_A + M_X}$$

ΠC = velocity of light,

M_A = Atomic mass of A

M_X = atomic mass of X

The stretching vibration frequency is inversely proportional to μ_{A-X} and directly proportional to the force constant, f_{A-X}. The force constant is a direct measure of the strength of a bond.

Assuming that A- X in the above expression is an Sn-X moiety in an organotin compound, the force constant of the Sn-X bond is determined by the bond strength. Where Sn and X have close electronepativity values bond polarity of Sn-X is minimal and electron density changes on Sn might not influence much the strength of the Sn-X bond. This could be why the Sn-C bond stretching vibration frequency is observed to be little influenced by changes in the electron density around the Sn nucleus[10]. But where X is much more electronegative than Sn, the strength of the Sn-X bond would be expected to decrease with increase in the electron density around the Sn. This is because the polarity caused by the difference in the electronegativities of Sn and X, which induces an electrostatic attraction of X to Sn, is partially neutralised with



increase in the electron density around Sn. The Sn - X bond elongates even more and becomes weaker.

Since adduct formation with a Lewis base of an organotin halide would increase the electron density around Sn, the

force constant of the Sn - X bond, where X is the halogen, would weaken with adduct formation, leading to a decrease in the stretching vibration frequency. The Sn-X bond therefore would be expected to shift to longer wavelengths with adduct formation.

This postulation seems to explain the observation of beattie et al[9,10], that the Sn-Cl bond stretching frequencies in stannic chloride and methyltin chloride shifted downfield with complexation of the Sn with pyridine. The Sn-Cl stretching frequencies shifted below 200cm^{-1} in the dimethyltin dihalides as they complexed with pyridine, while in stannic chloride, it shifted from 364cm^{-1} to 324 cm^{-1} with complexation. It is possible that other factors might influence the shift, but the most prominent would be the strength, or force constant, of the bond.

ii. Observed stretching frequencies of the pyridine, 3- and 4- acetyl and benzoyl-pyridine complexes of methyltin, phenyltin, and stannic chlorides.

The Sn-Cl bond.

The corollary for bond assignment has been derived from the reports of Beattie et al[9,10], Pollar et al[17], Gill, Mitchell, and Popor et al[38,39,40].

The Sn-Cl stretching vibration frequencies for the pyridine adducts of trimethyltin and dimethy-tin chlorides come below 200cm^{-1} and so are not observable in the 200-4000cm^{-1} range. The Sn-Cl stretch for the corresponding adducts of methyltin, trichloride, diphenyltin dichloride, phenyltin trichloride, and stannic chloride occur above 200cm^{-1}. The frequencies of the observed bands for the pyridine and ketopyridine adducts are listed in Table 7. The assignments are, however, tentative; confirmable only through appropriate calculations which are beyond the scope of this work.

Compared with the parent organotin halide, the shifts of the Sn-Cl stretch in the adducts seem to reflect the binding strength (see section B) of the ligands. For a given organotin Lewis acid, the shift is highest for the pyridine adduct and lowest for the 3-acetylpyridine adduct. For $MeSnCl_3$. 2Py for example, the shift is 80cm^{-1}, and 65cm^{-1} for $MeSnCl_3$. bis-3-acetylPyridine. The binding strength of the ligand would determine the magnitude of this shift, as a stronger Lewis base would, in the absence of steric hindrance, bind more strongly with the organotin Lewis acid, thereby increasing the electron density on the Sn and decreasing the Sn-X bond strength the more, making it absorb at longer i.r. wavelengths.

The acetyl and benzoyl groups are electron withdrawing; when on the meta position of the pyridine ring, their electron withdrawing effects make the pyridine a weaker donor. The shifts in the adducts have been observed to decrease in the following order:

$MeSnCl_3.2Py$ > $MeSnCl_3$.bis-4-Be.Py> $MeSnCl_3$.bis-4-Ac-Py > $MeSnCl_3$.bis-3-Be.Py> $MeSnCl_3$.bis-3-Ac.Py.

The corresponding Ph_2SnCl_2, $PhSnCl_3$, and $SnCl_4$ adducts virtually follow a similar order.

It has also been noticed that the magnitude of the shifts decreases with

TABLE 7

Some i.r. absorption frequencies of the adducts

Compound	O-H	C-H	C=O	C=C arom. (py)	Sn-Ph	Sn-Me Rock	Sn-Cl
Me_3SnCl						790s	
Me_2SnCl_2						790s	330s
$MeSnCl_3$						795s	370s
$SnCl_4$							360s
$PhSnCl_3$							370vs
Ph_2SnCl_2							255s
Py		3075w		1580s			
$Me_3SnCl.Py$	-	3050vw	-	1600s		795m	
$Me_2SnCl_2.2Py$		3050w		1600s		795m	

Table 7 (Contd.)

Compound	O-H	C-H	C=O	C=C arom. (Py)	Sn-Ph	Sn-Me Rock	Sn-Cl
$MeSnCl_3$.2Py		3050w		1600s		795w	290s
$SnCl_4$.2Py		3050w		1605s			330s
$PhSnCl_3$.2Py		3050w		1605s	1060m		285s
Ph_2SnCl_2.2Py		3040w		1600s	1065m		250s
4-Be.Py		3030w	1660vs	1580s			
Me_3SnCl.4-Be.Py		3040vw	1660s	1595		790m	
Me_2SnCl_2.bis-4-Be.Py		3060w	1660s	1600s		790m	
$MeSnCl_3$.bis-4-Be.Py		3040w	1660s	1600s		795w	292s
$SnCl_4$.bis-4-Be.Py		3070w	1665s	1600s			335s
$PhSnCl_3$.bis-4-Be.Py		3030w	1665s	1595s	1065m		300s
Ph_2SnCl_2.bis-4-Be.Py		30040w	1660s	1590s	1065m		270s
4-Ac.Py		3030m	1700s	1580s			
Me_3SnCl.4-Ac.Py		3030vw	1695s	1595s		790m	
Me_2SnCl_2.bis-4-Ac.Py		3030w	1700s	1595s		795m	
$MeSnCl_3$.bis-4-Ac.Py		3040w	1700s	1600s		795w	295s
$SnCl_4$.bis-4-Ac.Py		3060m	1700s	1610s			335s
$PhSnCl_3$.bis-4-Ac.Py		3030w	1700s	1595s	1060m		300s
Ph_2SnCl_2.bis-4-Ac.Py		3045w	1700s	1600s	1065m		270s
3-Be.Py		3040m	1660s	1580s			
Me_2SnCl_2.bis-3-Be.Py		3060w	1660s	1600s		795m	
$MeSnCl_3$.bis-3-Be.Py		3050w	1665s	1595s		795w	300s
$SnCl_4$.Bis-3-Be.Py		3060w	1660s	1600s			345s
$PhSnCl_3$.bis-3-Be.Py		3030w	1660s	1590s	1060w		325s
Ph_2SnCl_2.bis-3-Be.Py		3040w	1660s	1590s	1075m		275s
3-Ac.Py		3040m	1680s	1580s			
Me_2SnCl_2.bis-3-Ac.Py		3030w	1680s	1595s		795m	

Table 7 Contd.)

Compound	O-H	C-H	C=O	C=C arom. (Py)	Sn-Ph	Sn-Me Rock	Sn-Cl
$MeSnCl_3$.bis-3-Ac.Py		3040w	1685s	1595s			305s
$SnCl_4$.bis-3-Ac.Py		3050w	1690s	1595s			350s
$PhSnCl_3$.bis-3-Ac.Py		3030w	1680s	1590s	1060w		325s
Ph_2SnCl_2.bis-3-Ac.Py		3040w	1680s	1600s	1065w		280s
2.Be.Py		3040w	1660s	1580s			
$MeSnCl_3$.2-Be.Py		3060w	1605s	1590s		795m	310s
$SnCl_4$.2-Be.Py		3110	1600s	1600s			325s
$PhSnCl_3$.2-Be.Py		3060w	1610s	1595s	1065w		320s

increasing number of halogen atoms on the Sn; this effect is more noticieable in the pyridine adducts of the methyltin and stannic chlorides. Sn - Cl stretch shifts from $360cm^{-1}$ in $SnCl_4$[17] to $324cm^{-1}$ in $SnCl_4.2Ph$; from about $360cm^{-1}$ in $MeSnCl_3$ to about $285cm^{-1}$ in $MeSnCl_3.2Py$; and from about $320cm^{-1}$ in Me_2SnCl_2 to below $200cm^{-1}$ in $Me_2SnCl_2.2Py$. This could be explained by the fact that the more halogens there are bonded to an Sn atom, the less the share of the electron density increase effect on the Sn due to adduct formation, on each Sn-Halogen bond.

NO. 5 100 0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

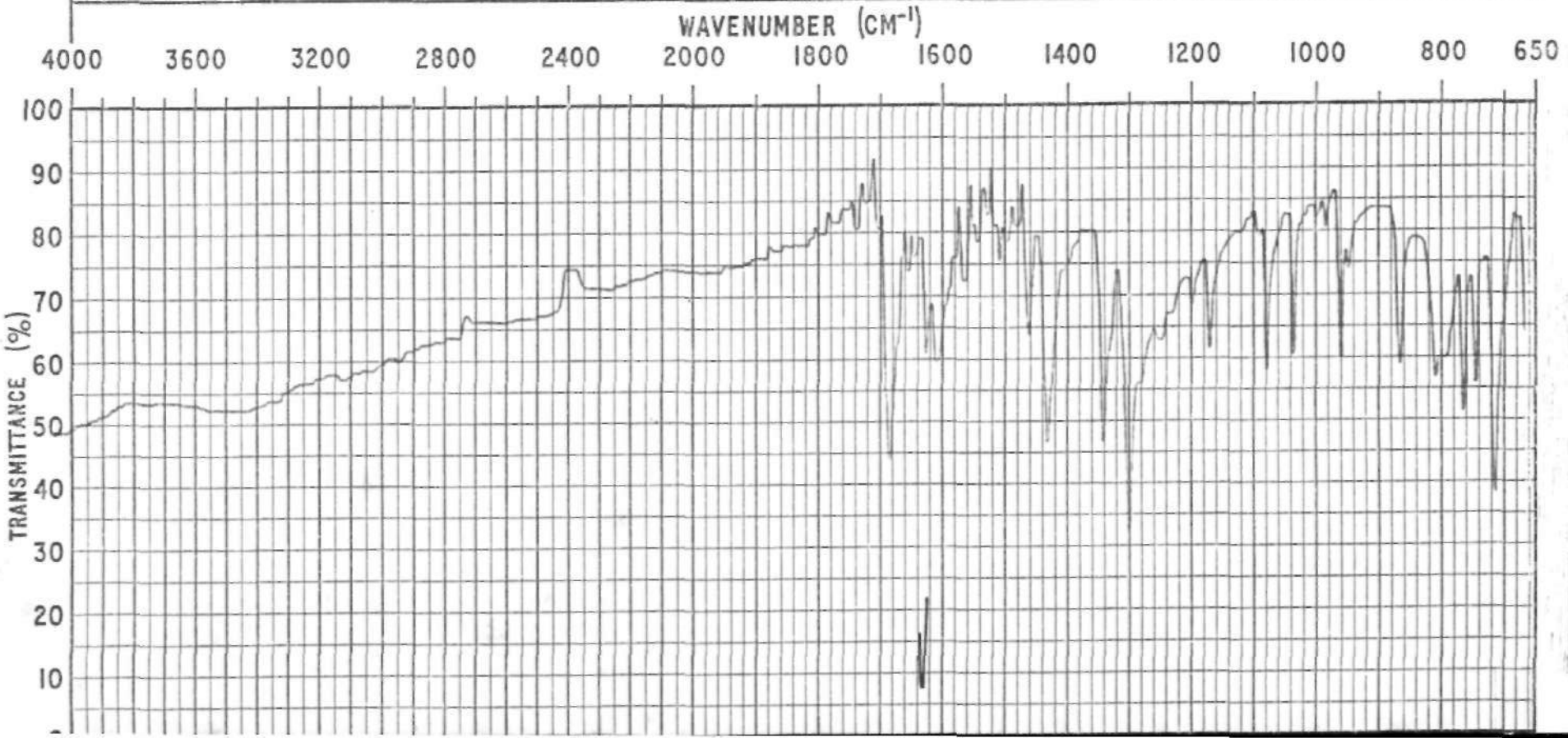
PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1 $Me_3SnCl \cdot NO_2\text{-}CO\text{-}O$

DATE 5/8/80

OPERATOR Bonnie



SAMPLE

SPECTRUM NO.

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED slow

SLIT

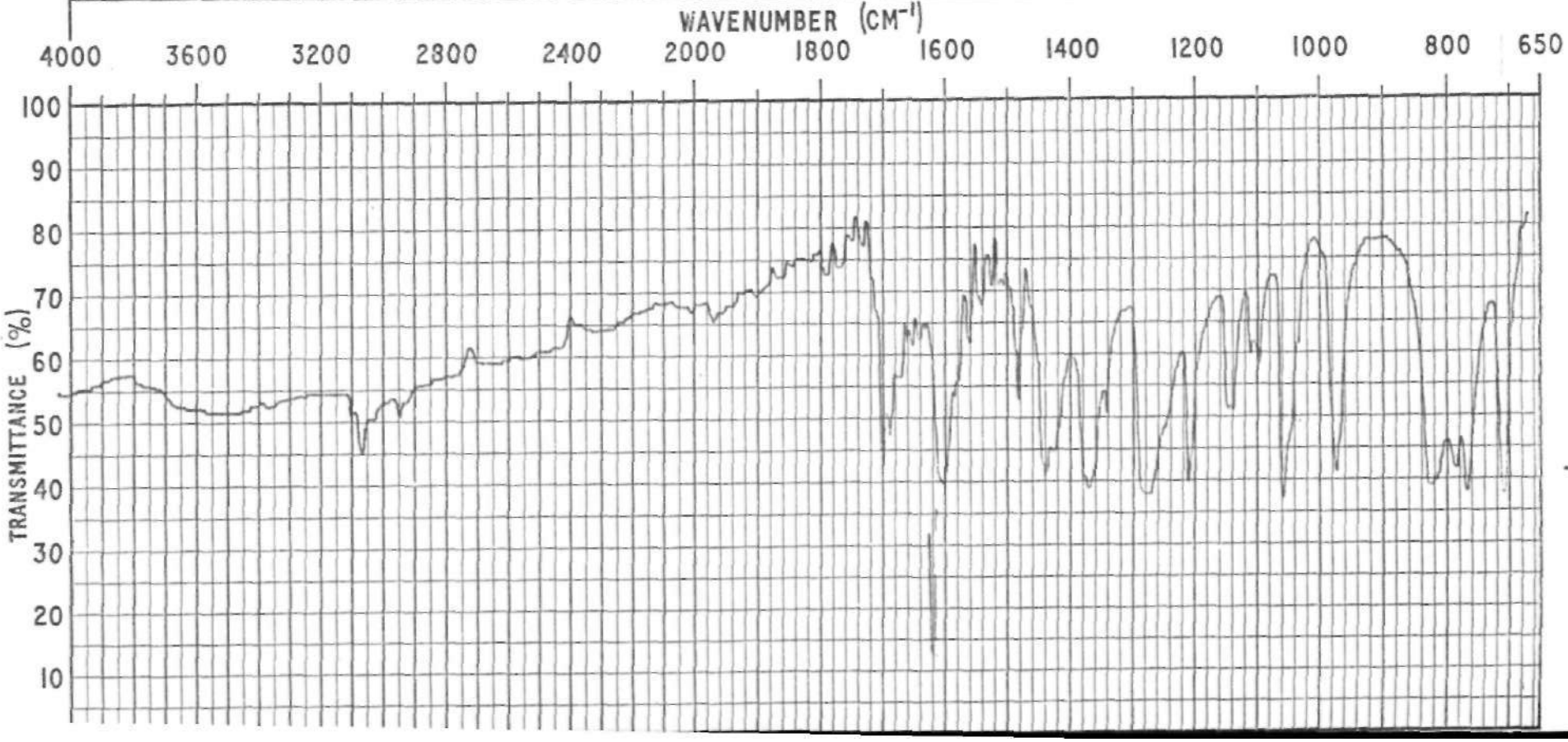
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I $Me_2SnCl_2 \cdot 2$ [O] CO-Me

DATE 1/8/80

OPERATOR Benise



SAMPLE

SPECTRUM NO.

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

PERKIN-ELMER

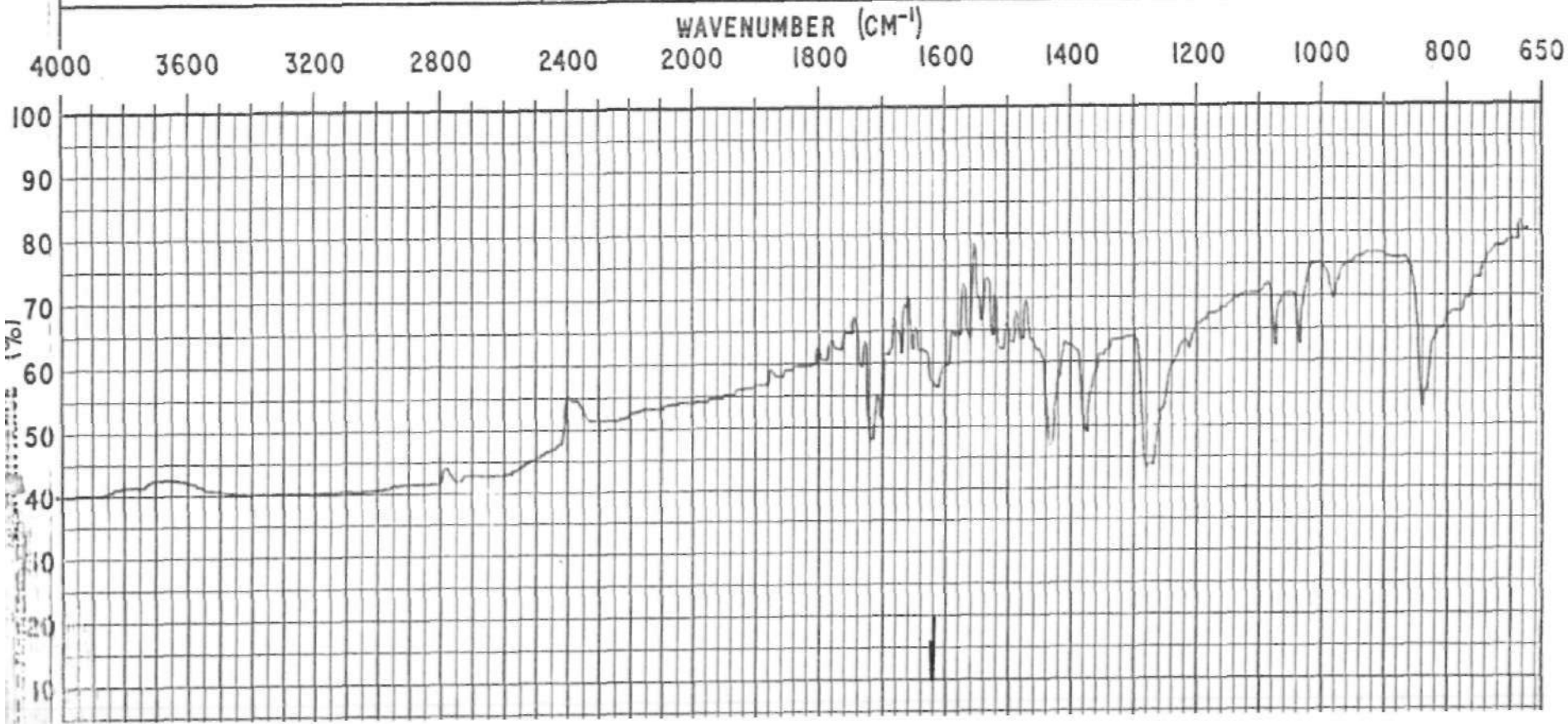
SPECTRUM NO.

SAMPLE I

Me $SnCl_3$ ~~2~~ ~~[illegible]~~ ~10 Mo

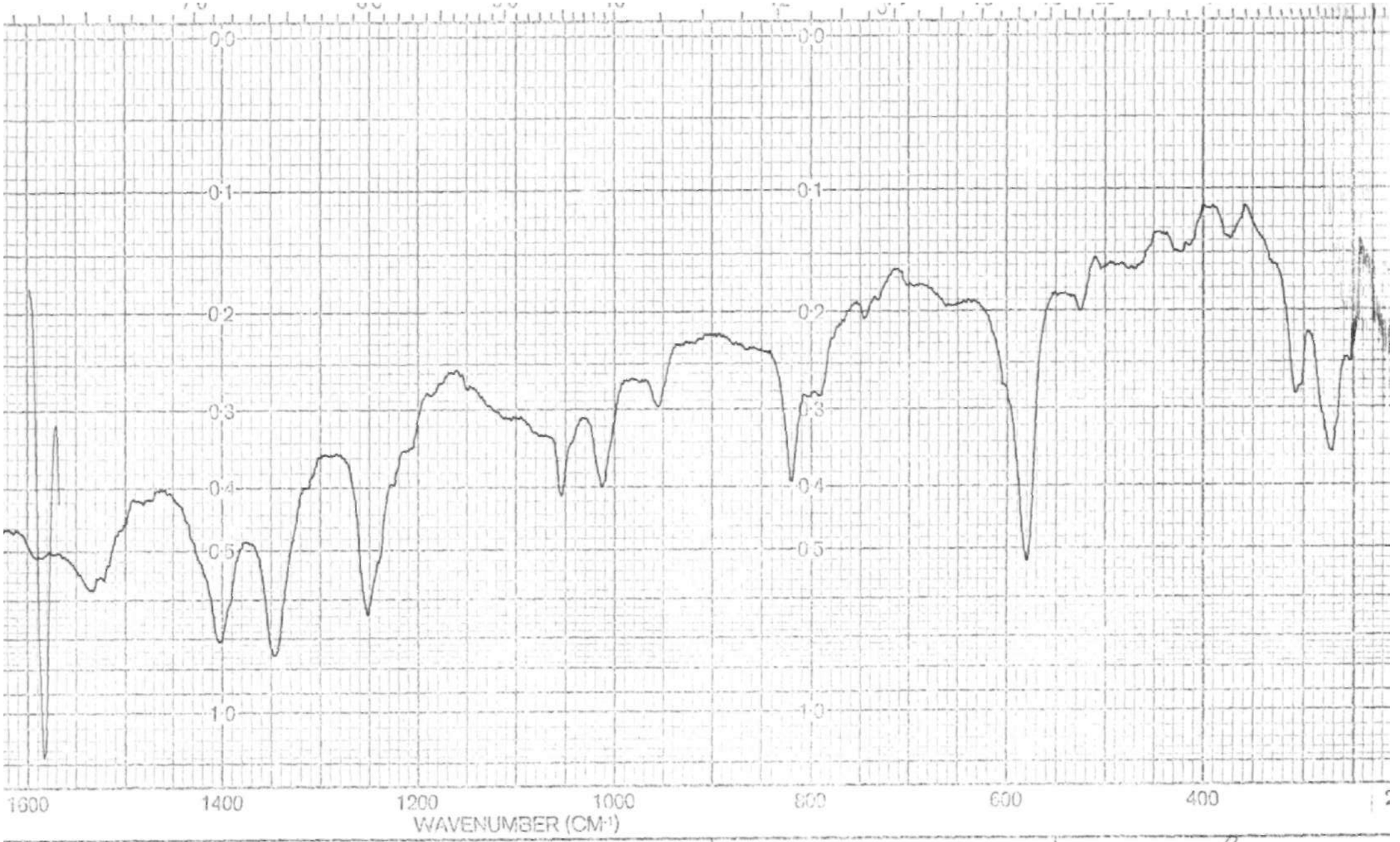
DATE 7/8/80

OPERATOR Bernie



SAMPLE

SPECTRUM NO.



REMARKS

Sample : $MeSnCl_3 \cdot 2$ $-CO \cdot Me$

Phase : CS_2

SCAN MODE 1.5 min
SLIT N TIME CONSTANT Auto

PERKIN ELMER
PART No. 5100 4366

OPERATOR Bonire
DATE 10/2/81

REF No.

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

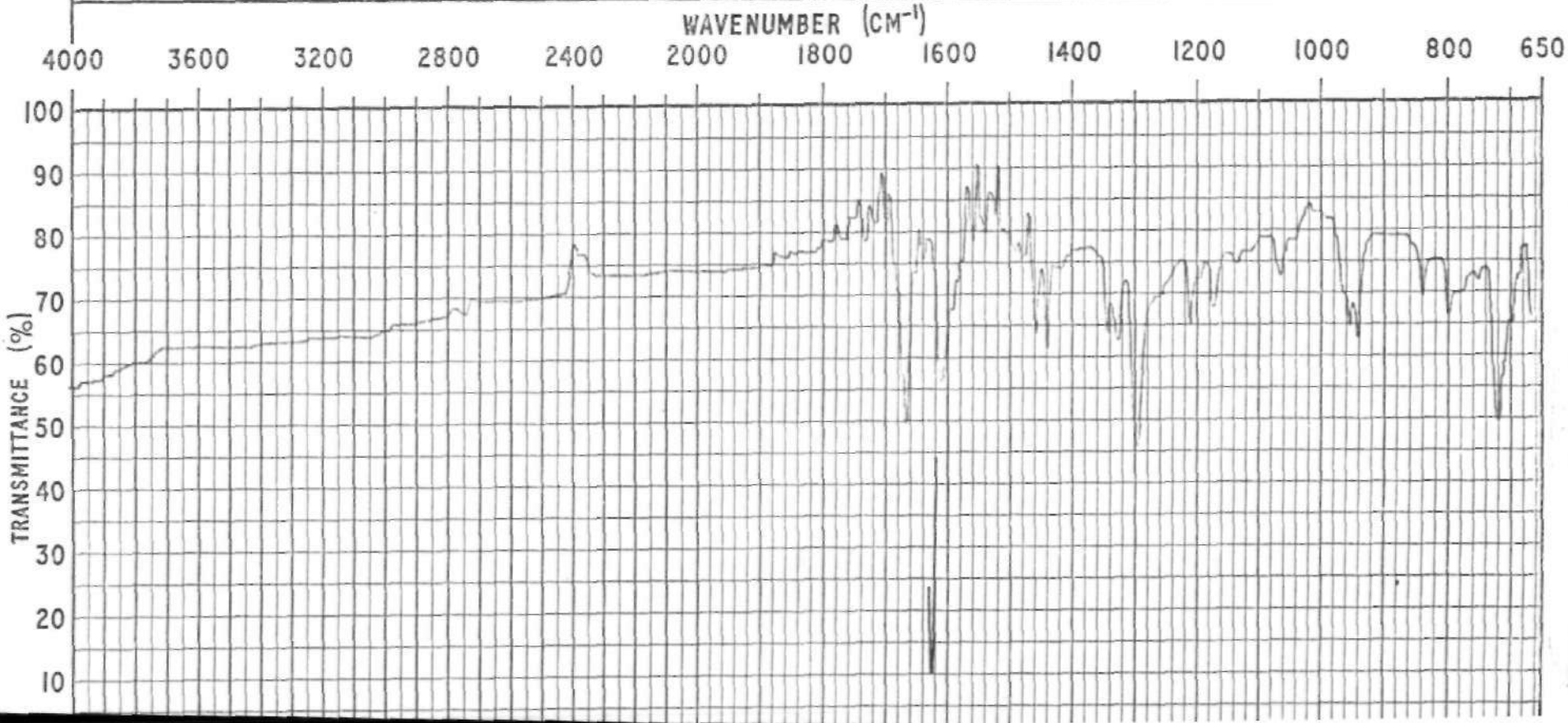
PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1 Me_2SnCl_2 2 NO -CO-O

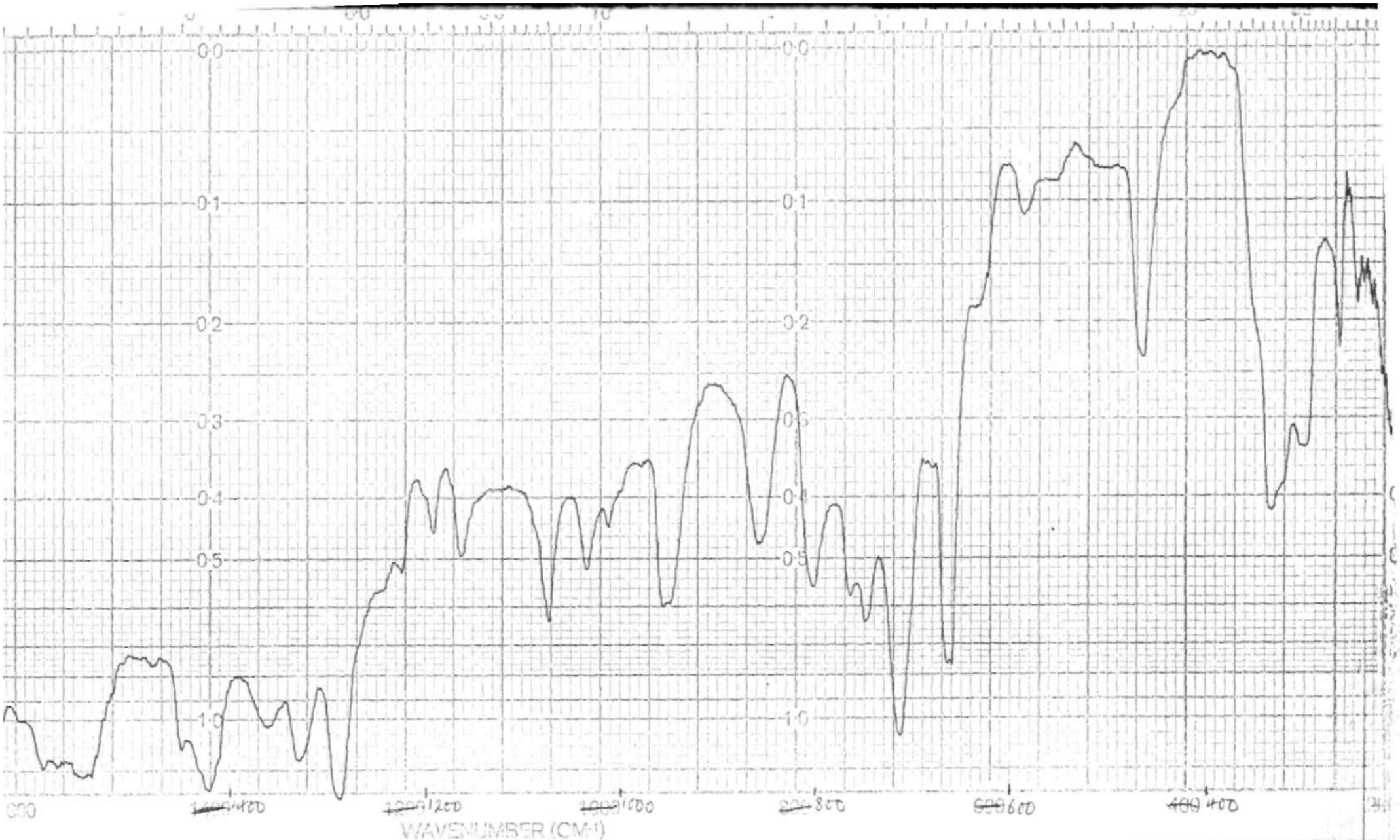
DATE 7/8/80

OPERATOR Bonine



SAMPLE

SPECTRUM NO.



REMARKS

Sample : $PhSnCl_3 \cdot 2$ 

Phase : CsI

SCAN MODE 15 min
SLIT H TIME CONSTANT Auto

PERKIN ELMER
PART No. 5100 4366

OPERATOR Bonire
DATE 10/2/81

REF No.

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

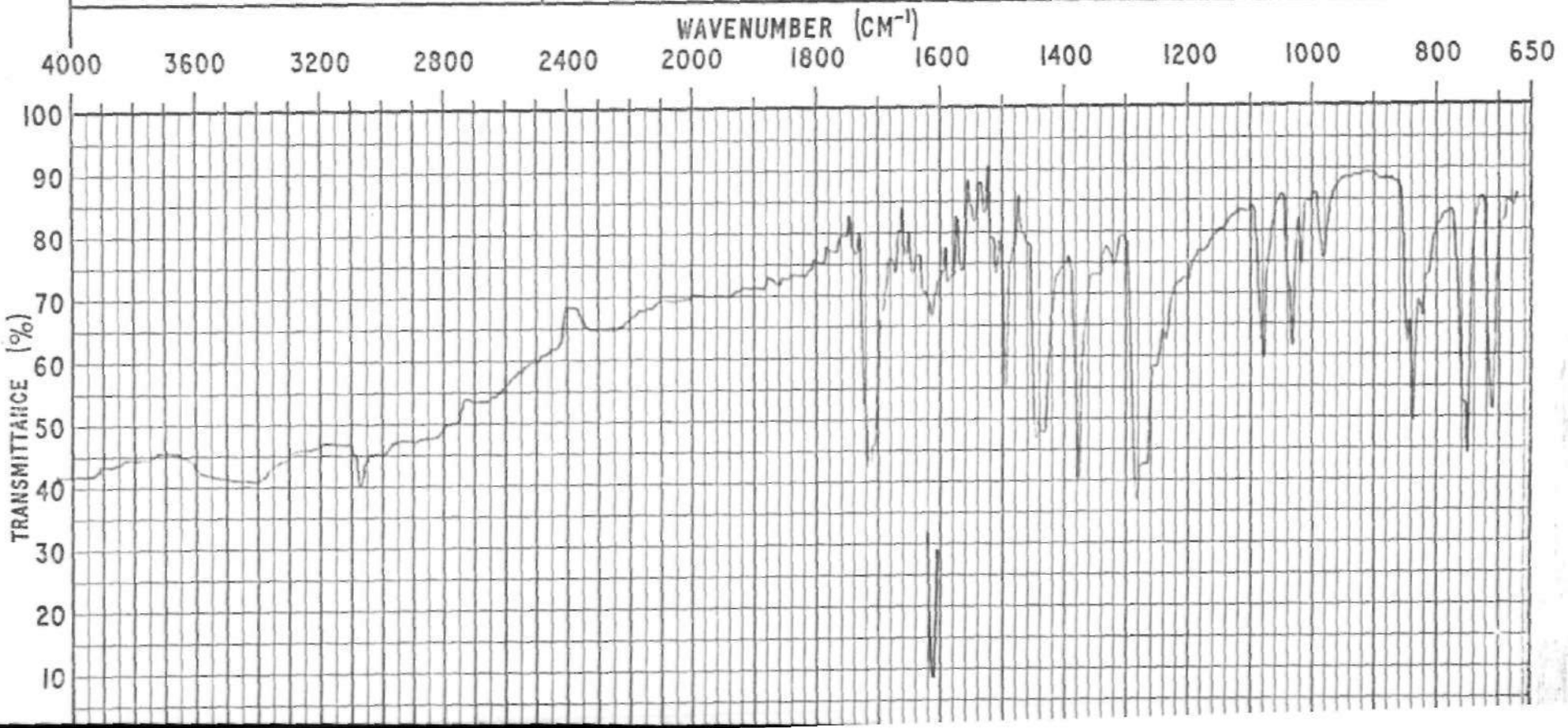
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I $Ph_2SnCl_2 \cdot 2$ NO-CO·Me

DATE 6/8/80

OPERATOR Bonise



SAMPLE

SPECTRUM NO.

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

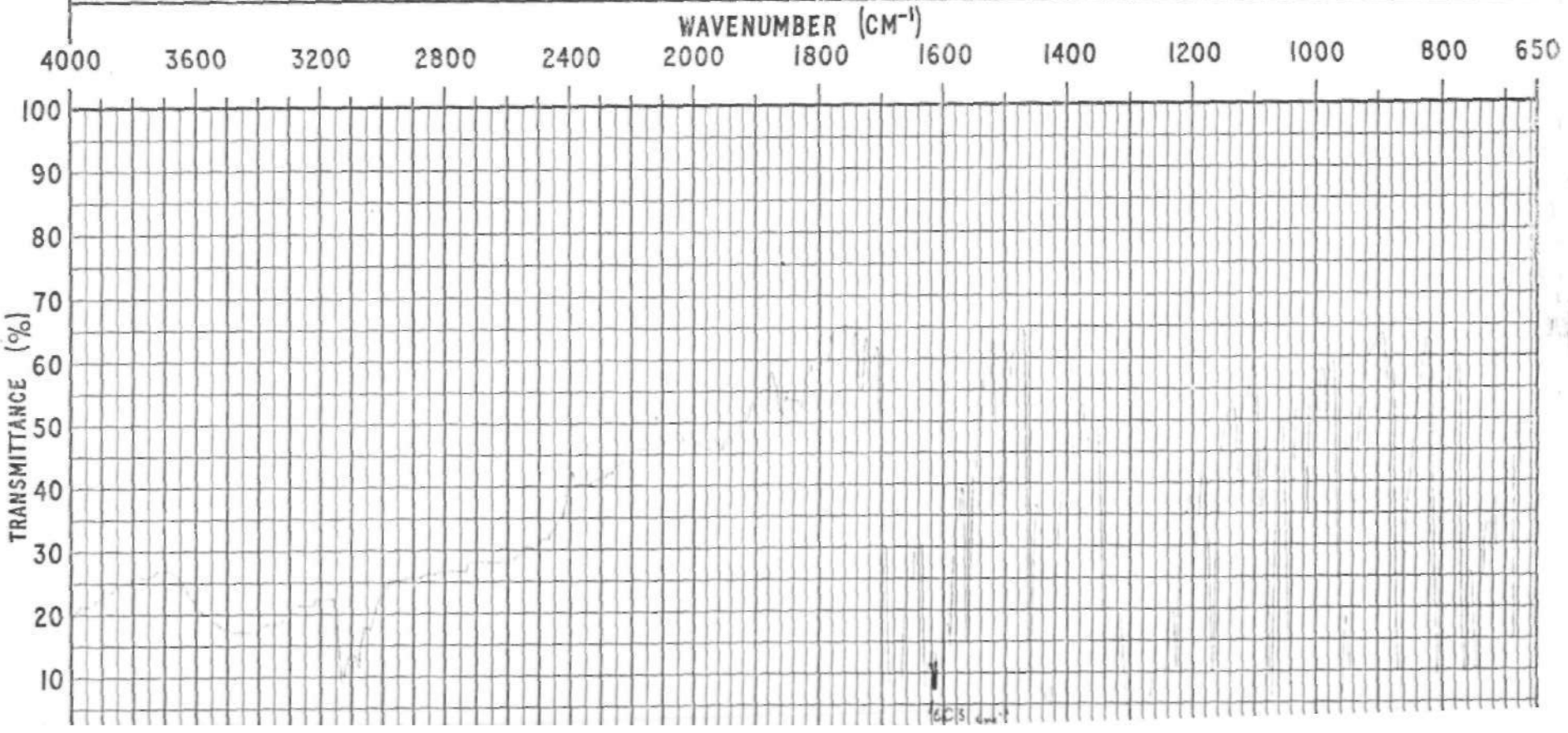
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I $SnCl_4 \cdot 2$  $\cdot CO \cdot Ph$

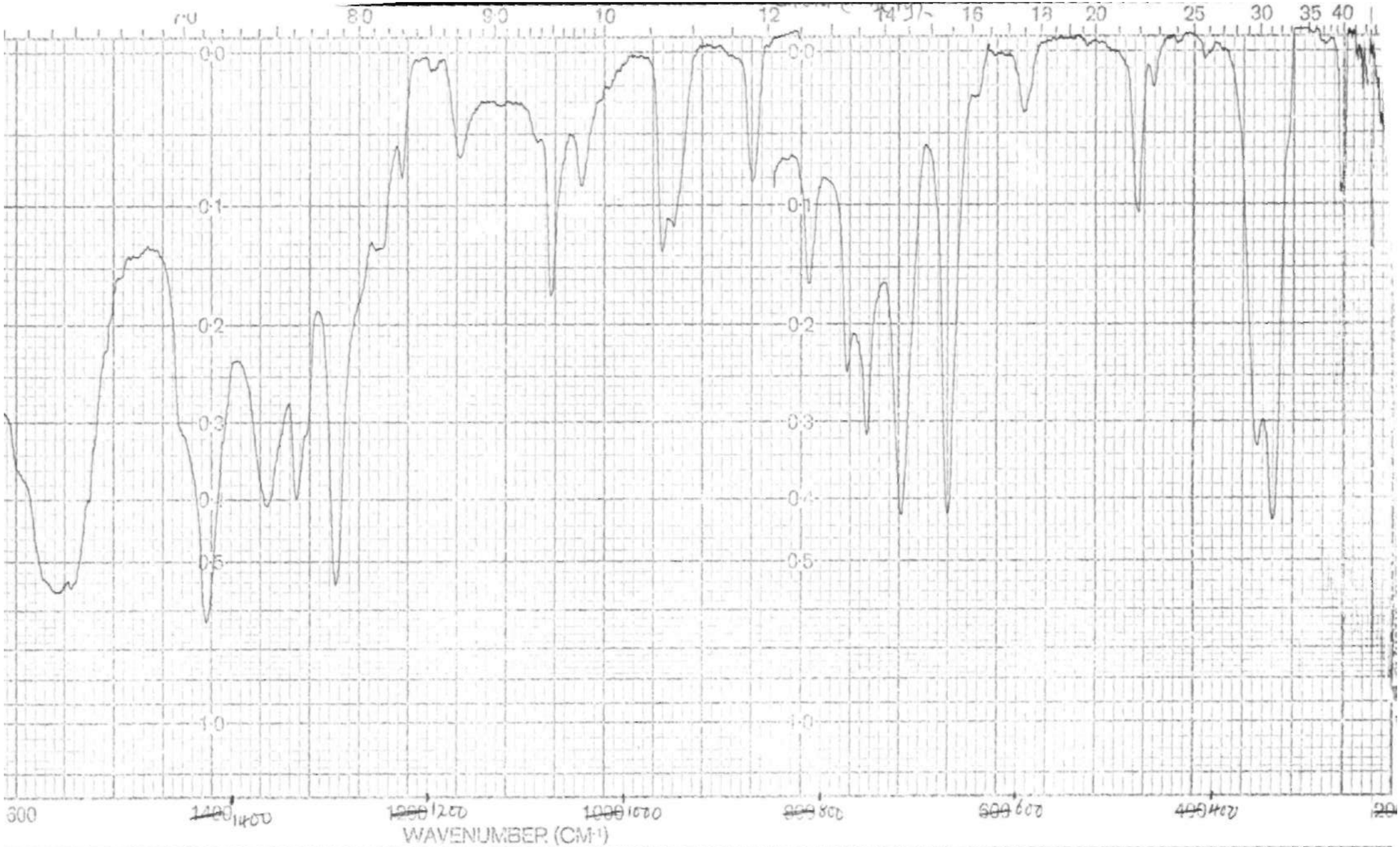
DATE 31/7/80

OPERATOR Bernie



SAMPLE

SPECTRUM NO.



REMARKS Sample : $SnCl_4$ 2 NO 10 C Phase : CS]	SCAN MODE 15 min SLIT N TIME CONSTANT fast	OPERATOR Bonine DATE 10/2/81
	PERKIN ELMER PART No. 5100 4366	REF No.

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

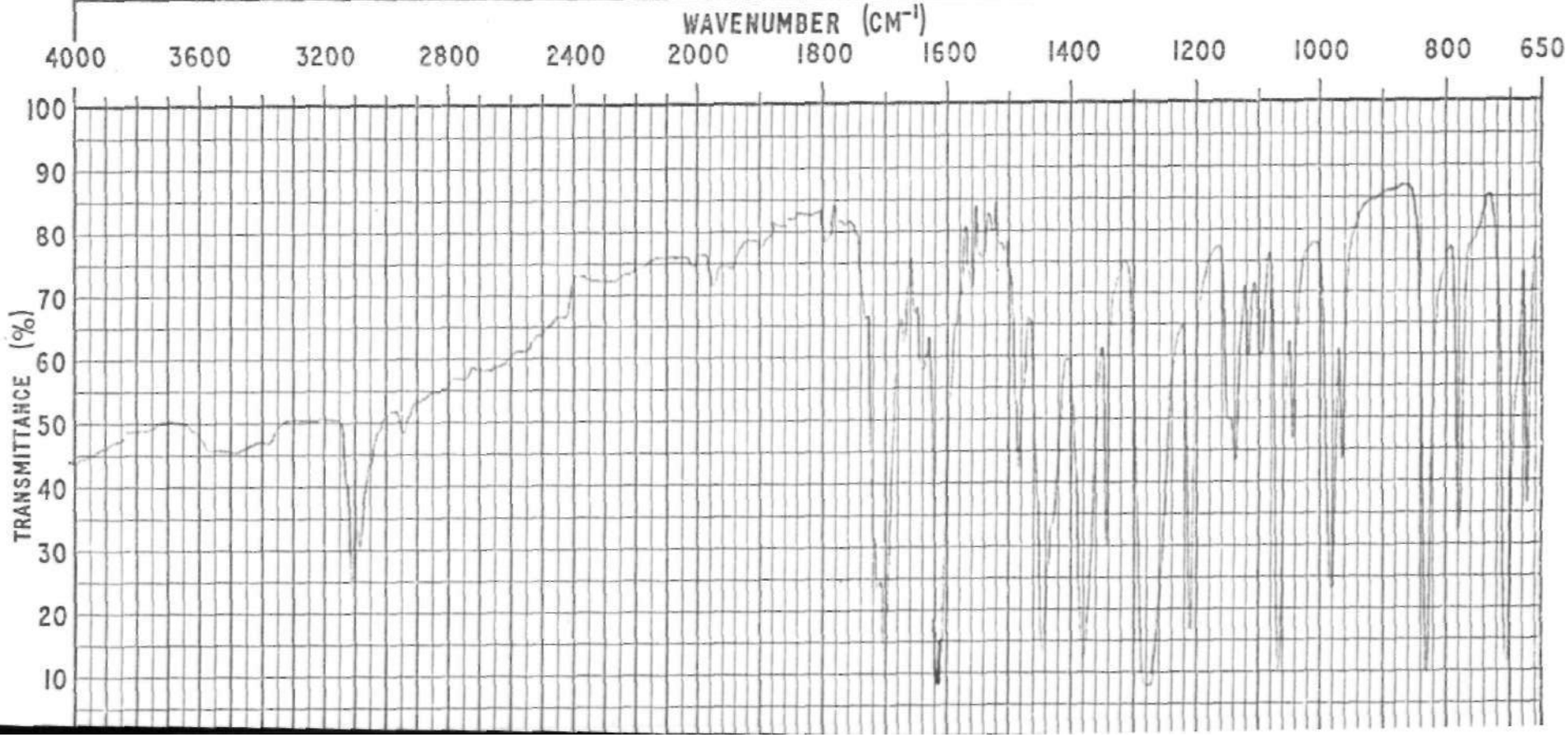
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I $SnCl_4 \cdot 2$  in Me

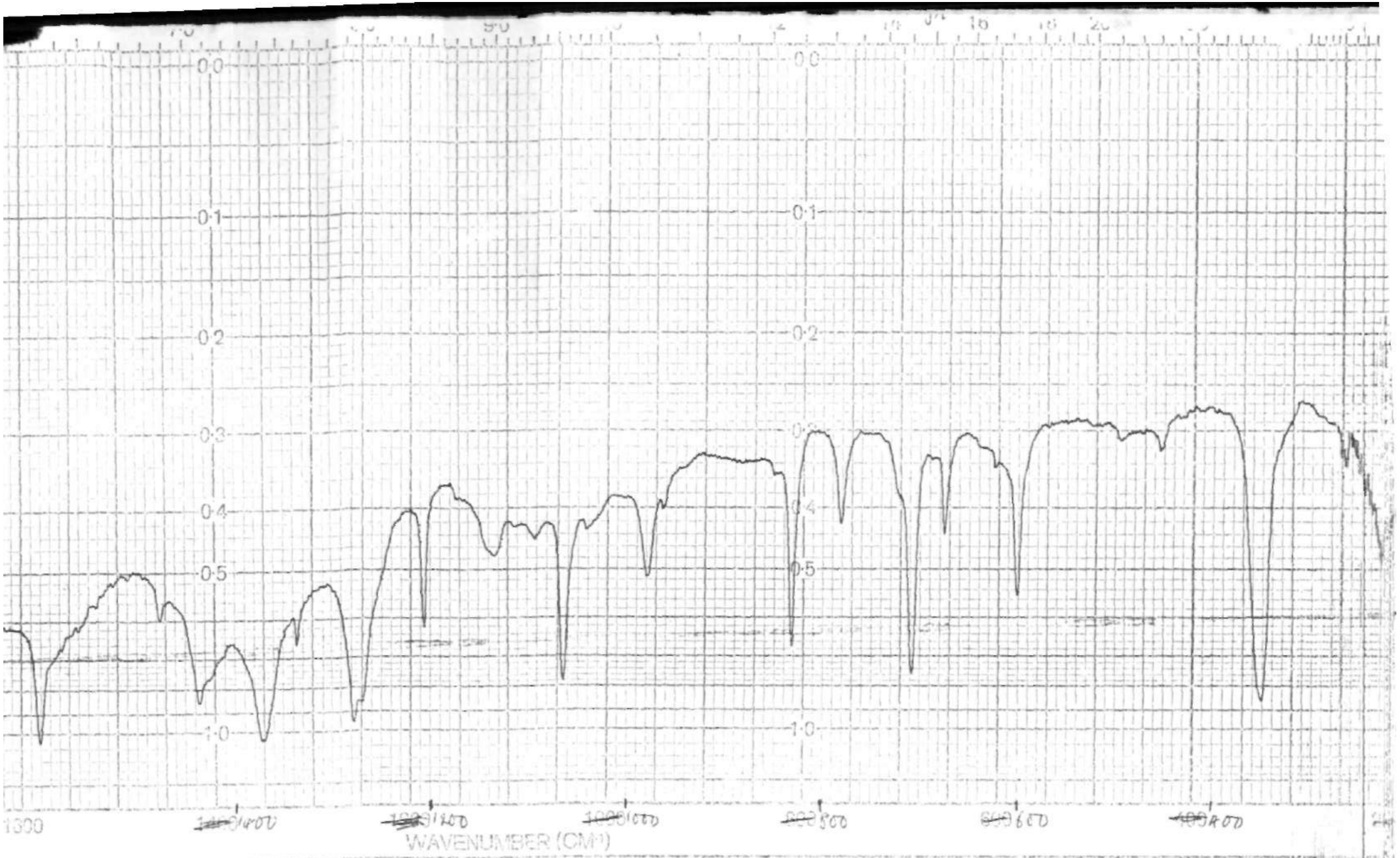
DATE 5/8/80

OPERATOR Benine



SAMPLE

SPECTRUM NO.



REMARKS Sample : $SnCl_4 \cdot 2$ [O]$_{CO\,Me}$

Phase : Cs I

SCAN MODE 15 min
SLIT M TIME CONSTANT Auto

PERKIN ELMER
PART No. 5100 4266

OPERATOR Bernie
DATE 10/2/81

REF No.

The Pyridine C=C bond.

Gill, Mitchell, and Popov et al[38,39,40] have observed that most of the pyridine i.r. bands shift to higher frequencies as the pyridine coordinates on a Lewis acid. This is only to be expected, for reasons given earlier in the explanation of the n.m.r. downfield shift of the pyridyl protons with complexation of the pyridine. The tendency to neutralize the positivity created on N by coordination of the pyridine on some Lewis acid, would conceivably cause a contraction and thus strengthening of all the bonds in the ring. The stretching frequency of any of the bonds would therefore increase. Gill et al[38,39,40] have noticed that the pyridine C=C stretch at 1580cm^{-1} in the uncomplexed ligand shifts to about 1600cm^{-1} as the pyridine complexes. This has been the corollary used to tell whether there is coordination or not between an organotin chloride and pyridine.

All the pyridine and ketopyridine adducts of the organotin and stannic chlorides prepared showed this shift. The shift was however higher in the pyridine adducts than the keto-substituted pyridine adducts. (see table 7). This too seems to be a reflection of the binding strength of the ligand, for the more strongly a ligand donates to a Lewis acid, the more positive the donor atom becomes and the more the contraction

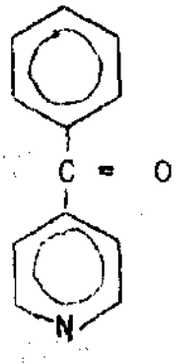
of the bonds of the ligand.

This observed shift seems to confirm the bonding between the organotin chloride and stannic chloride Lewis acids and the ligands (pyridine, 3- & 4-acetyl- and benzoyl-substituted pyridines).

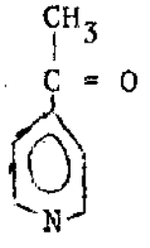
The >C=O stretch.

The >C=O stretch on the 2-ketopyridines complexed with transition metals[14,15,16] was observed to shift to lower frequencies with complexation. This could be predicted from the fact that coordination of the O of the >C=O could be likened to a situation in which the >C=O forms a hydrogen bond: the >C=O stretching vibration frequency decreases and the absorption band broadens.

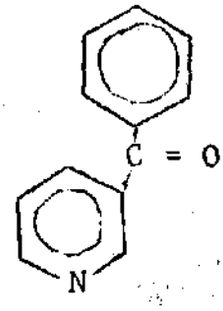
This provides the criterion for a decision as to which of the two sites on the complexed ketopyridines actually binds to the Sn.



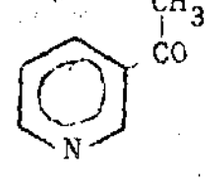
LIV



LIII



XLI



LV

In the above ligands, either or both N and O could bind on the Lewis acid as a complex is formed. Conceivably, the N end is freer and would therefore bind in preference to the C=O site. I.r. spectroscopy has conformed this in this work: compared with the spectrum of the free ligand, no appreciable shift of the C=O stretching frequency to lower frequencies is observed in all the 3- and 4-acetyl and benzoyl-pyridine adducts of the methyltin, phenyltin, and stannic chlorides studied. Since elemental analysis has indicated that the diorganotin, monoorganotin, and stannic chlorides are in the ratio of 1:2 Lewis acid: Lewis base in their complexes with the 3- α 4- acylpyridine adducts, while trimethyltin chloride is in 1:1 proportion with the 4-acylpyridines in their complexes, it follows that the 3- α-4-acetyl - and benzoyl-pyridines act as monodentate ligands when they bind on organotin and stannic chloride Lewis acids. Also, they bind with their N rather than O, as evidenced in the pyridine C = C stretching frequency shift in the complexes, while no shift in frequency is exhibited by the C = O stretch.

The preference for N-coordination over O-coordination, since both the N and O ends of the ligands are reasonably sufficiently sterically free to bind in adduct formation,

could be due mainly to the higher electronegativity of oxygen compared with that of nitrogen. This makes it more difficult for O to spare its electron pairs for dative bonding.

iii. 2-Acetyl and benzoyl-pyridine, and 2-pyridine carboxaldehyde complexes of methyltin, phenyltin, and stannic chlorides.

2-Benzoylpyridine Adducts.

2-Benzoylpyridine forms isolable adducts with only methyltin trichloride, phenyltin trichloride, and stannic chloride. Most remarkable in the i.r. spectra of the isolated adducts is the shift of the C=O stretch at ~ 1660cm^{-1} in the uncomplexed Lewis base to about 1600cm^{-1} in the adducts. This goes to conform, as earlier found by other workers[14,15,16] that the carbonyl of the Lewis base also coordinates with the Lewis acid in the complex. Elemental analysis has indicated that methyltin trichloride, phenyltin trichloride, and stannic chloride form 1:1 complexes with the Lewis base. Sn in the Lewis acids is known, and has been found in this work, to be hexacoordinated as it complexes. If follows then that 2-benzoylpyridine acts as a bidentate ligand to the Lewis acids:

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

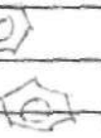
THICKNESS

SCAN SPEED Slow

SLIT

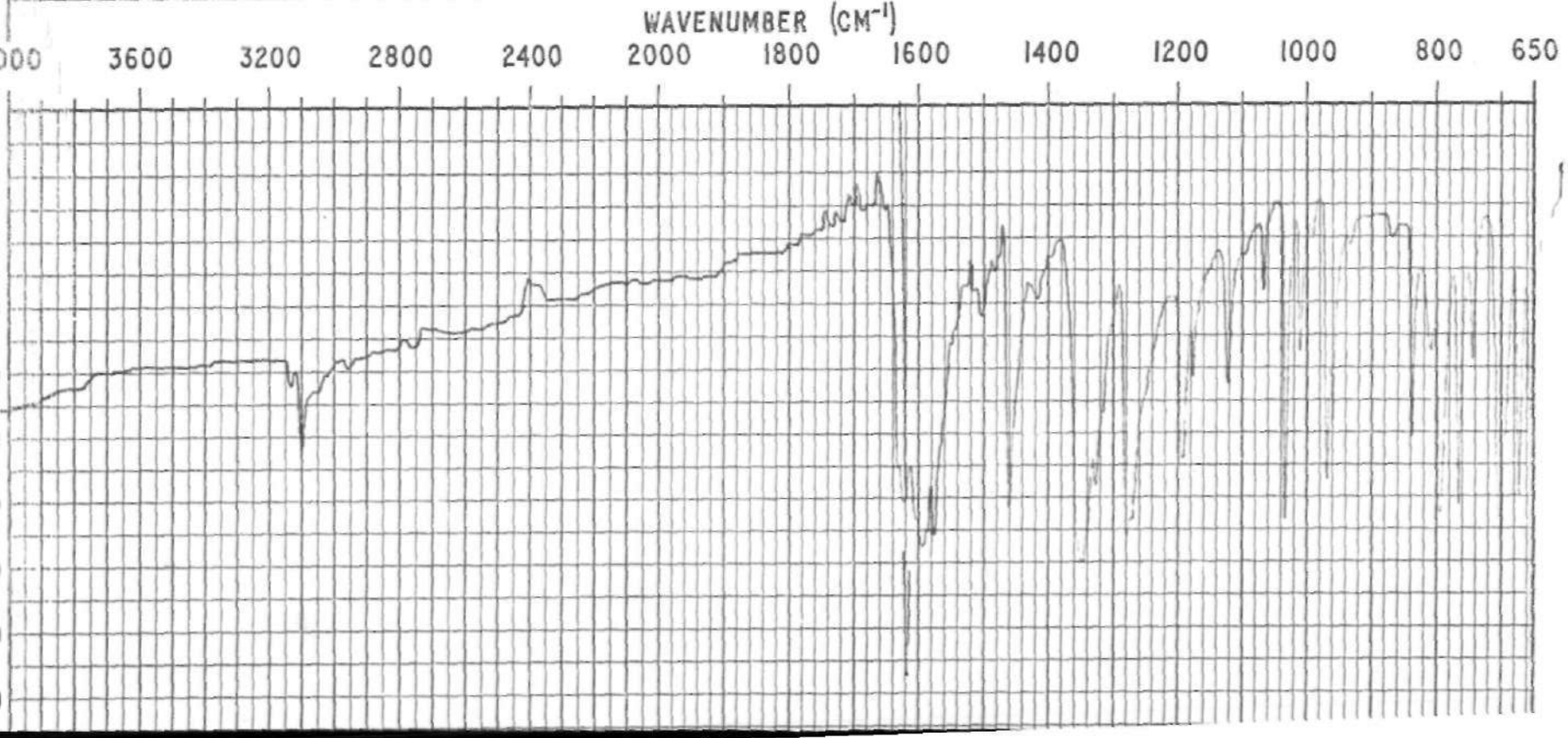
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I MeSnCl, 

DATE 30/10/80

OPERATOR Bonnie



SAMPLE

SPECTRUM NO.

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

PERKIN-ELMER

SPECTRUM NO.

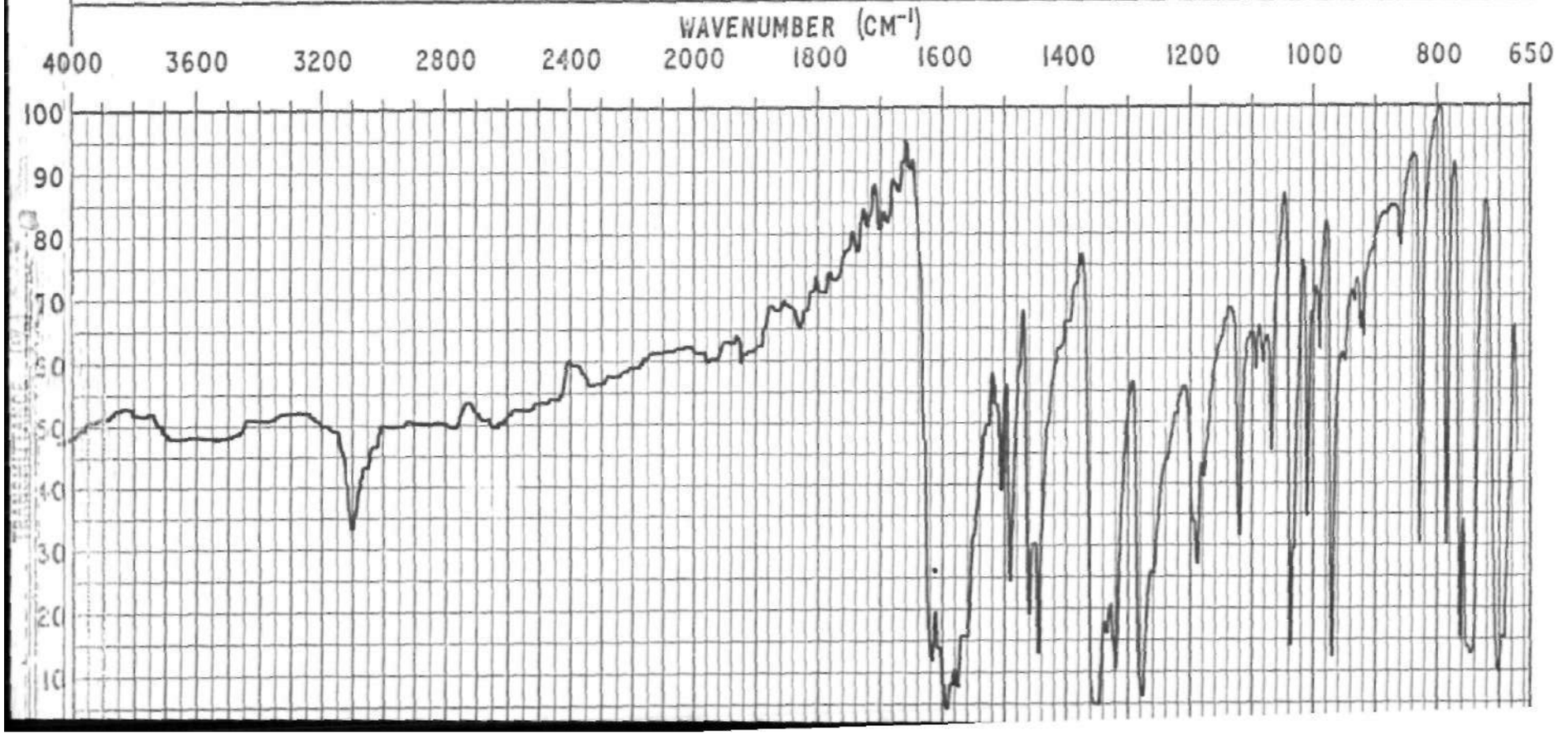
SAMPLE 1 $PhSnCl_3$ (C) Oz. (O)

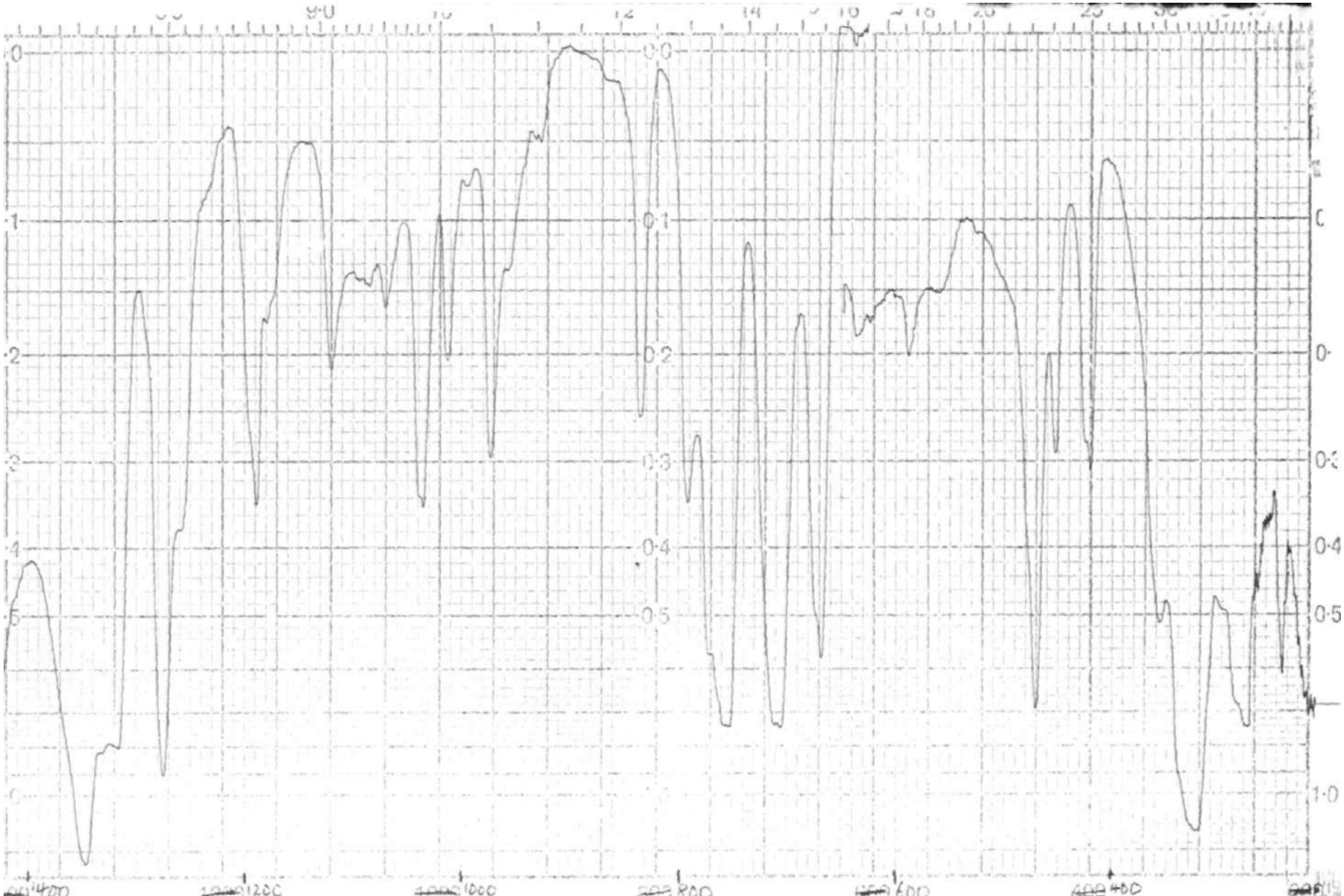
DATE 30/10/80

OPERATOR Bonin

SAMPLE

SPECTRUM NO.

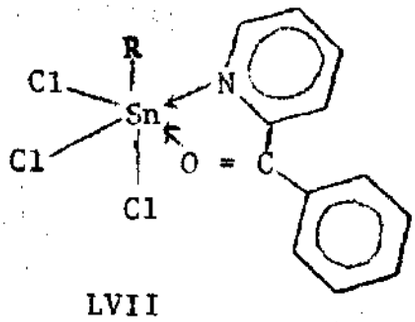




Sample : $PhSnCl_3$ · H_2O
Phase : CS I

SCAN MODE 15 min
SLIT N TIME CONSTANT Auto
PERKIN ELMER
PART No. 5100 4366

OPERATOR Bonire
DATE 10/2/81
REF No.



LVII

where R = Me, Ph, or Cl

Coordination of the Lewis base carbonyl on the Sn is quite feasible. Not only is the hexacoordination of the Sn satisfied, but a possibly stable five-membered ring is formed as a result of the coordination of the N and O on the Sn. It is perhaps the geometry of the Lewis base then that allows the O to bind along with the N on Sn, unlike the case with the 3- and 4- analogous keto substituted pyridines.

2-Acetylpyridine Products

The mode of reaction of 2-acetyl pyridine with the methyltin, phenyltin, and stannic chlorides still remains a puzzle. Elemental analysis results for the products of reaction of $SnCl_4$, $PhSnCl_3$, and Ph_2SnCl_2 with the Lewis base agree well with those expected for 1:2 Lewis acid: Lewis base complexes. The infrared spectra of the products

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

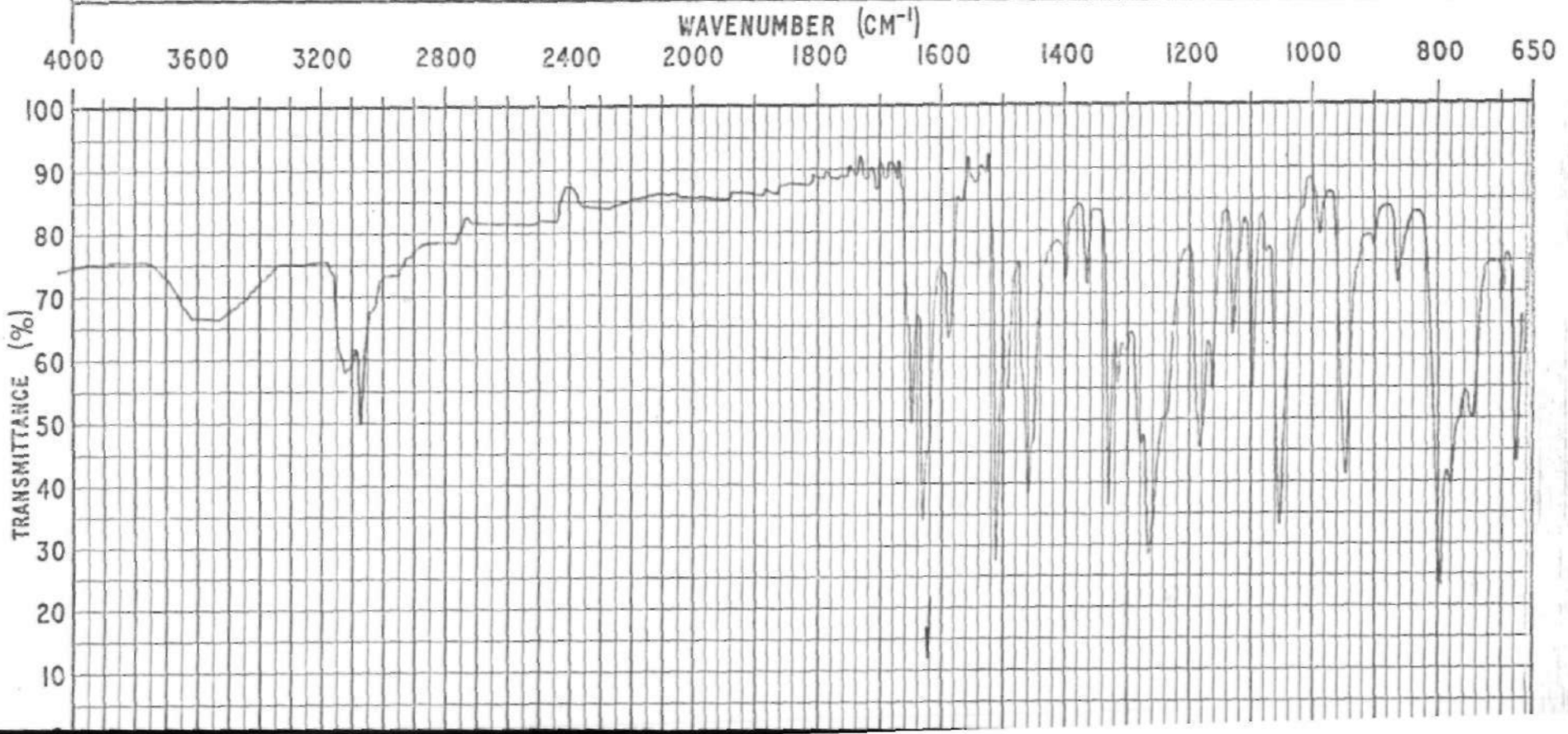
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I Product of $MeSnCl_3$ + 2-Ac-Py

DATE 31/10/80

OPERATOR Banire



SAMPLE

SPECTRUM NO.

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

SCAN SPEED Slow

SLIT

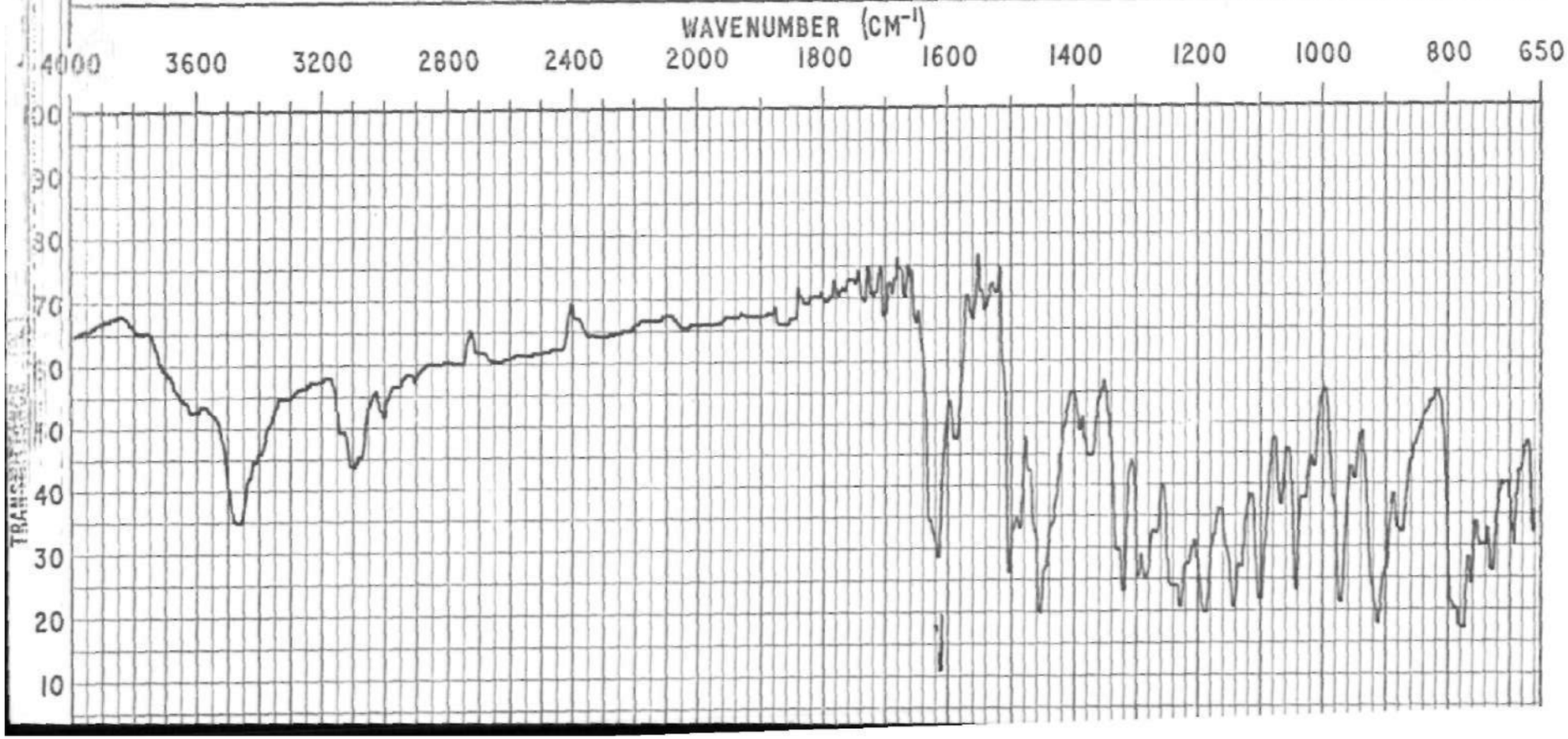
PERKIN-ELMER

SPECTRUM NO.

SAMPLE I Product of $SnCl_4 + 2$ [illegible] 60 mg

DATE 31/10/80

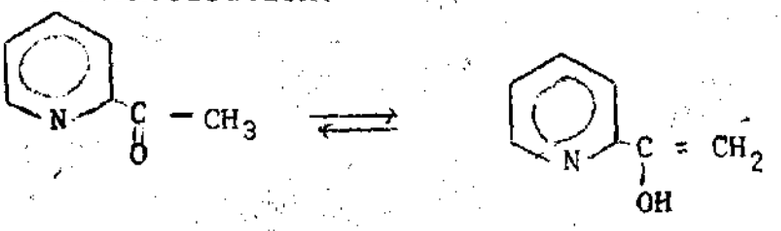
OPERATOR Bonino



SAMPLE

SPECTRUM NO.

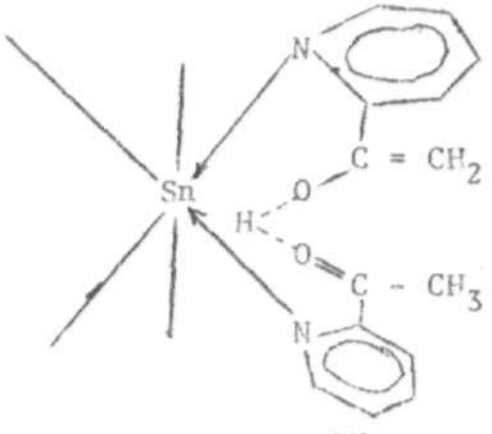
however have shown the C = O band at ~ 1700cm^{-1} in the uncomplexed Lewis base to be absent in the spectra of the products. Instead, new strong bands at ~ 1600cm^{-1}, due probably to coordinated C = O or C = C stretch, have been observed in the spectra of the products. Also, a new band appears at ~ 3450cm^{-1} in the spectra of the three products. This band is assignable to -OH, but the only conceivable way by which an -OH could have been produced in the products is through tautomerisation:



LVIII LIX

However, this new band at 3450cm^{-1} is not present in the spectrum of the free Lewis base, and unless the OH enhances the stability of the product in some way, there is no reason why the tautomer bearing it should be preferred in the complexes. The elemental analysis results of the three products agree with those expected for the 1:2 complexes. N.m.r. spectra of the products have not shown distinct signals

for vinylic protons, but vinylic C=C stretch that would be at ~ 1645cm^{-1} could not be said to be absent, as the new band at about 1600cm^{-1} extends to almost 1650cm^{-1}. The only mode of coordination that could be suggested, if only tentatively and speculatively, is



LX

This structure could account for the absence of the C=O stretch at ~ 1700cm^{-1}, the emergency of a new band between 1600 and 1650cm^{-1} (coordinated C = O); the appearance of the new band at 3450cm^{-1}; the diminished -CO.CH$_3$ signal at ~ δ2.70ppm in the n.m.r. spectra of the products; and the low melting temperatures of the products compared with the 3- α 4-acyl substituted pyridine adducts. Such a complex

would not be expected to be very stable.

The CH_3 of the acetyl substituent in 2-acetylpyridine influences the mode of reaction of the ligand. In the absence of steric hindrance, 2-benzoylpyridine gave clean simple 1:1 adducts with the Lewis acids. 2-Benzoylpyridine bears no α-hydrogens. Therefore, tautomerism leading to the above suggested mode of bonding cannot arise. Where the acetyl groups are on the 3- α 4- positions of the pyridyl, they are probably geometrically too far apart to interact. These suggestions, however, are still only speculative, and would require further work for confirmation.

The products of reaction of the methyltin chlorides with 2-acetylpyridine have not been analytically identifiable, unlike the products of reaction with the phenyltin chlorides. This seems to suggest that the $-CO.CH_3$ of the 2-acetylpyridine and the methyl on Sn in the methyl tin chlorides somehow influence or participate in the reaction of the Lewis base with the methyltin chlorides. 2-Benzoylpyridine gave straight-forward adducts with $SnCl_4$, $PhSnCl_3$, and $MeSnCl_3$; 2-acetylpyridine has given at least analytically and therefore stoichiometrically understandable products in its reaction with $SnCl_4$ and $PhSnCl_3$ but the

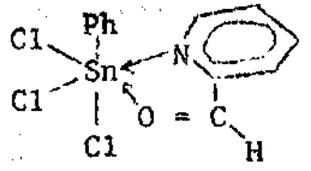
methyltin chlorides react with 2-acetyl-pyridine to give even analytically yet to be understood products.

Unlike the products of reaction of $SnCl_4$, $PhSnCl_3$, and Ph_2SnCl_2, the i.r. spectra of the products of reaction of $MeSnCl_3$ and Me_2SnCl_2 with 2-Acetyl pyridine have not shown any band at ~ 3400cm^{-1}. The >C=O band expected at ~ 1700cm^{-1}, as present in the spectrum of the clean Lewis base, has also been found to be absent. New bands, appear between 1600 and 1650cm^{-1}. These might be due to aromatic C=C, vinyl C=C, or coordinated >C=O. A number of new bands have sprung in the fingerprint region, while some that were present in the spectrum of the free Lewis base are absent from that of the complex.

2-Pyridine Carboxaldehyde.

Only phenyltin trichloride reacted with 2-pyridine carboxaldehyde to give a stable, analytically and spectroscopically identifiable product: a 1:1 adduct. The i.r. spectrum shows, among others, a shift of the >C=O stretch from ~ 1720cm^{-1} in the uncomplexed Lewis base to ~ 1630cm^{-1} in the complex. This strongly suggests the participation of the >C=O in complexation of the Lewis base. The aromatic C=C stretch has also shifted slightly to a higher frequency in the complex.

These suggest that 2-pyridine carboxaldohyde, although a poor unstable Lewis base, acts as a bidentate ligand towards organotin Lewis acids.



LXI

The fortunate isolation of this product goes further to substantiate the suggestions made on the mode of reaction of 2-acetyl pyridine with organotin Lewis acids. 2-Pyridine carboxaldehyde cannot exist in any tautomeric form as 2-acetylpyridine would. It would therefore bind simply like 2-benzoylpyridine, although its probable easy oxidation to a carboxylic acid could make the products unstable.

REMARKS

ORIGIN

PURITY

PHASE

CONCENTRATION

THICKNESS

SCAN SPEED

SLIT

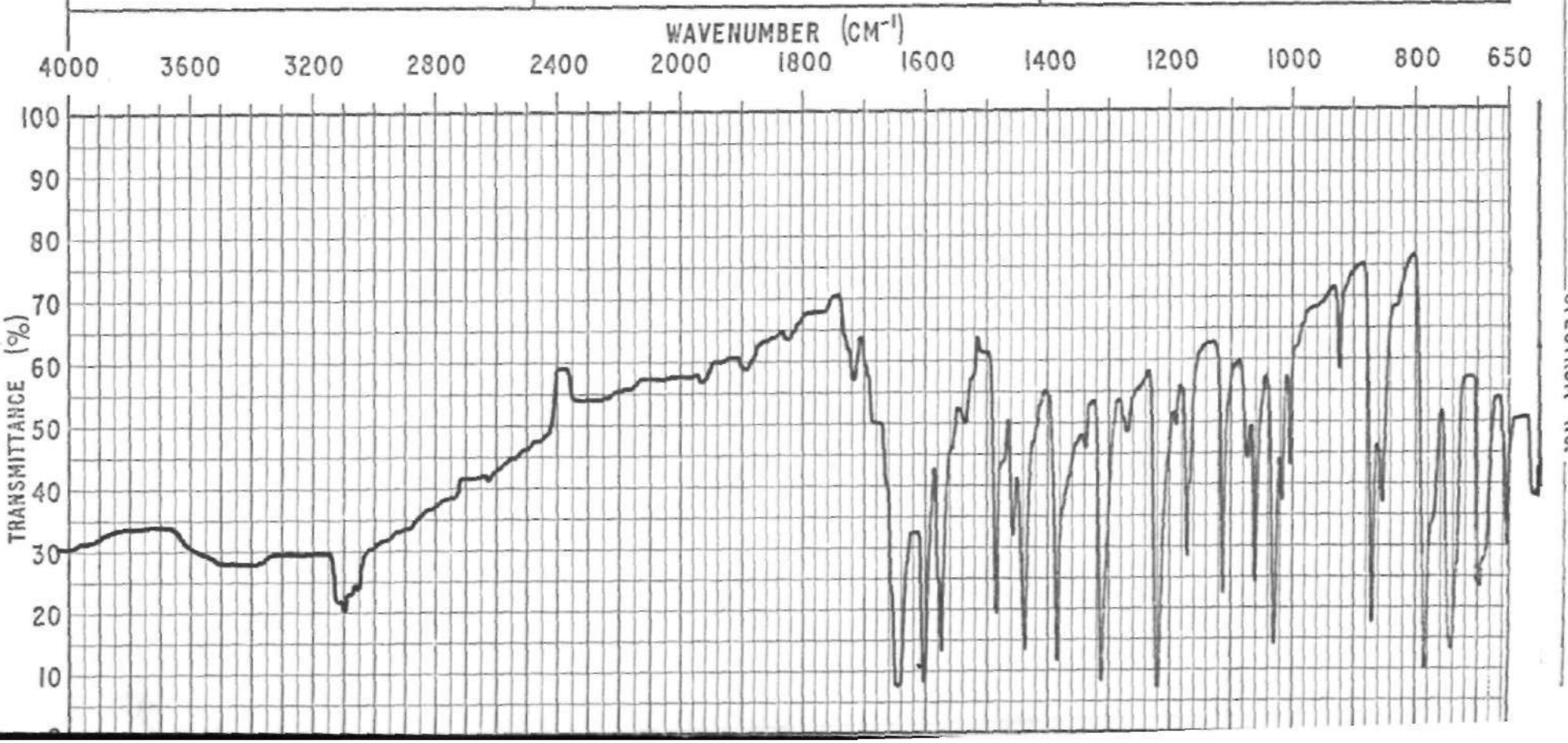
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SPECTRUM NO.

SAMPLE

DATE

OPERATOR



SAMPLE

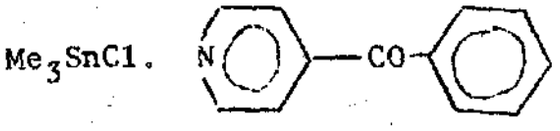
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(g) Structures of the methyltin, phenyltin, and stannic chloride pyridine adducts.

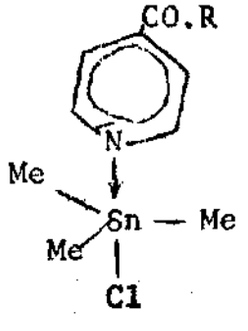
X-ray crystallography has shown $Me_3SnCl.Py$ to be of a regular trigonal bipygramidal structure, with equitorial methyl groups[8]. It is conceivable therefore that the structures of



and



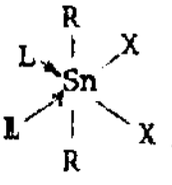
would also be trigonal bipyramidal with equatorial methyl groups. Some degree of distortion is expected in the structures. however, since 4-acetyl and 4-benzoyl-pyridines are weaker donors than pyridine. However, since the substituents of the Lewis bases are in the para-position, steric interaction that might alter the trigonal bipyramidal structure is unlikely. viz:



where R = Me, or Ph

XXXII

As a result of i.r. and Mossbauer spectroscopic studies, adducts of dimethyl and diphenyl tin dichlorides with monodentate ligands have been assigned the octahederal structure with trans Me or Ph groups[52].



LXII

where R = Me, or Ph

H = halogen,

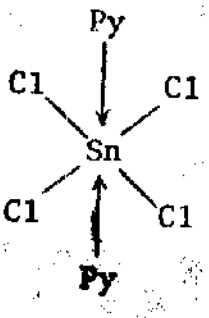
L = Lewis base.

The above structure has actually been assigned to $Me_2SnCl_2.2Py$[52]. The Keto-substituted pyridine Lewis bases studied in this work have their keto-substituents in the 2-, 3- or 4- positions of the pyridine ring. The 2-substituted acyl-pyridines add on to organotin and stannic chlorides in ways different from that observed for 3- and 4-acylpyridines as already discussed; and would therefore be expected to have a different structure. Whether the above structure still holds for the new acyl-pyridine adducts would be a good field to examine further.

Unfortunately, absence of the necessary instrumentation has made it impossible to undertake that task in the present work.

The structures of the monoorganotin trihalide pyridine adducts have not been successfully arrived at yet[52]. The structures of the pyridine and acylpyridine adducts would therefore make a good field of study.

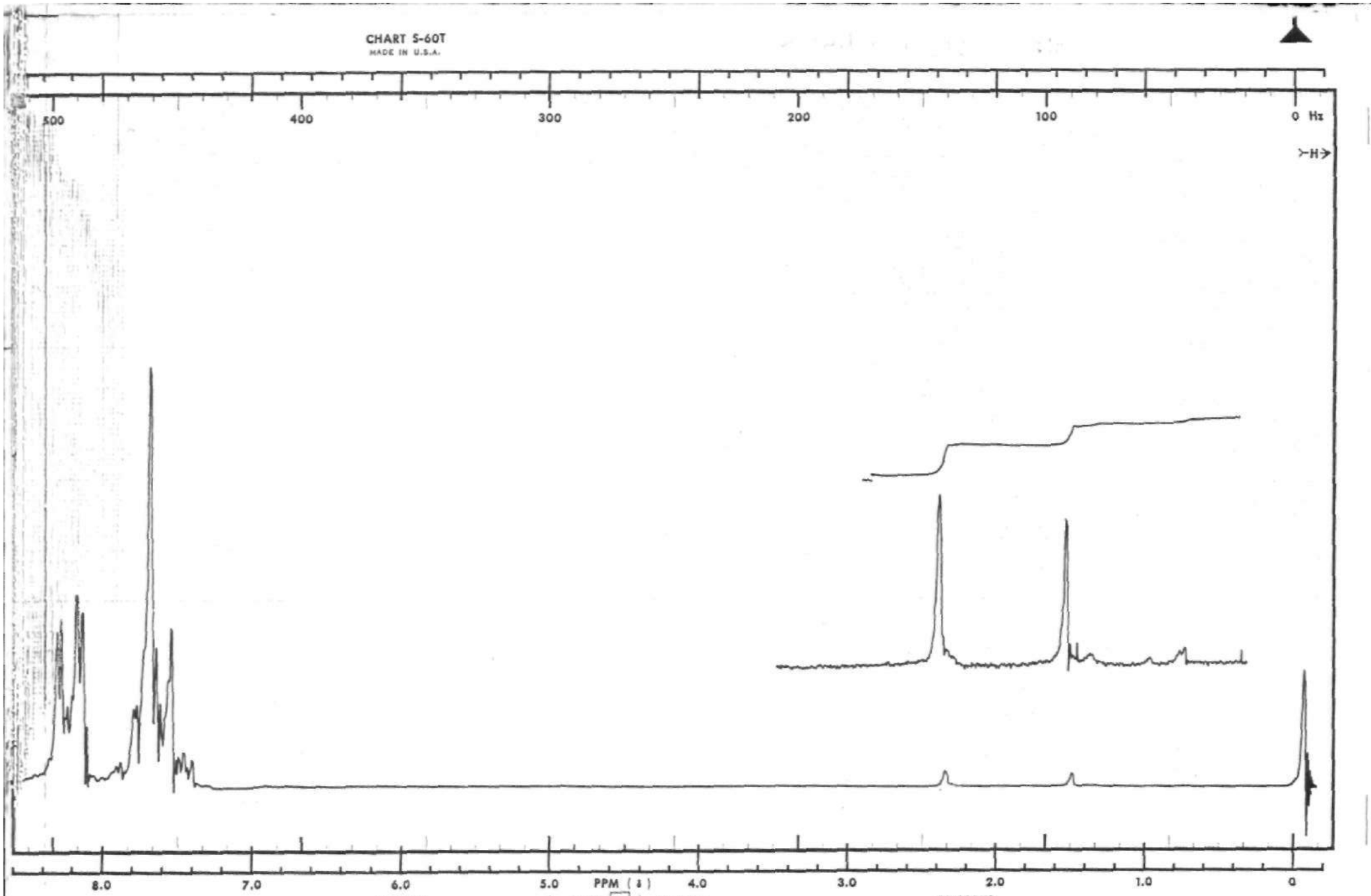
Stannic chloride pyridine adduct has been intensively studied[9,10]. $SnCl_4.2Py$ is thought to have its Lewis base ligands in the trans - form, and its halogen ligands in a square plane.



LXIII

The keto-substituted pyridine adducts of $SnCl_4$ prepared in this work most likely would be of trans configuration too, for steric freedom.

CHART S-60T
MADE IN U.S.A.



MANUAL AUTO ☐

SWEEP OFFSET (Hz): 0.0V
SPECTRUM AMPLITUDE: 12
INTEGRAL AMPLITUDE: 6
SPINNING RATE (RPS): 42

SWEEP TIME (SEC): 50 250 (250)
SWEEP WIDTH (Hz): 25 50 100 250 500 (500)
FILTER: LK 2 3 4 5 6 7 8 (2)
RF POWER LEVEL: 2.1 (.05)

SAMPLE: $Me_2SnCl_2 \cdot 2NO-CH_3$

SOLVENT: Nitrobenzene

REMARKS:

varian

60 MHz NMR

(b) Strength of the Lewis bases.

Potentiometric titrimentric methods are, usually, the most widely used methods for determining the strength of weak acids and bases. The strength of a base B is a measure of its degree of ionization, viz:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{\{BH^+\}\ \{OH^-\}}{\{B\}}$$

$$\{OH^-\} = \frac{K_b\ \{B\}}{\{BH^+\}}$$

$$\therefore\ pOH^- = pK_b + \log \frac{\{BH^+\}}{\{B\}}$$

or

$$pH = pK_w - pK_b - \log \frac{\{BH^+\}}{\{B\}}$$

where the weak base is gradually neutrilized with a strong acid, at half neutrilization,

$$\{BH^+\} = \{B\}$$

$$\therefore\ \log \frac{\{BH^+\}}{\{B\}} = 0,$$

making

$$pH = pK_w - pK_b = pK_a$$

or

$$pK_b = pK_w - pK_a \simeq pOH$$

At half neutrilization then.

$$pH = pK_a,$$

and

$$pOH = pK_b$$

The strengths of the Lewis bases pyridine, 4-picoline, 4-vinylpyridine, 4-benzoylpyridine, and 4-acetylpyridine were studied by titrating their 0.10M solutions in 20% aqueous ethanol solutions with 0.10M HCl acid. The titrations were monitored with a pH-meter. The different values of pH of the mixtures were plotted against the volumes of titre used, and the various pK_a values for the base at half neutrilization obtained from the graphs.

Neutrilization curves for 4-Picoline, 4-vinylpyridine, pyridine, 4-acetylpyridine, and 4-benzoyl pyridine.

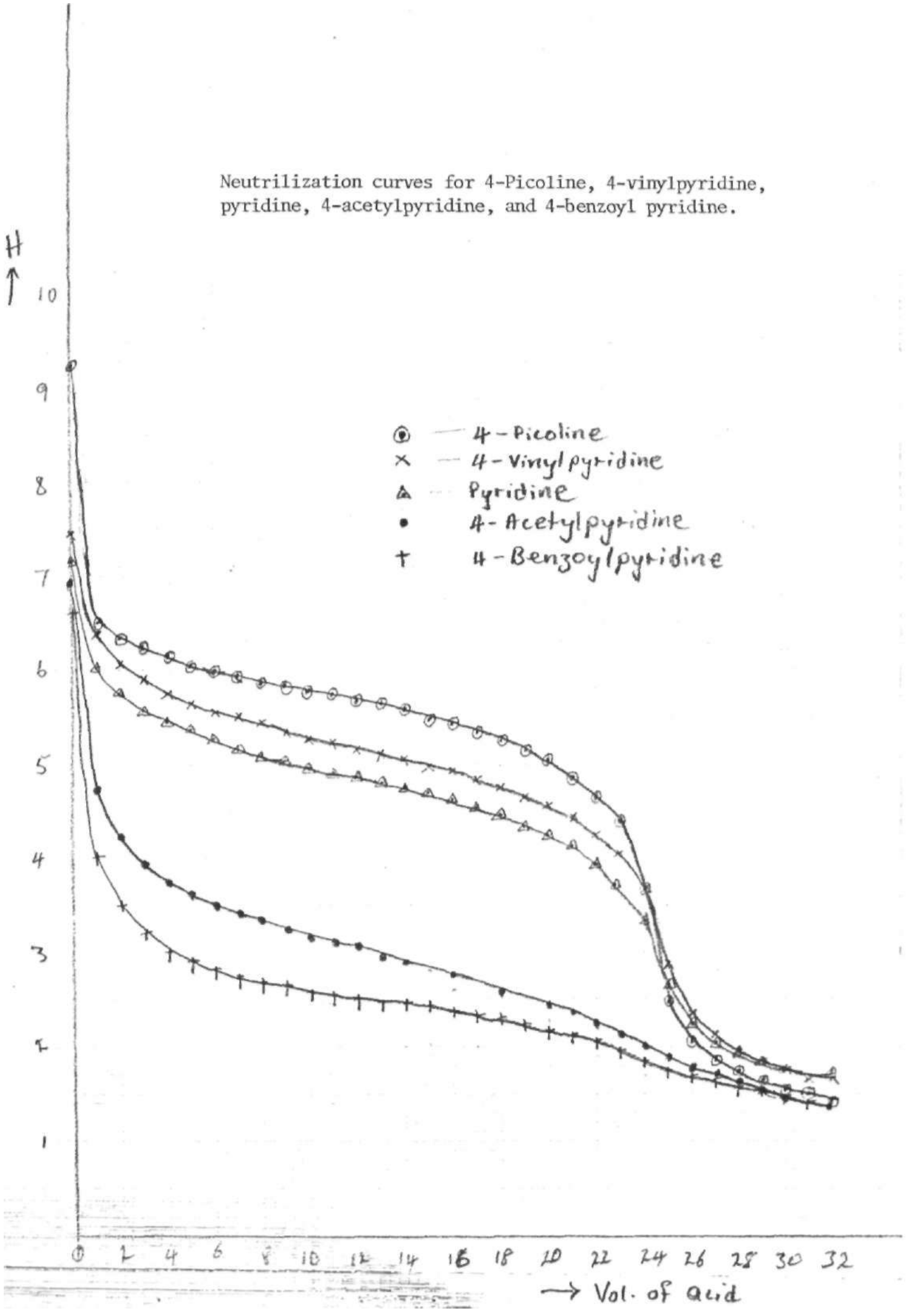
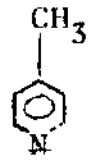
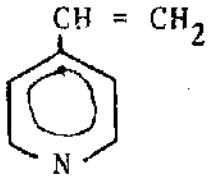
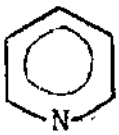
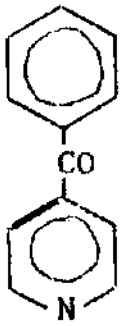
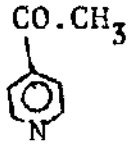


TABLE 8

Pyridine and some substituted pyridines, their pK_b's, and the respective values of the ^{119}JSn-C-H of their complexes with Me_2SnCl_2 (0.01M).

Lewis base	pK_b	Complex	^{119}JSn-C-H
	8.36	$Me_2SnCl_2.2$ 	cps 96.0
	8.87	$Me_2SnCl_2.2$ 	92.0
	9.17	$Me_2SnCl_2.2$ 	88.0
	11.49	$Me_2SnCl_2.2$  CO.Ph	82.0
	10.96	$Me_2SnCl_2.2$  CO.Me	81.0

(c) Relationship between the basicities of the ligands and the J Sn-C-H of their Methyltin chloride complexes.

Only the Lewis base ligands with their substituents in the the para-position were chosen, to ensure little or no steric interference of the substituents in the complexes. The main effects of the substituents on the N of the pyridine then would be mesomeric and/or inductive.

The titrations have shown that the Lewis bases, by measure of their pK_b, have their strength in the order.

4-Picoline > 4-vinylpyridine > Pyridine > 4-Acetylpyridine > 4-Benzoylpyridine.

There was however the difficulty of solubilizing the 4-benzoylpyridine well enough for a good titration.

The dimethyltin dichloride adducts with the Lewis bases have their $J^{119}Sn$-C-H in the following order of magnitude.

Me_2SnCl_2.bis-4-Me.Py > Me_2SnCl_2.bis-4-Vi.Py >
LXIV LXV

Me_2SnCl_2.2Py > Me_2SnCl_2.bis-4-Be.Py > Me_2SnCl_2.bis-4-Ac.Py
LXVI

where

4 - Me.Py = 4-picoline

4 - Vi.Py = 4-vinylpyridine

Py = Pyridine

4 - Be.Py = 4-benzoylpyridine

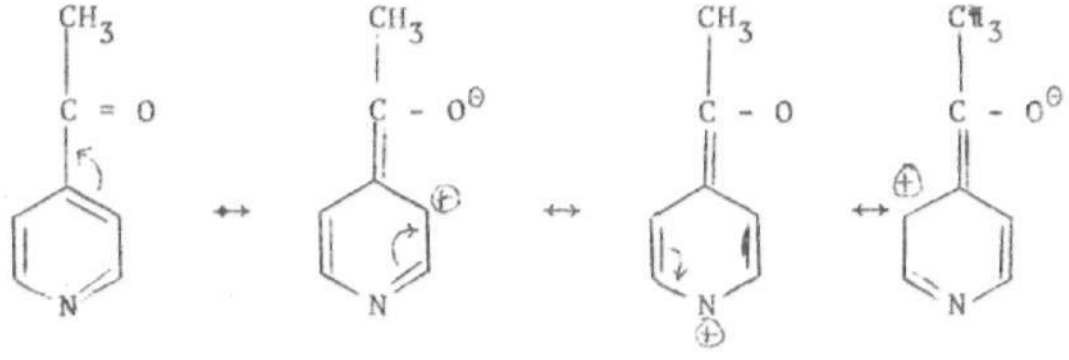
4 - Ac.Py = 4-acetylpyridine

It can then be seen that at constant temperature and molar concentration in a given solvent that interacts as little as possible with the solutes, the J Sn-C-H of the complex formed by a Lewis base with a given methyltin halide increases with increase in the strength of the base, provided the substituents on the Lewis base offer no steric hindrance in the association of the base with the Lewis acid. The relationship seems direct and linear, at least for pyridine and the stronger bases.

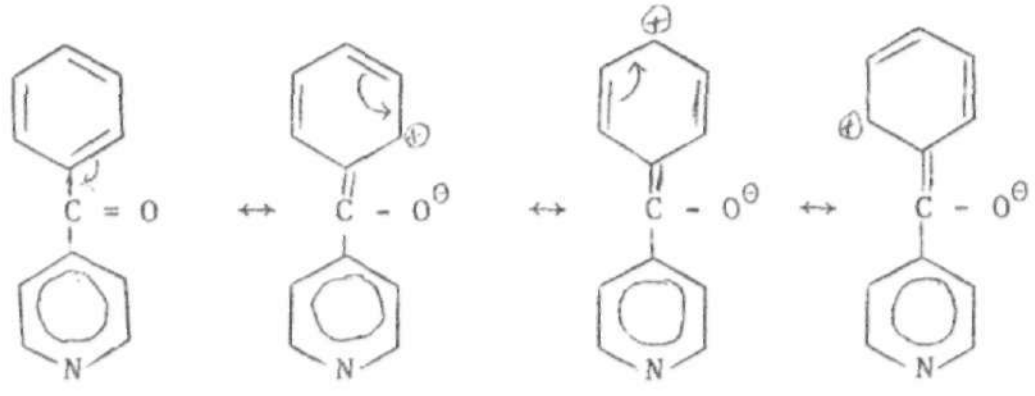
The JSn-C-H could thus be used in correlating the comparative strengths, i.e. the relative pK_b's of Lewis bases, especially the strengths of a Lewis base and its substituted derivatives, where titrimetric methods are difficult.

This method appears advantageous over titrimetric methods for determining the relative strength of bases, for the problem of having to solubilize the bases in necessarily

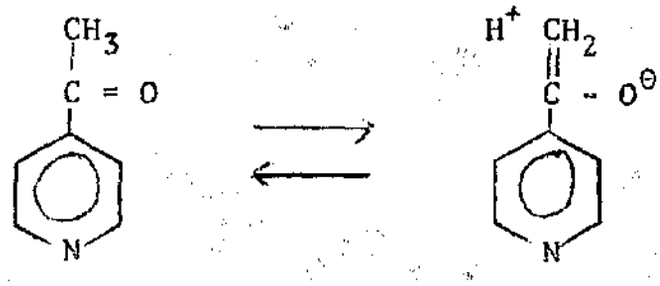
polar media for a good titration does not arise. For example, the bulky benzoyl substituent of 4-benzoylpyridine probably was responsible for the difficulty in solubilizing the base, which eventually made the determination of the pK_b of the base difficult, and the resulting pK_b value unreliable. But by simple logic, it could be predicted that 4-benzoylpyridine would be a stronger Lewis base than 4-acetylpyridine:



whereas



The methyl of 4-acetylpyridine has predominantly no more than an inductive effect on the molecule. Hyperconjugation involving its methyl could be possible:



but in our opinion, this involves the breakage of a σ - C - H bond and would therefore not be energetically as favoured as a mesomeric drift of electrons from the pyridyl ring. The phenyl of 4-benzoylpyridine on the other hand, takes care by mesomerism, of the mesomeric effect the $\rangle C = O$ would have had on the pyridine ring; the phenyl ring being preferred for the mesomerism since its Π-electrons are freer than those of the pyridyl ring that is already datively bonded in its complex and is therefore more 'electron deficient'. The net effect then would be that 4-benzoylpyridine emerges a stronger base than 4-acetylpyridine. The J Sn-C-H values have shown this to be at least tentatively true (see table 8).

(d) The Increase in J Sn-C-H for Methyltin Chlorides with Complexation.

If it is true that the Fermi contact term is a major contributor to the J Sn-C-H, implying that JSn-C-H increases with increasing % s-character of the bond - as postulated by Ramsey[42], Karplus and Anderson[43] - then J Sn-C-H should decrease in the following order, with decreasing % s-character of the hybrid bond:

$$sp > sp^2 > sp^3 > sp^3d > sp^3d^2$$

$$s\% = 50 \quad 33\tfrac{1}{3} \quad 25 \quad 20 \quad 16\tfrac{2}{3}$$

But it is commonly observed that J Sn-C-H for methyltin chlorides increases from trimethyltin chloride to methyltin trichloride, in a given solvent. The most reasonable explanation for this is the ionization or partial ionization in the solvent, of the methyltin chlorides, the completeness of which would decrease from $Me_3SnCl \rightarrow MeSnCl_3$ with increasing nuclear charge from $Me_3Sn^+ \rightarrow MeSn^{3+}$. The effect of this would be a tendency of sp^3 character in Me_3SnCl towards sp^2 in Me_3Sn^+, sp^3 in Me_2SnCl_2 towards 'sp' in Me_2Sn^{2+}. and sp^3 in $MeSnCl_3$ towards 'sp' in

$$Me_3SnCl \rightleftharpoons Me_3Sn^+ + Cl^- \quad \text{.....xxxvii}$$

$$Me_2SnCl_2 \rightleftharpoons Me_2Sn^{2+} + 2Cl^- \quad \text{.....xxxviii}$$

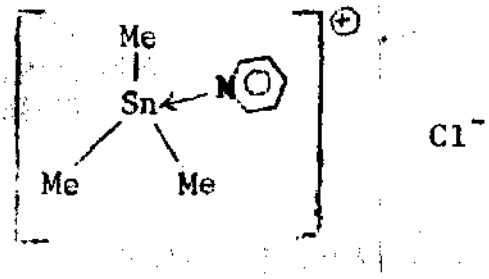
$$MeSnCl_3 \rightleftharpoons MeSn^{3+} + 3Cl^- \quad \text{.....xxxix}$$

This would imply an increase of the s-character as the methyltin halides are dissolved in the solvents. The s-character would increase with increase in completeness of the ionization, which in turn would increase with increasing dielectric constant of the solvent. This then would explain the observed increase of J Sn-C-H for Me_3SnCl across Me_2SnCl_2 to $MeSnCl_3$, and its increase also with increase in the polarity of the solvent, as commonly observed.

It is observed that J Sn-C-H increases for a methyltin chloride as it complexes with a Lewis base. Beattie et al[9,10] have derived from their i.r. studies that the hybridization of Sn in organotin halides changes from sp^3 to sp^3d or sp^3d^2 as the complex forms. But following the line of thought of Anderson et al[42,43,44], JSn-C-H should decrease as the methyltin halide complexes, and not increase as observed. In explaining the increase, Petrosyan et al[18], supporting their arguments with Bent's secondary rehybridization theory proposed that there is no rehybridization as the methyltin halide complexes. The Lewis acid - Lewis base interaction, they proposed, is a p - d donor acceptor interaction, which merely increases the electron density on the Sn and leads to the

increase in J Sn-C-H. This proposal might be acceptable for some ligands, but not for pyridine that has its only N unhybridized p - orbital participating in the formation of the aromatic system of the ring. The lone pair of electrons that are donated in coordination occupy an sp^2 hybrid orbital. The p-d donor-acceptor model of Petrosyan et al cannot therefore hold.

Van den Berghe et al[46] have proposed the existence, in aqueous or other polar media, of $Me_3SnCl.Py$ as

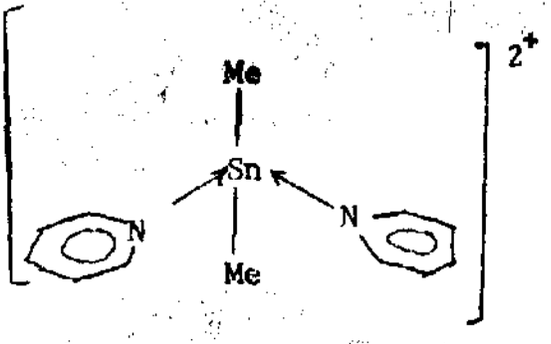


LXVII

supporting their proposal with Kraus and Greer's observation that the electrical conductivity of trimethyltin halide solutions in ionizine solvents increased on the addition of pyridine[47].

This would mean that coordination would enhance the ionization of the complex. And usually, pyridine adducts of methyltin halides are soluble most often only in reasonably polar media, supporting the possible idea of ionization of the complex. If the methyltin halide

halogens and Sn ionize then and the Lewis base molecules take the place of the halogens on the Sn, it would only imply that the hybridization of the Sn of the complex in solution very likely does not change much from that of the parent organotin halide in the solution; the Lewis base molecules most likely only enter the inner coordination sphere of the Sn, leaving the electron withdrawing halogens in the outer sphere.



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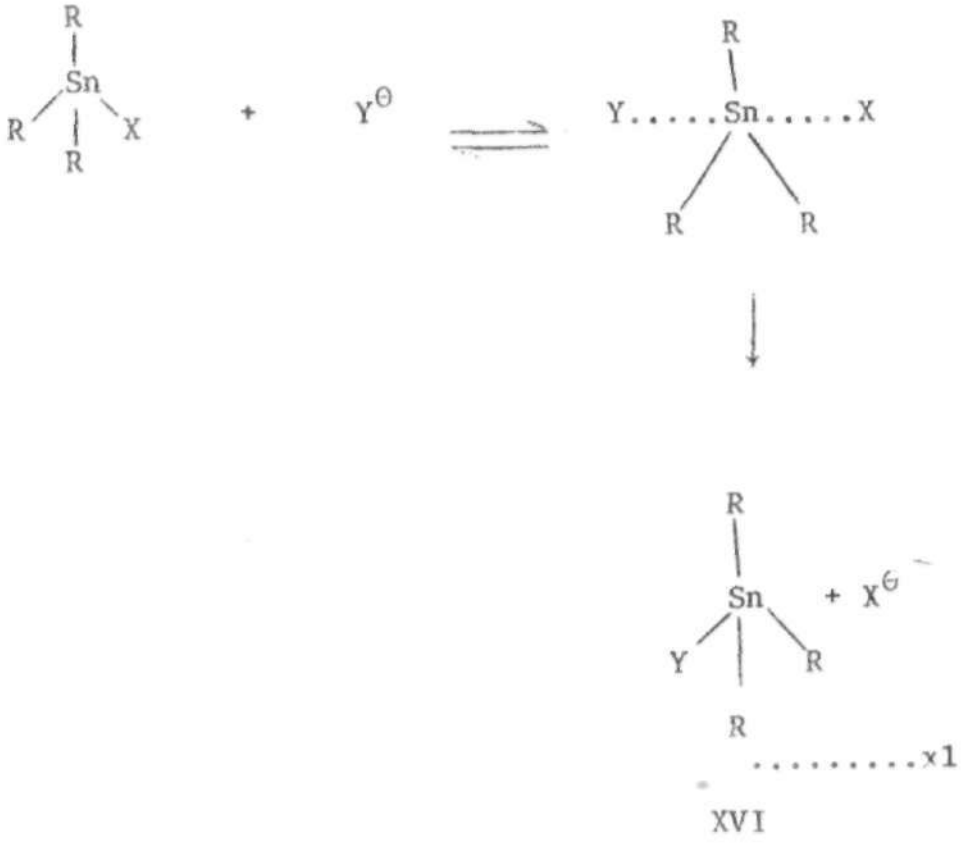
But the positive charge induced on the N of the Lewis base as a result of dative bonding would repel the positive Sn centre, making the Sn - Lewis base bond elongated and the hybridization state perhaps even a little different from complete sp^3; it would tend towards a state of sp^2 or sp^1 - a hybrid state with increased s-character in short. Also, the Lewis base, though it develops a positive charge on coordination, is electron donating,

implying a net increase in the electron density around Sn ef the complex in solution compared with that around the Sn of the Lewis acid in solution. All these effects, in our view, collectively account for the increase in the J Sn-C-H values of the methyltin halides on complexation with the pyridines, as opposed to the p-d donor - acceptor idea of Petrosyan et al[18].

SECTION C

(a) Reactions of the pyridine adducts of methyl and phenyltin chlorides.

Anderson's studies of the nucleophilic substitution reactions of organotin halides and pseudohalides[20], and Eaborn's on organosilicon halides and pseudohalides[21] suggest that nucleophilic substitution reactions of organotin halides occur in an SN2 fashion.



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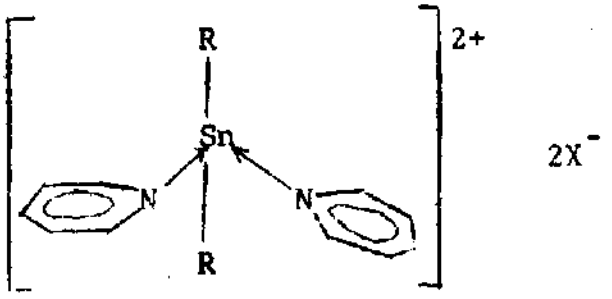
The suggestion appears to be supported by the fact that most of the reactions were carried out in non-polar media. If SN2 really is the mechanism of the substitution reactions of the organotin halides, then it would be difficult, if not impossible, for organotin halide adducts to undergo nucleophilic substitution reactions, for the intermediate in the above equation has a pentacoordinated Sn, and Sn in the adducts is already either penta or haxa-coordinated on the basis of steric crowding therefore, the organotin halide adducts might not be able to undergo substitution reactions.

However, Anderson and Eaborn[20,21] observed that silver salts were outstandingly effective as reagents for substitution reactions of organotin and organosilicon halides and pseudohalides. Also, they drew up their "conversion series" on the basis that the preferential substitution of a nucleophile on an organotin was determined by the relative affinity of Sn for the nucleophile. They also proposed that silver served the role of pulling the halogens and pseudohalogens off the Sn, to form more stable silver halides and pseudohalides.

Now, if ionic or at least partially ionic silver is to be able to pull the halogens and pseudolahalogens off the Sn, then the halogen and pseudohalogen substituents must possess

some ionic character since the polarizability and polarizing power of chlorine especially and silver respectively, are not extremely high. The polarization of the Sn-halogen bond is quite feasible, since halogens are more electronegative than tin.

It had been suggested earlier in this work that adducts, especially pyridine adducts of methyltin halides, when they solubilize (and they do only in fairly polar media), most probably exist in forms having the Lewis bases in the inner coordination sphere, and the halogens in the outer coordination sphere. viz



This proposal implies that it would not be very difficult to remove the halogen substituents with some suitable halogen abstractor like a silver salt, once the adduct dissolves in the medium. On this basis, some substitution reactions of the many such reactions have been found to occur.

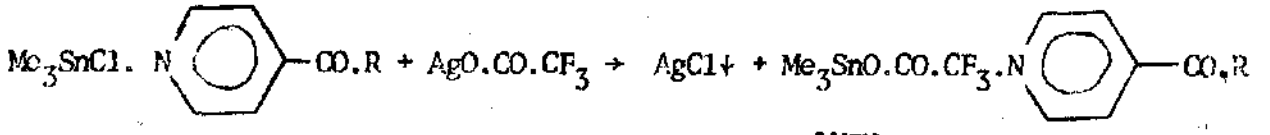
(b) Reactions with Silver trifluoroacetate.

Silver trifluoroacetate, because of its solubility in many organic solvents, was found to be easier to work with than the other silver salts, as stoichiometric amounts of the reagents could then be measured and dissolved in the solvent of choice. Dried acetone was chosen as the reaction medium.

i. 4-Acetylpyridine and 4-Benzoylpyridine adducts of the methyltin chlorides.

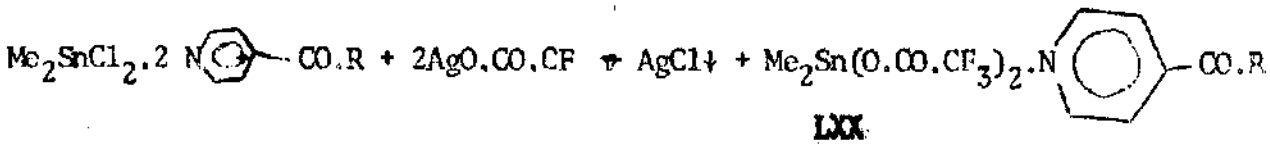
Hot solutions of the adducts and silver trifluoroacetate were made and then mixed. In all cases, a white precipitate of silver chloride was formed; the precipitate was coagulated through boiling of the reaction mixture and then filtered off. Clear filtrates were obtained, indicating the solubility of the products in the medium. The solvent was removed by evaporation, but recrystallization of the crude product had to be done only in non-polar media as the products dissociated in even slightly polar media, giving the insoluble, polymeric methyltin trifluoroacetate, especially in the case of 4-acetylpyridine and 4-benzoylpyridine adducts of dimethyltin bistrifluoroacetate.

Elemental analysis, i.r. n.m.r., and mass spectroscopy have shown all the adducts obtained to be 1:1 :



LXIX

....1i



LXX

....xii

where R = Me,Ph

The products were obtained as light yellow crystalline needles.

The trimethyltin trifluoroacetate adducts were higher melting than their parent trimethyltin chloride adducts, whilst dimethyltin bistrifluoroacetate adducts were lower melting than their dimethyltin dichloride analogues. The easy dissociation of the dimethyltin bistrifluoroacetate adducts in polar solvents to give dimethyltin bistrifluoroacetate and the Lewis base suggests that the Lewis acid-Lewis base bond is weak.

The 4-acylpyridine adducts of methyltin trichloride reacted with silver trifluoroacetate to give, not the expected methyltin tricarboxylate adducts, but rather larger amounts of the trifluoroacetate salts of the pyridine Lewis bases. The reason for this is not exactly clear, but Ford et al[26] have observed that methyltin tricarboxylates hydrolyse easily:

$$R - Sn(O.CO.R^1)_3 + H_2O \rightarrow R \cdot Sn(O)\ O.CO.R$$

LXXI LXXII

$$+ 2R^1.CO.OH$$

...Xliii

In our reactions therefore, the methyltin tristrifluoroacetate produced from the reaction of the methyltin trichloride moiety of the adduct might have picked up even trace amounts of water in the highly deliquescent acetone solvent:

$$MeSnCl_3.2\ N\langle\bigcirc\rangle CO.R + 3AgO.CO.CF_3 \rightarrow 3AgCl\downarrow$$

XXXVI

$$/ \cdot MeSn(O.CO.CF_3)_3.2\ N\langle\bigcirc\rangle CO.R$$

....xliv

$$MeSn(O.CO.CF_3)_3 + H_2O \rightarrow Me - Sn(O).CO.CF_3 + 2CF_3CO.OH$$

...xlv

LXXV

$$CF_3.CO.OH + N\langle\bigcirc\rangle CO.R \longrightarrow R.CO\langle\bigcirc\rangle \overset{+}{N}H\ \bar{O}COCF_3$$

LXXXVI

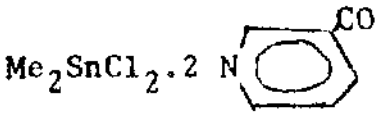
where R = CH_3, C_6H_5.

Most R.Sn(O) O.CO.R[1] compounds are known[26] to be high melting powders that dissolve only in very few organic solvents. It is likely therefore that the MeSn(O) O.CO.CF_3 precipitated with the silver chloride.

The insoluble nature of the reaction product of $MeSnCl_3$ with AgO.CO.CF_3 was confirmed when the reaction was carried out in acetone. The product remained suspended in the mixture. A trial of the reaction of the adducts in non-polar media did not succeed as the reactants were grossly insoluble in the media.

ii. 3.Acetylpyridine and 3-benzoylpyridine adducts of the methyltin chlorides.

The dimethyltin dichloride adducts reacted, in dried acetone, with AgO.CO.CF_3 to give dimethyltin bistrifluoroacetate and not the pyridine adduct. The reason for this might be steric interference of the mota-substituent of the pyridine Lewis base, since even when its substituent is on the para-position of the pyridine ring from where there can't have be much steric interference with the Lewis acid substituents, the Lewis acid-Lewis base bond is not very strong.



XXXIII

$$Me_2SnCl_2.2\ N\text{(3-CO.R)} + 2AgO.CO.CF_3 \longrightarrow Me_2Sn(O.CO.CF_3)_2 + 2\ N\text{(3-CO.R)} + 2AgCl\downarrow \quad \ldots xlvii$$

where R = Me,Ph.

The 3-ketosubstituted pyridine adducts of methyltintrichloride, like the analogous 4-ketosubstituted pyridine adducts, gave trifluoroacetate salts of the pyridine Lewis base on reaction with silver trifluoroacetate instead of any pyridine adduct of methyltin tricarboxylate. The reasons might be similar to those given for the mode of reaction of $AgO.CO.CF_3$ with $MeSnCl_3.2$  above.

iii. 3- and 4-keto-substituted pyridine adducts of the phenyltin chlorides.

No isolable pyridine or substituted pyridine adduct of triphenyltin chloride could be prepared.

The diphenyltin dichloride and phenyltin trichloride adducts reacted with silver trifluoroacetate to give, apart from silver chloride, the trifluoroacetate salt of the Lewis base as the only isolable product. But the analogous dimethyltin dichloride adducts of the 4-ketosubstituted pyridines reacted, as reported earlier in this work, to give isolable adducts. The outcome of the reaction of the diphenyltin dichloride adducts with silver trifluoroacetate therefore led to the probing of how diphenyltin dichloride reacts with silver trifluoroacetate, especially since there is no known literature report on it. The results are discussed below.

iv. The Pyridine adducts of methyltin and phenyltin chlorides.

Trimethyltin chloride - pyridine adduct reacted with silver trifluoroacetate to give silver chloride and a thick, unstable oil, which solidified only below $0^{\circ}C$, and which could not be distilled as its pyridine kept coming off.

Dimethyltin dichloride bis-pyridine also reacted with silver trifluoroacetate to give AgCl and an unstable low melting ($42^{\circ}C$) solid. Its pyridine kept coming off, leaving behind a white, high-melting solid that proved to be dimethyltin bistrifluoroacetate.

The reaction of $Me_3SnCl.Py$ and $Me_2SnCl_2.2Py$ with $AgO.CO.CF_3$ most probably gave the expected adducts, but the pyridine Lewis base ligands are so labile that the products are unstable at room temperature.

$$Me_2SnCl_2.2Py + 2AgO.CO.CF_3 \rightarrow \underset{\text{LXXVIII}}{Me_2Sn(O.CO.CF_3)_2.2Py} + 2AgCl\downarrow \quad ...xlviii$$

$$xMe_2Sn(O.CO.CF_3)_2.2Py \rightarrow \underset{\text{LXXVII (polymer)}}{\{Me_2Sn(O.CO.CF_3)\}_x} + 2xPy \quad .....xlix$$

Diphenyltin dichloride.bis-pyridine and phenyltin trichloride bis-pyridine both reacted with silver trifluoroacetate in acetone, but sense on the nature of the products could not be made from the analyses of the products, especially after purification in hydrocarbons. Of the products, only pyridinium trifluoroacetate could be identified. It was eventually found (see section D) that diphenyltin dichloride reacts with silver trifluoroacetate to give a ditin compound, the molecule of which coordinates internally and so would not take on a Lewis base.

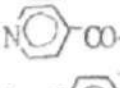
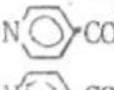
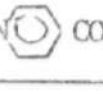
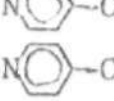
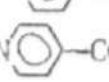
c. Spectral Properties of the Methyltin Carboxylate Adduct.

i. N.m.r.

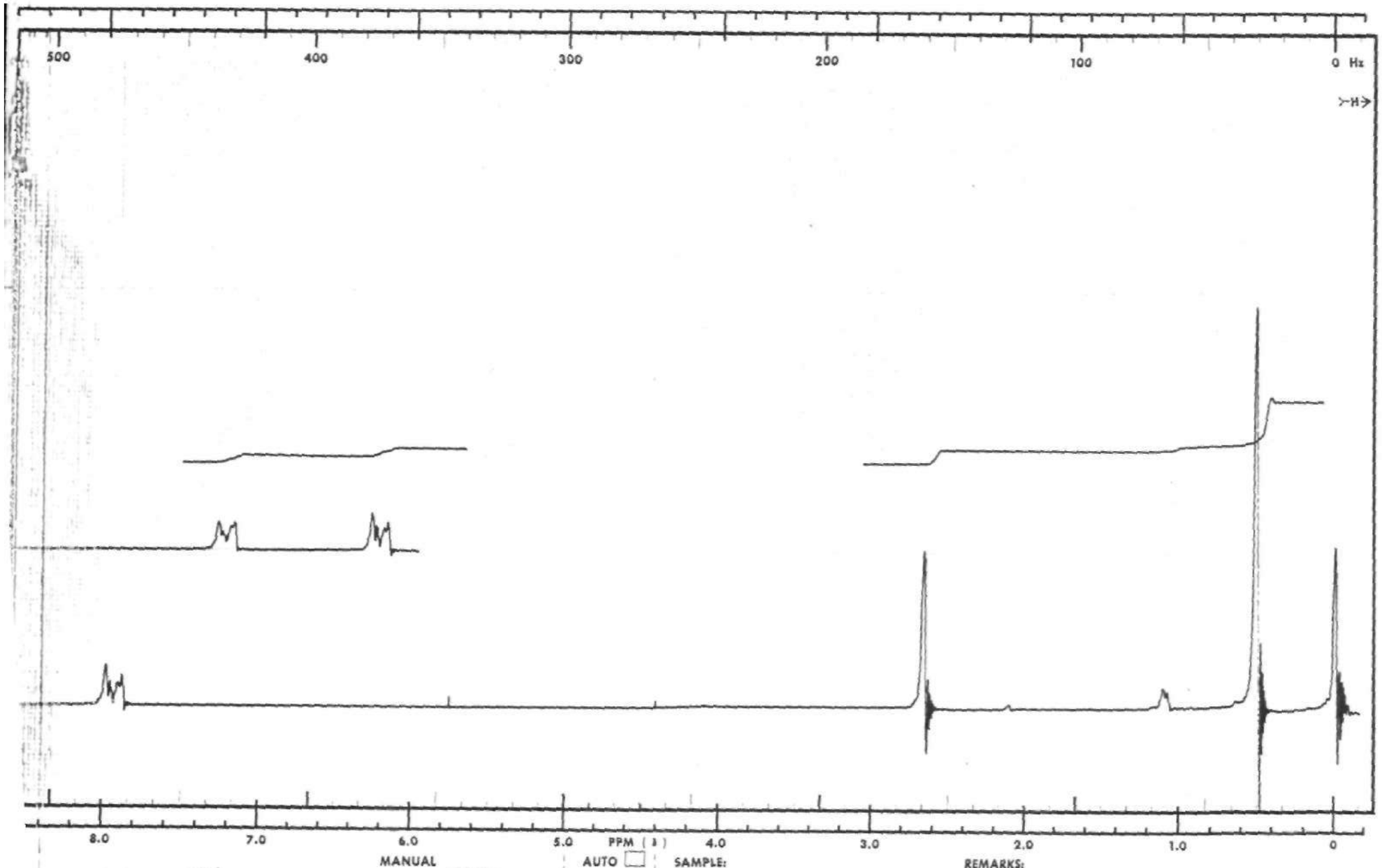
The methyltin carboxylate adducts, unlike their methyltin chloride analogues, dissolve readily in acetone. But to facilitate comparison, deuterodimethyl sulphoxide was chosen as the solvent. The proton magnetic resonance spectral data for the 4-acetylpyridine and 4-benzoylpyridine adducts of trimethyltin and dimethyltin trifluoroacetates as well as their methyltin chloride analogues are tabulated below.

Table 9

P.m.r. chemical shifts of the methyltin carboxylate and chloride pyridine adducts

Compound	δppm (d-DMSO)				
	Sn-CH_3	-CO.CH_3	Pyridyl-m-H	Pyridyl-o-H	-CO-
$(CH_3)_3SnO.CO.CF_3.N$ $CO.CH_3$	0.50	2.65	7.90	8.95	-
$(CH_3)_3SnO.CO.CF_3.N$	0.50	-	-	8.96	7.80
$(CH_3)_2Sn(O.CO.CF_3)_2.N$ CO^{CH_3}	0.92	2.65	7.85	8.86	-
$(CH_3)_2Sn(O.CO.CF_3)_2.N$	0.92	-	-	8.96	7.80
$(CH_3)_3SnCl.N$ $-CO.CH_3$	0.60	2.70	7.98	8.98	-
$(CH_3)_3SnCl.N$	0.60	-	-	9.00	7.80
$(CH_3)_2SnCl_2.2\ N$ $CO.CH_3$	1.14	2.70	7.98	8.98	-
$(CH_3)_2SnCl_2.2N$	1.15	-	-	9.00	7.80

MADE IN U.S.A.



EP OFFSET (Hz): 102
CTRUM AMPLITUDE: 2.5
EGRAL AMPLITUDE: 5
NING RATE (RPS): 42

MANUAL
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 6

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:

REMARKS:

Me3Si-O-CO-CF3 · NO - 20 mg

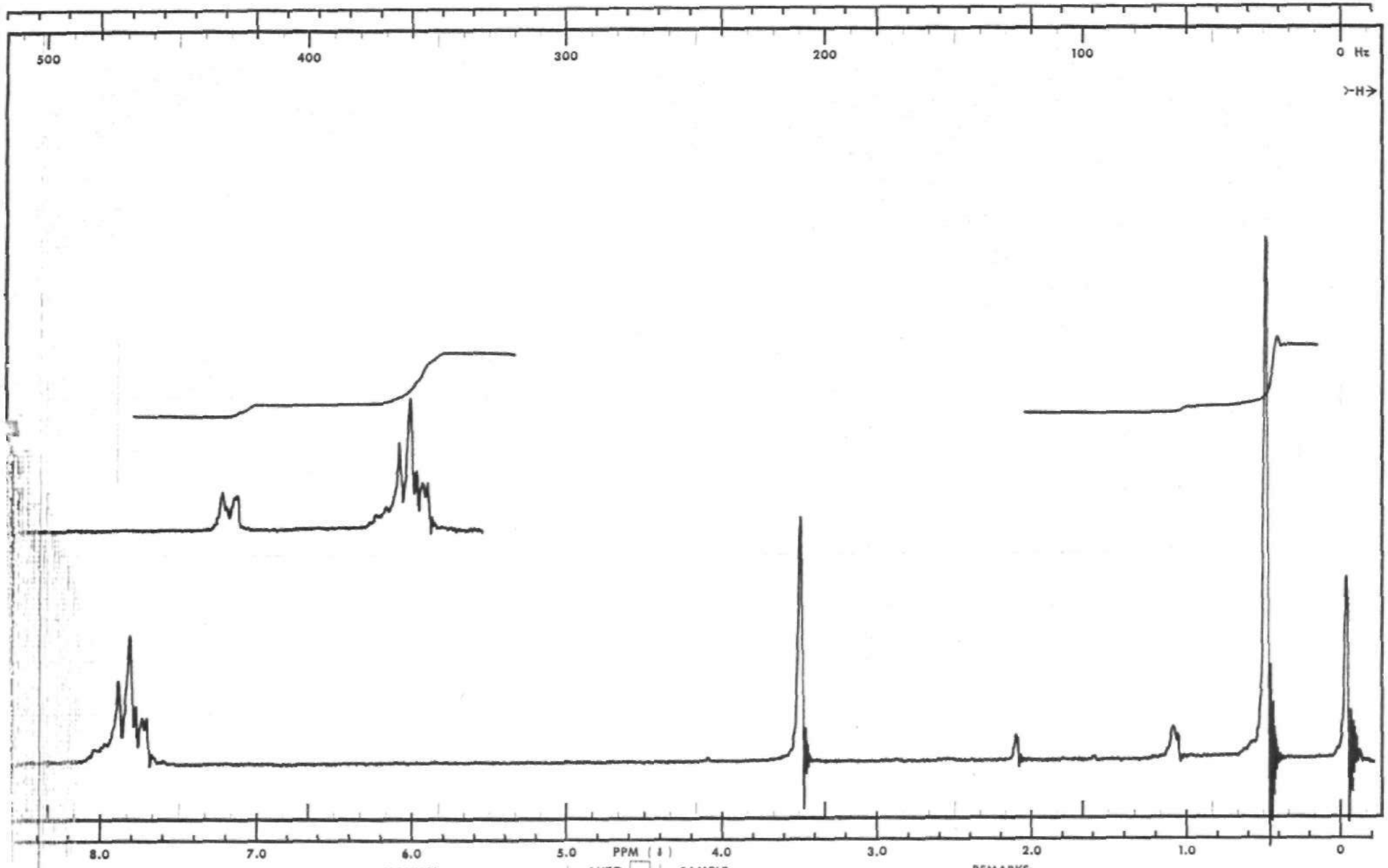
SOLVENT: d-DMSO

varian
analytical instrument division

DATE: 7/6/81

OPERATOR: Bonne

60 MHz NMR
SPECTRUM NO.



MANUAL | AUTO ☐

SWEEP OFFSET (Hz): 100	SWEEP TIME (SEC): 50 250		(250)
SPECTRUM AMPLITUDE: 6.3	SWEEP WIDTH (Hz): 25 50 100 250 500		(500)
INTEGRAL AMPLITUDE: 5.0	FILTER: 1 2 3 4 5 6 7 8		(2)
SPINNING RATE (RPS): 40	RF POWER LEVEL: 0.1		(.05)

SAMPLE:

REMARKS:

$Me_3SnC(O)CF_3 \cdot N(O)-CO-(O)$

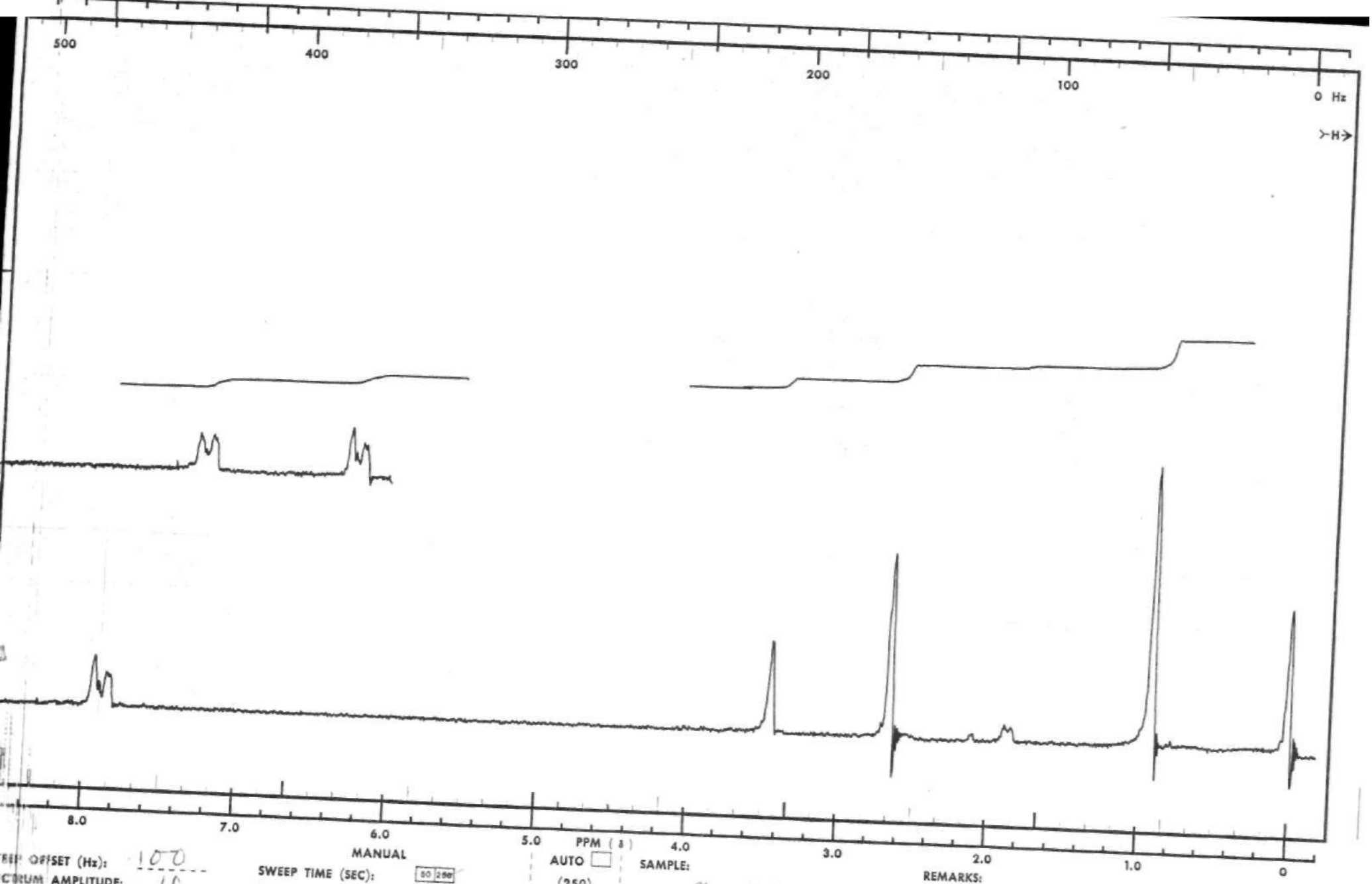
SOLVENT: d-DMSO

varian
analytical instrument division

DATE:

OPERATOR: Bernice

60 MHz NMR
SPECTRUM NO.



REF OFFSET (Hz): 100
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: 3
SPINNING RATE (RPS): 40

MANUAL
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 0.1

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:

REMARKS: MeNSO(CF3)2 · NO2 40 mg

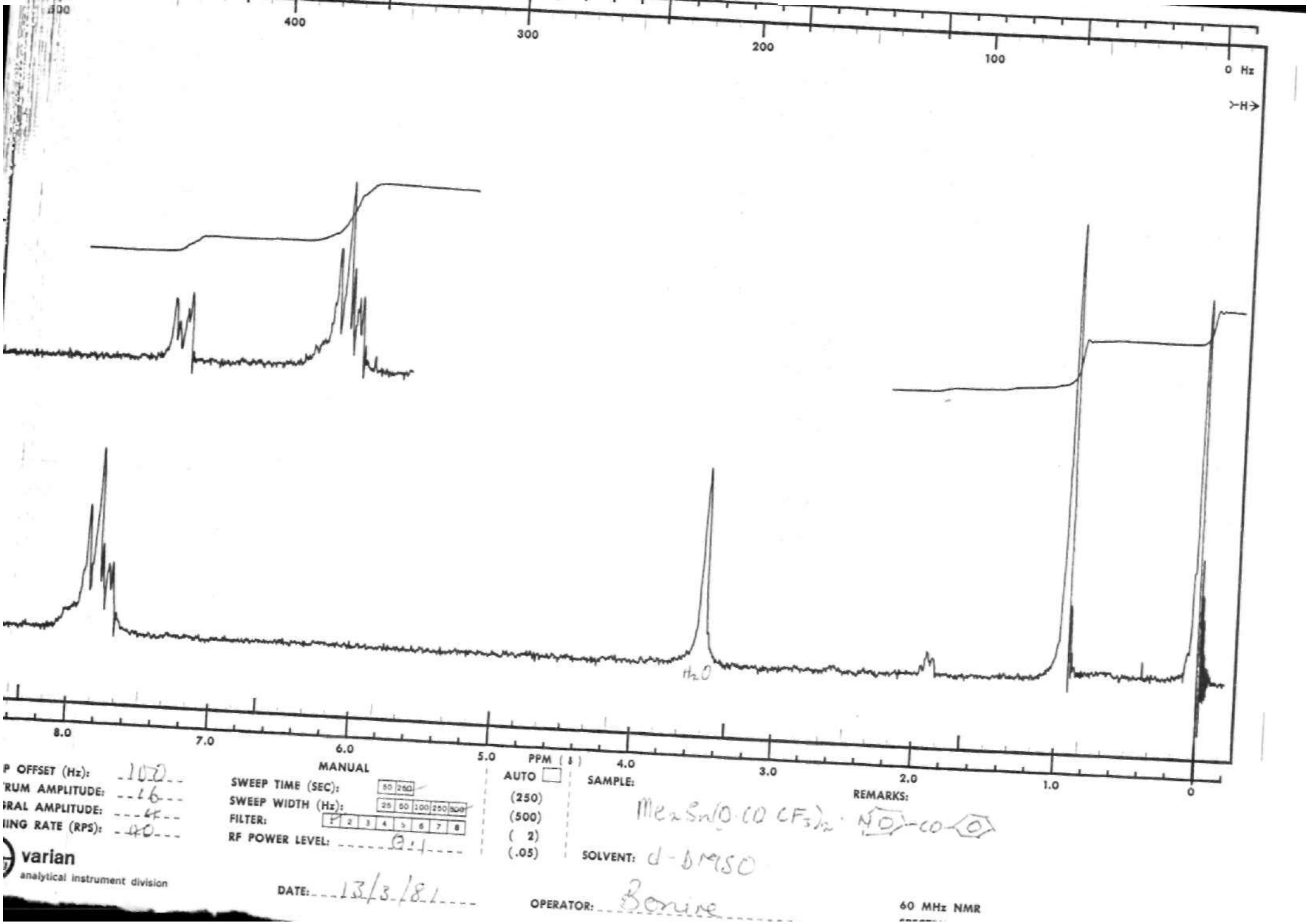
SOLVENT: d-DMSO

varian
analytical instrument division

DATE: 9/6/21

OPERATOR: Berline

60 MHz NMR
SPECTRUM NO.



P OFFSET (Hz): 100
RUM AMPLITUDE: 16
RAL AMPLITUDE: 4
ING RATE (RPS): 40

varian
analytical instrument division

MANUAL
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 0.1

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:

$Me_2Sn(O(CO)CF_3)_2 \cdot$

SOLVENT: d-DMSO

REMARKS:

DATE: 13/3/81

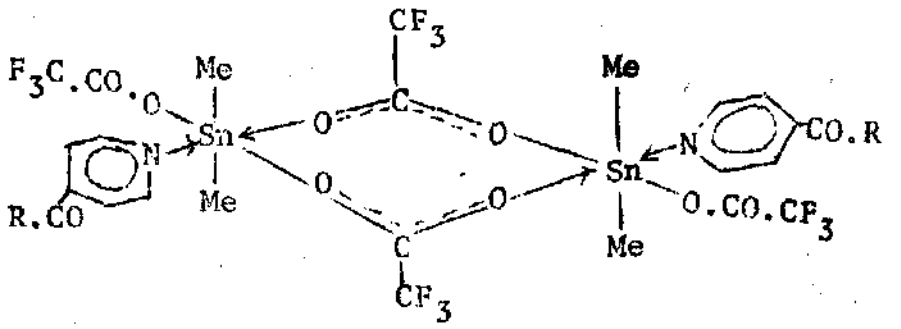
OPERATOR: Bonine

60 MHz NMR

From the table, it could be seen that the $Sn-CH_3$ δ values for the methyltin carboxylate adducts are generally lower than the δ values for the corresponding methyltin chloride adducts, the shifts appearing higher than for the trimethyltin species. This implies that the $Sn-CH_3$ protons in the methyltin carboxylate adducts are better shielded than the $Sn-CH_3$ protons of the methyltinchloride adducts. In our view, there are two main reasons for this:

i. The electron withdrawing ability of the trifluoroacetate group might be less than that of chlorine. This would leave the electron density on Sn in the methyltin carboxylate adducts higher than in the Sn of the methyltin chloride adducts, implying that the $Sn-CH_3$ in the former would be less deshielded due to inductive effect than in the latter.

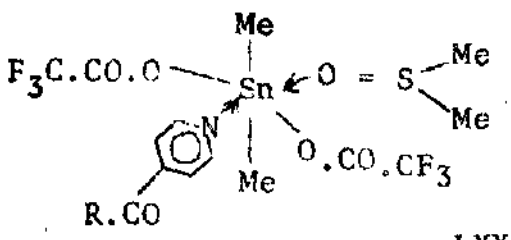
ii. It is thought (see below) that dimethyltin bistrifluoroacetate adducts exist in the solid as dimers, the carboxyl group being the bridge between the two moieties of the dimer.



LXXXIX

where R = Me, Ph

In dimethyl sulphoxide solution, the solvent molecules would complete with the O → as well as the N→ coordinate bonds and it is likely that the DMSO solvent molecules are better donors than the C - O→ moiety of the CF_3.COO group. The effect would be the breaking of the Sn←O-C coordinate bond to form an Sn ← O=S ; The effect therefore breaks the dimeric nature of the methyltin carboxylate adduct in DMSO solution, and a new type of adduct if formed:

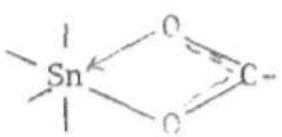


LXXX

DMSO most probably would be a better donor than the C...O moiety of CF_3.COO group, meaning an increase of the electron density around Sn and therefore a reduced electron withdrawal

by inductive mechanism, from the Sn-CH_3 hydrogen atoms. The Sn-CH_3 are thereby more shielded in the methyltin carboxylate adduct than in the methyltin chloride adduct.

The Sn - O.CO.CF_3 bond in the methyltin carboxylate adducts might not ionize as easily as the analogous Sn-Cl moiety in the methyltin chloride adducts, possibly because of a lower electron withdrawing power of the CF_3.COO group compared with Cl, due to possible synergic bonding of the CF_3.CO.O ($p\pi$ - $d\pi$) oxygen to the Sn



This possible synergic effect would keep the Sn-O.CO.CF_3 bond stable, as well as keep the electron density around Sn high. Also, after solvation by solvent molecules, the electron withdrawing effect of the CF_3 moiety in the CF_3.COO group would be reduced, implying an overall reduction of the electron withdrawing power of the CF_3COO group from the Sn. The synergic effect, coupled with the solvation effect, would explain why the Sn-Me protons in the trimethyltin carboxylate adducts are more shielded than they are in the trimethyltin chloride adducts.

These postulations seem to be supported by the fact that the $Sn-CH_3$ proton signals of the methyltin carboxylate adducts in acetone, a poorer donor solvent than DMSO, have higher δ values than they have in DMSO, although the values are not as high as those for the analogous methyltin chloride adducts.

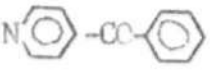
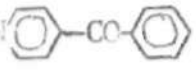
The ligand protons have lower δ - values in the methyltin carboxylate adducts than in the analogous methyltin chloride adducts, suggesting that the Lewis base ligands are more loosely bound to the Lewis acid in the former than in the latter.

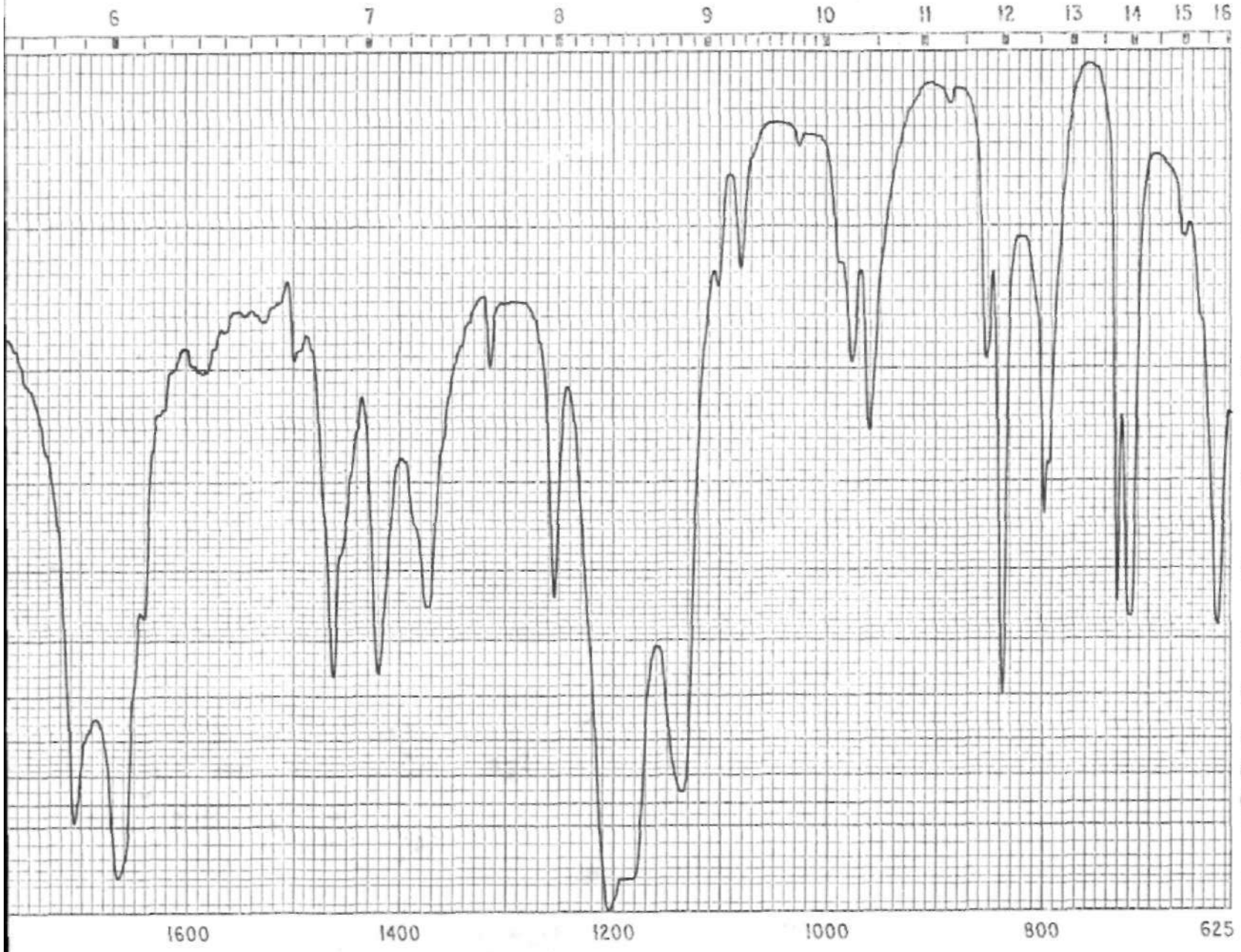
d. Infra Red.

Adducts of the methyltin carboxylates are a relatively new class of organotin compounds. Graddon et al[51] recently reported a thermodynamic study of the reaction of some organotin carboxylates with some Lewis bases via titrations, but no attempt was made to isolate and study the products they suspected were formed in solution. Mossbauer spectroscopy could provide more concrete evidence on the nature of the Sn-O bonds in the methyltin trifluoroacetate adducts prepared in this work. However, non-availability of the required instrumentation has not allowed that option at this time. The data available from the i.r. spectra is tabulated (10) below

Table 10

I.r. absorption frequencies of the methyltin carboxylate Pyridine adducts.

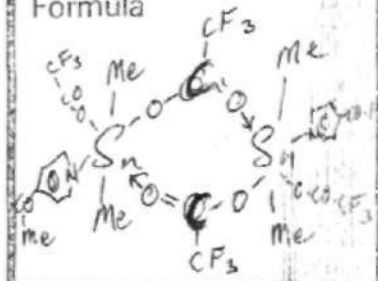
Compound	Stretching vibration frequencies, cm^{-1}						
	C-H arom.	C=O OCO	C=C arom	C-O	C-F	Sn.Me Rock	Sn ← O
$Me_3SnO.CO.CF_3.N$	3050w	1650-1710	1600w	1410m	1200s	795s	300m
$Me_3SnO.CO.CF_3.N$	3030w	1650-1710s	1600m	1410m	1200s	790s	305m
$Me_2Sn(O.CO.CF_3)_2.N$	3100w	1620-1720s	1585m	1410m	1200s	795m	300m
$Me_2Sn(O.CO.CF_3)_2.N$	3100w	1620-1720s	1600m	1410m	1200s	795m	300m



Sample

Dimethyltinbis[trifluoro-acetate - 4-acetylpyri...

Formula



Phase

Nujol

Thickness

Reference

Operator

Bonire

Date 19/5/77

Spectrophotometer

PYE UNICAM LTD CAMBRIDGE ENGLAND

PERKIN-ELMER

ORIGIN

PURITY

PHASE

CONCENTRATION KBr

THICKNESS

SCAN SPEED Slow

SLIT

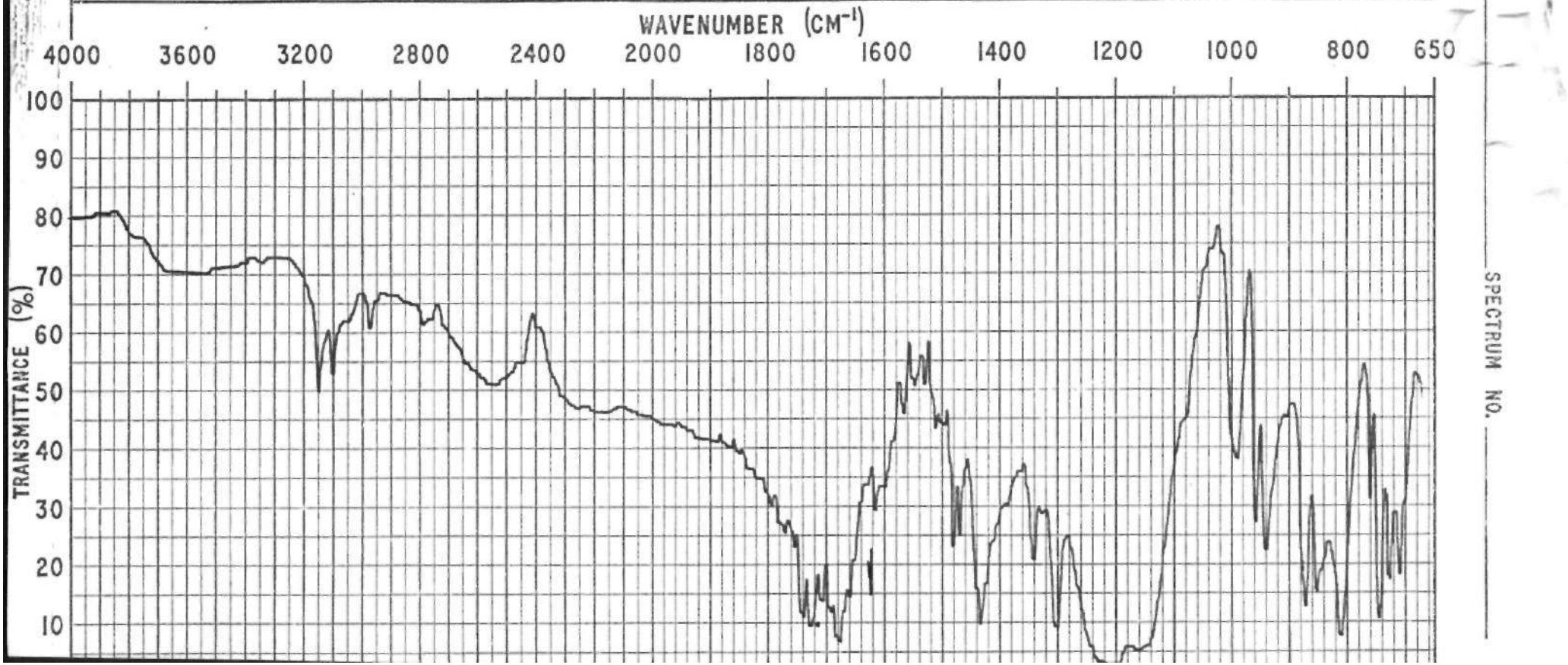
SPECTRUM NO.

SAMPLE I

[Me$_2$Sn(O$_2$C·CF$_3$)$_2$·MeC$_6$H$_4$CO$_2$H]$_2$

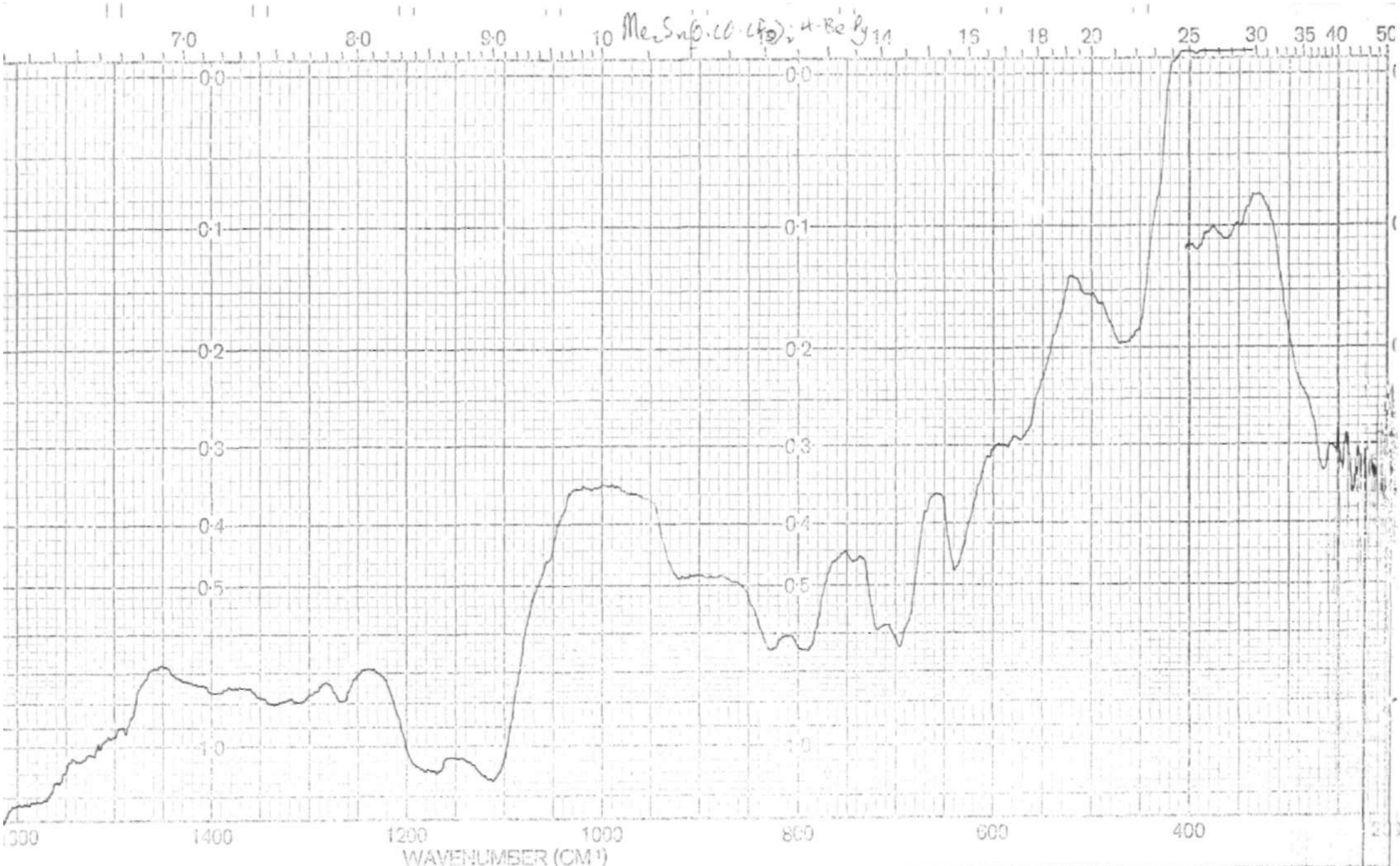
DATE 24/1/81

OPERATOR Bonnie



SAMPLE

SPECTRUM NO.



REMARKS Sample $Me_2Sn(O{\cdot}CO{\cdot}CF_3)_2$  Phase: C_8 ?	SCAN MODE 15 min SLIT N TIME CONSTANT fast PERKIN ELMER PART No. 5100 4366	OPERATOR Bonnie DATE 10/2/01 REF No.

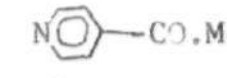
e. Mass Spectra

The mass spectra of trimethyltin trifluoroacetate 4-acetylpyridine and dimethyltin bistrifluoroacetate 4-acetylpyridine were run. Some of the mass units obtained in the spectra as well as their assignments are reported below.

Table 11

Mass spectra of $Me_3SnO.CO.CF_3.L$ and $Me_2Sn(O.CO.CF_3)_2.L$

Compound: $Me_3SnO.CO.CF_3.L$		$Me_2Sn(O.CO.CF_3)_2.L$	
Mass Unit	Fragment	Mass Unit	Fragment
120	Sn^+	120	Sn^+
121	$(C_7H_7NO)^+$	121	$(C_7H_7NO)^+$
150	$(Me_2Sn)^+$	135	$(MeSn)^+$
165	$(Me_3Sn)^+$	361	$\{Me_2Sn(O.CO.CF_3)_2\}^+$
263	$(Me_2SnO_2C.CF_3)^+$	497	$\{Me_2Sn(O.CO.CF_3)_2.L\}^+$
278	$(Me_3SnO.CO.CF_3)^+$	873	$\{(Me_2Sn(O.CO.CF_3)_2.L\}^+$

where L =  (C_7H_7NO)

The highest mass unit obtained in the spectrum of trimethyltin trifluoroacetate 4-acetylpyridine is 278, which is assigned to $(Me_3SnO.CO.CF_3)^+$. But present in the spectrum was also a 121 mass unit, which is assignable to 4-acetylpyridine molecular ion.

The highest mass unit obtained in the spectrum of dimethyltin bistrifluoroacetate 4-acetylpyridine is 873, which is assignable to $\{(Me_2Sn(O.CO.CF_3)_2\}_2.N\langle\bigcirc\rangle-CO.Me)^+$, strongly suggesting that the adduct exists as a dimer.

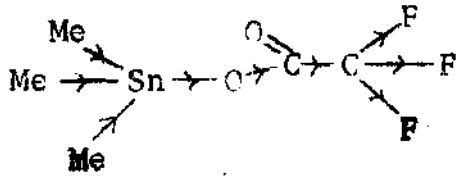
Structural Deductions from the Spectra.

Of particular interest would be the OCO and C = O bands in the i.r. spectra of the methyltin carboxylate adducts. It has been observed[8] that most methyltin carboxylates are polymeric, with bridging OCO; and such OCO bands in i.r. have been observed to be broad. In the i.r. spectrum of $Ph_3SnO.CO.CF_3$, Ford et al[26] have assigned the broad band around 1650cm^{-1} to the symmetric stretch of OCO.

The i.r. spectrum of $Me_3SnO.CO.CF_3.N\langle\bigcirc\rangle-CO.R$, where R = Me or Ph, would be expected to show bands for the C=O of the Lewis base ligand, and of the $CF_3.CO.O$. A broad band at 1650 - 1710 cm^{-1} has been obtained in the i.r. spectrum of the compound. Elemental analysis and n.m.r. have shown the compound to be a 1:1 adduct, and 4-acetylpyridine as well as 4-benzoylpyridine have been found, as earlier reported in this work, to bind only through the nitrogen, to organotin Lewis acids. The >C=O of the ligand would therefore be a sharp band at ~ 1700cm^{-1}; the >C=O stretch

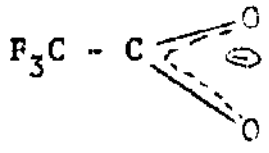
of the uncomplexed ligand absorbs at $1680cm^{-1}$.

Ester stretching vibrations absorb ~ $1735-1750cm^{-1}$, while carboxylate anions are commonly known to have broad bands at ~ $1610cm^{-1}$ and sharp ones at ~ $1400cm^{-1}$. In a $CF_3.COO$ case, the electron withdrawing effect of the CF_3 group would most probably make the Sn-O bond strongly polarized.



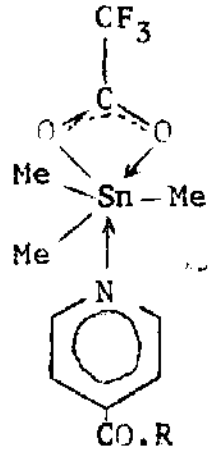
LXXXI

The -COO then, although basically an ester type, would have some anionic character, implying some character of



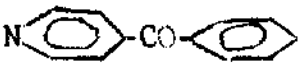
which would make the -COO i.r. band broad. Such a condition would make the -COO to be midway between a carboxylate anion and an ester type of -COO. The COO stretch would therefore be broad, be lower in frequency than the ester stretch at ~1730cm, but be higher than the free $-COO^-$ stretch et ~$1610cm^{-1}$. And indeed, the -COO stretch of the $Me_3SnO.CO.CF_3.N$$-CO.R$ (where R = Me or Ph) has been observed to come between 1650-$1710cm^{-1}$.

Sn in Me_3Sn compounds has most often been observed to be pentacoordinate[8], with planar methyls. Mass spectroscopy has not shown that $Me_3SnO.CO.CF_3.N$$-CO.Me$ exists in an associated form higher than the monomer. If the -COO really acts as a pseudobidentate ligand, then the structure of the adduct would most probably lie between a trigonal bipyramidal structure (confirmed by X-ray spectroscopy for $Me_3SnCl.Py$[8]) and some sort of distorted octahedron.

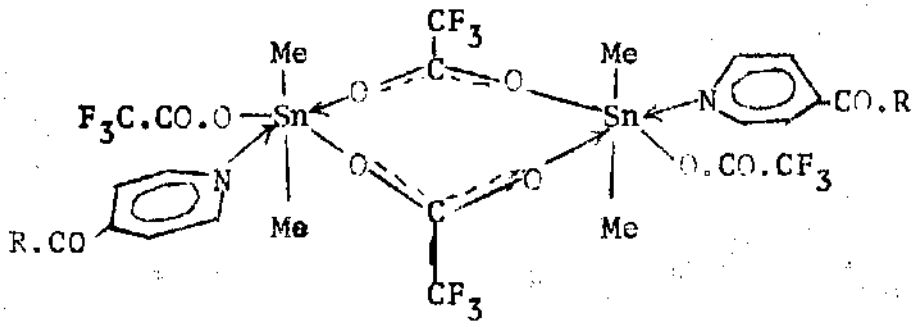


LXIX

where R = Me, or Ph.

The i.r. spectra of $Me_3SnO.CO.CF_3.N$$-CO.Me$ and $Me_3SnO.CO.CF_3.$$N$$-CO-$ are remarkably similar. Although the mass spectrum of the latter could not be obtained, the phenyl of the Lewis base is so positioned as to offer little or no steric interaction to render the proposed structure implausible on the basis of the available experimental and literature evidence.

The mass spectrum of $Me_2Sn(O.CO.CF_3)_2.N$$CO.Me$ has shown a mass unit assignable to $\{\{Me_2Sn(O.CO.CF_3)\}.\ N$$CO.Me\}$ strongly suggesting that the adduct exists in the solid state as dimer. The only feasible structure that can be written for the dimeric state is



LXXXIX

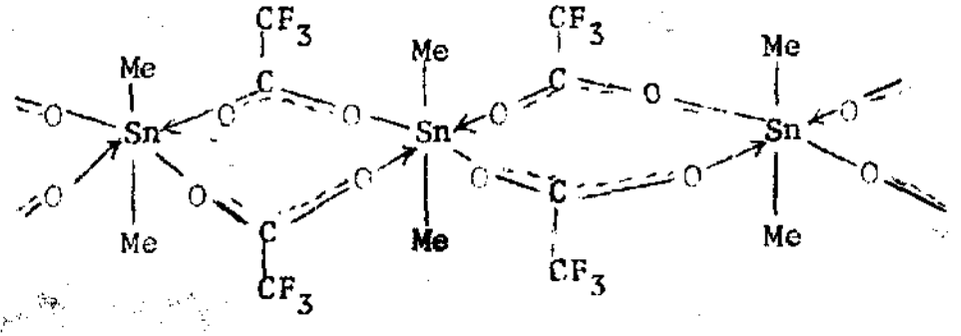
where R = Me (and feasible for Ph)

This structure ensures the hexacoordination common with diorganotin adducts. The bridging OCO and the free COO of the trifluoroacetate groups, and the >C=O of the ligand would combine to give a broad absorption band for the >C=O, which would lie between the ester stretching and the bridging and free carboxylate stretching frequencies for reasons given above. And indeed the carbonyls combine to give a broad absorption band between 1620 and 1720cm^{-1}. The methyls of Me_2Sn hexacoordinated compounds have been found to be axial[8].

Assuming that the same holds for the methyltin carboxylate adducts, then with the other information from elemental analysis and p.m.r. already discussed, the above structure is suggested for $Me_2Sn(O.CO.CF_3)_2.N$⬡—CO.R, where R = Me or Ph, for although the mass spectrum of $Me_2SnO.CO.CF_3)_2.N$⬡—CO⬡ could not be obtained, its i.r. spectrum is similar to that of the analogous 4-acetylpyridine adducts- and there is no compelling ground to suggest that the adducts would have different structures.

The suggested structures are, nonetheless, still merely tentative. The methyltin carboxylate adducts, to the best of our knowledge, are being reported for the first time. Only appropriate calculations and X-ray diffraction studies could confirm or show the actual structures of the adducts.

The instability of $Me_2Sn(O.CO.CF_3)_2.N$⬡—CO.R in polar solvents could be due to solvent clearage of the Sn ← N⬡—CO.R bond, thereby allowing for the formation of the more stable polymer[8], $\{Me_2Sn(O.CO.CF_3)_2\}_x$



LXXVII

Chemistry of Substitution Reactions.

It will appear that the main principle guiding substitution reactions of organotin compounds is the tendency of the tetravalent tin, basically of sp^3 hybridisation, to form covalent bonds. The closer the "effective electronegativity" of Sn moiety in its compound and that of the nucleophile, the more stable the bond between the two moieties is likely to be. Anderson[20] and Eaborn[21] observed that Si and Sn were more affinitive for some nucleophiles than for others; they proceeded to draw "conversion series". They gave logical reasons, but they seemed not to see that where there would be increase in the covalent nature of the Sn - element to be formed in a reaction, the reaction was feasible - if only there would be a way of stripping off the element or group already on Sn, to give room for the new one. This, in our view, is why $SnMe_4$ is extremely stable, while $SnCl_4$ is extremely unstable;

SECTION D

(a) Reaction of the Phenyltin chlorides with Silver Trifluoroacetate.

Anderson[20] and Eaborn[21] have carried out several studies of nucleophilic substitution reactions in organotin and organosilicon compounds, respectively. Poller[19] has stressed the ease with which the halogens of organotin halides can be replaced by a variety of nucleophiles in preparative work. Eaborn[21] has found silver salts exceptionally effective in his nucleophilic substitution reactions of the organosilicon compounds.

The ease of the use of organotin halides, especially the chlorides, in preparing other organotin compounds, as earlier suggested, is most likely due to the high electronegativity of the halogen compared with that of tin. This renders the Sn-X (X = halogen) bond polar, with the tin becoming partially positively charged while the halogen is negatively charged. The Sn centre thus becomes susceptible to nucleophilic attacks. And where the halogen could be easily removed by some metal ion, the nucleophilic substitution is fast indeed.

Silver trifluoroacetate, fortunately, is soluble in many organic solvents, making it possible to weigh and dissolve stoichiometric amounts of it and organotin chlorides in suitable organic media, for nucleophilic reactions. Mixing of the

solutions produces silver chloride, which is filtered off; and the organotin trifluoroacetate, which remains in solution.

$$R_ySnX_{(4-y)} + (4y)AgO.CO.CF_3 \rightarrow RySn(O.CO.CF_3)_{4-y} + (4y)AgCl\downarrow$$

LXXX1 LXXXII 1

i. Triphenyltin Chloride

Triphenyltin trifluoroacetate has reportedly[26] been prepared from the reaction between triphenyltin hyroxide and trifluoroacetic acid. However, this and another report[48] have pointed out that the phenyl-tin bond could be cleaved by carboxylic acids.

$$Ph_3SnOH + R.CO.OH \rightarrow Ph_3SnO.CO.R + H_2O$$

XX1 LXXX111 ..... 1i

$$Ph_3SnO.CO.R + 2R.CO.OH \rightarrow PhSn(O.CO.R)_3$$

LXXX1V

$$+ 2C_6H_6 \quad ....1ii$$

LXXXV

$$PhSn(O.CO.R)_3 + H_2O \rightarrow PhSn(O)O.CO.R$$

LXXXV1

$$+ 2RCO.OH \quad .....1iii$$

In this work, triphenyltin trifluoroacetate, has been prepared from triphenyltin chloride and silver trifluoroacetate in dried acetone - a method which, to the best of our knowledge, had not previously been used for that synthesis.

$$Ph_3SnCl + AgO.CO.CF_3 \rightarrow Ph_3SnO.CO.CF_3$$

LXXXV11 XX11

$$+ AgCl\downarrow \quad ....1iv$$

The method removes any loss of $Ph_3SnO.CO.CF_3$ through the above side reactions, and also enhances the purity of the product, as the silver chloride co-product is easily removed by filtration.

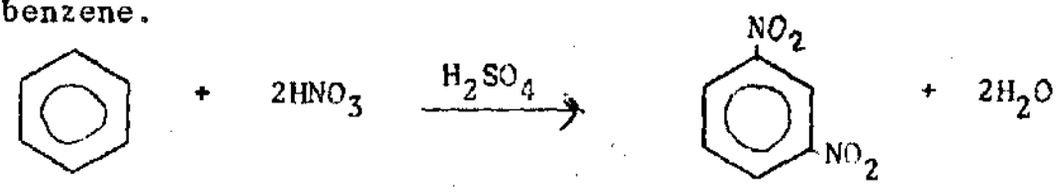
ii. Diphenyltin dichloride.

Having successfully prepared $Ph_3SnO.CO.CF_3$ in good yield (73%) from Ph_3SnCl and $AgO.CO.CF_3$, it was thought that an analogous reaction of Ph_2SnCl_2 with $AgO.CO.CF_3$ would yield $Ph_2Sn(O.CO.CF_3)_2$ as an isolable product, viz

$$\underset{\text{XVII}}{Ph_2SnCl_2} + 2AgO.CO.CF_3 \rightarrow \underset{\text{LXXXVIII}}{Ph_2Sn(O.CO.CF_3)_2} + 2AgCl\downarrow \quad \text{.....lv}$$

The reaction was carried out in dried acetone. The precipitated silver chloride was coagulated by boiling the mixture, and after filtration, the solvent was removed by evaporation. An oil was left. All efforts, including prolonged cooling and trituration with cold light petroleum, failed to make the oil solidify. By accident, a petrol mixture of the oil was boiled, and a white amorphous solid gradually separated out. A fresh sample of the oil was therefore extracted into a quantity of aromatic hydrocarbon-free 40-60 light petroleum, and the mixture was carefully warmed to boiling. The clear solution turned turbid, and eventually, a white powdery substance was precipitated as the heating continued. The precipitation continued over the 48 hour period of boiling. The powder was filtered off, and the filtrate distilled. N.m.r. and GLC showed that benzene had been

produced in the reaction. Further, treatment of the distillate with 1:1 mixture of concentrated sulphuric and nitric acids yielded a mass of yellow crystalline needles which spectroscopy and elemental analysis showed to be m-dinitrobenzene, confirming that the reaction of the oil in the light petroleum produced benzene.



LXXX1X ...1vi

Elemental analysis results of the white powder agree with the empirical formula $PhSn(O.CO.CF_3)_2$. The powder neither melted nor decomposed on heating to 360°C.

iii. Phenyltin trichloride.

Phenyltin trichloride reacted with silver trifluoroacetate in dried acetone to give a mixture containing silver chloride. Filtration of the mixture followed by evaporation of the filtrate yielded a thick, reddish brown oil, which, on standing, hardened and solidified to give a non-volatile solid that could not be purified, as it neither dissolved in any suitable organic solvent, nor did it sublime below 360°C thereby making sublimation techniques unapplicable. The thick oil however was, to a good degree, extractible with 40-60 petrol, but slight warming of the petrol mixture led to a near instant precipitation of its content.

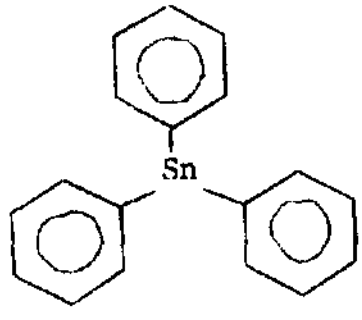
A dirty white powder was deposited. Spectroscopic monitoring of the reaction did not indicate that benzene was produced in the process of production of the powder, unlike what had been observed in the reaction of diphenyltin dichloride with silver trifluoroacetate.

Elemental analysis of the powder gave results that suggested an empirical formula of $PhSn(O.CO.CF_3)_3$. The powder neither melts nor decomposes below 360°C .

(b) Spectral properties of the product of reaction of $AgO.CO.CF_3$ with the phenyltin chlorides.

i. Nuclear Magnetic Resonance.

Triphenyltin trifluoroacetate dissolves readily in most organic solvents. Its spectrum in deuteroacetone showed a multiplet at δ7.40ppm, and another at δ7.80ppm. The former is the combined signal of the meta- and para-protons of the phenyls on the Sn, while the latter is the combined signal of the phenyl ortho-protons. The integral ratio

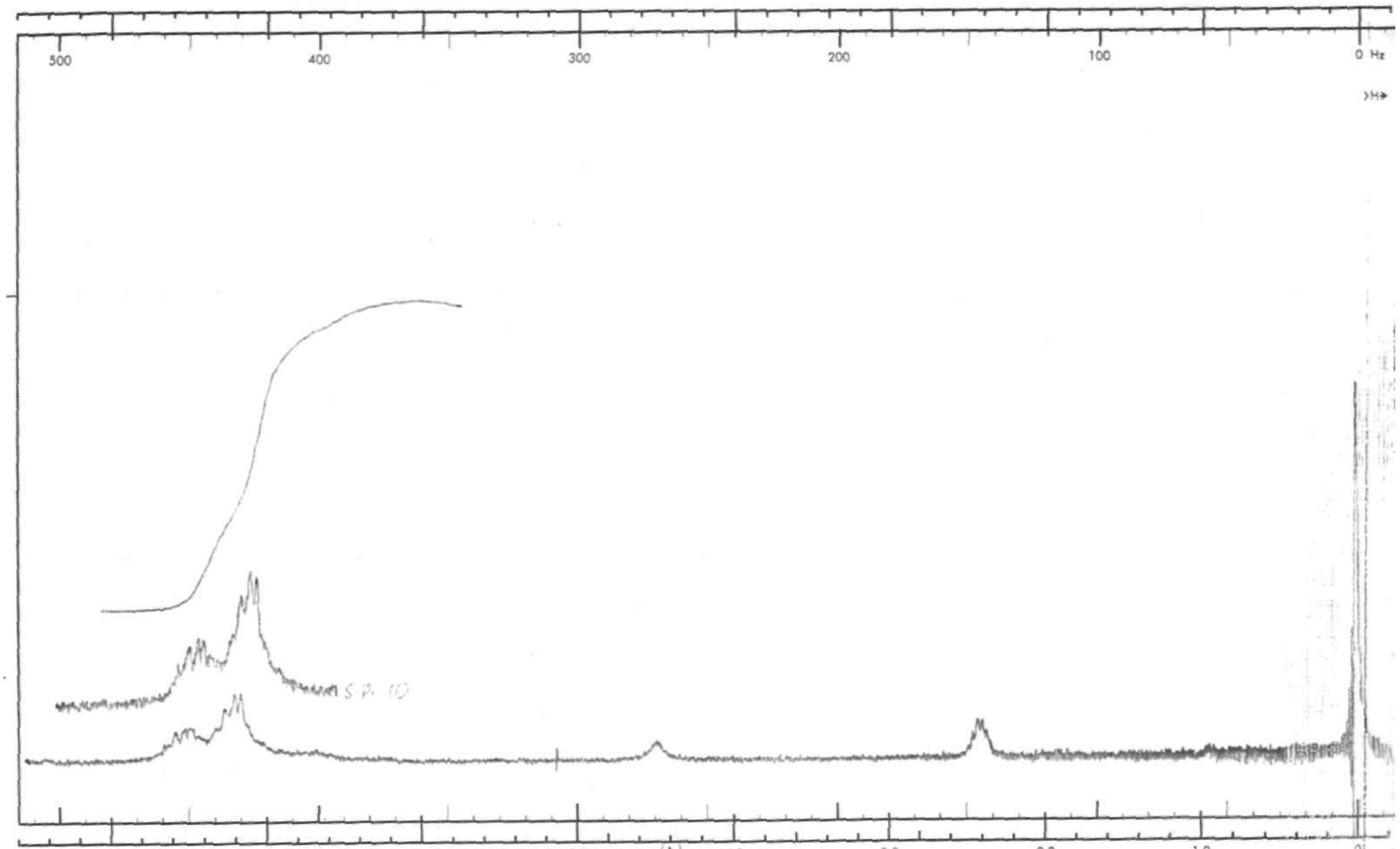


XC

of the former to the latter is roughly 3:2. The separation of the signals of the phenyl ring protons could be due to inductive effects through the Sn, of the $CF_3.CO.O-$ group on the Sn which passes along the sigma frame of the moiety and deshield the phenyl ortho-protons more than the meta and para-protons.

The isolated organotin product of the reaction of diphenyltin dichloride with silver trifluoroacetate, which has proved to be 1,2-diphenyl - 1,1,2,2- tetrakistrifluoroacetoxyditin (see below), dissolves only in highly polar, high solvating non-hydroxylic solvents like dimethylsulphoxide class. Its n.m.r. spectrum in deuterodimethyl sulphoxide shows a multiplet, assignable to the meta- and para-protons of the phenyl ring, at about δ7.40ppm; and a second multiplet at about 7.70ppm, assignable to the phenyl ortho-protons. Apart from the small signals of the few not fully deuterated molecules of the solvent, the product gives no other detectable signal.

The isolated product of the reaction of phenyltin trichloride with silver trifluoroacetate dissolved only with heating to near boiling, in dimethyl sulphoxide. The near colourless mixture turned orange as the product dissolved in the solvent, suggesting that a reaction might have occurred, rather than just dissolution of the product in the solvent. And indeed, the n.m.r. spectrum of the solution showed only a sharp signal similar to that shown by benzene, at δ7.30ppm.

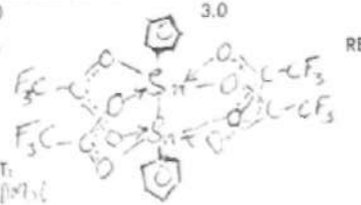


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SPECTRUM AMPLITUDE: 5
INTEGRAL AMPLITUDE: 3
SPINNING RATE (RPS): 0

MANUAL
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 0.1

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:



REMARKS:

SOLVENT: Acetone (DMSO)

STOHLER ISOTOPE CHEMICALS
49 JONES RD., WALTHAM, MASS. 02154, U.S.A.
IM BAUMGARTEN CH 3044 INNERBERG, SWITZERLAND
P.O. BOX 1134, MONTREAL 101, CANADA

DATE: 9/12/78

OPERATOR:

60 MHz NMR
SPECTRUM NO.

ii. Infra red spectra.

Band allocations in the i.r. spectra of the phenyltin carboxylates isolated from the reaction of the phenyltin chlorides with silver trifluoroacetate have been based on the findings of earlier researchers on similar compounds. It is commonly known that the -CO.O stretch shifts to lower frequencies, and symmetric (C_{2v}) bands appear at ~ 1570cm^{-1} and ~ 1400cm^{-1} where it is involved in polymeric or coordinate linkages[8]. Kriegsman[35] and Cummins[36] have also made a number of allocations, based on calculations and observation, to bonds linking Sn. The O → Sn coordination bond in organotin carboxylates is also known[17] to absorb at ~ 300cm^{-1}. On these bases, the following assignments have been made to some of the bands of the spectra.

Table 12

Infra red Spectral Bands

$Ph_3SnO.CO.CF_3$

Band frequency	Bond
3050, w cm^{-1}	aromatic C-H stretch
1640, vs, broad	OCO asymmetric
1440, m,	OCO symmetric
1220, vs, broad	C - F
1075, m,	aromatic (Sn-Ph) C-H deformation
990, m	SnOC stretch
300, s	Sn ← O

$Ph_2Sn_2(O.CO.CF_3)_4$.

Band Frequency	Bond
3030, vw cm^{-1}	Aromatic C-H stretch.
1610, s	OCO assymetric
1430, m	OCO symmetric
1200, vs	C - F
1075, w	aromatic (Sn-Ph) C-H deformation
995, m	SnOC stretch

Organotin carboxylate product of $PhSnCl_3$ + $3AgO.CO.CF_3$ $PhSn(O.CO.CF_3)_3$.

Band frequency	Bond
3060, vw	aromatic C-H stretch
1640, vs	OCO asymmetric
1440, m	OCO symmetric
1200, vs	C - F
1080, w	Sn - Ph aromatic C-H deformation
1005, m	SnOC stretch
300, s	Sn ← O

iii. Raman Spectra.

Vibrations that do not alter the dipole moment of a bond but the polarizability of the two elements of the bond are known[41] to be Raman active. The frequency of vibration of such a bond, measured as Raman shifts, could be expressed in wave. numbers:

NO. 5-100-0309

REMARKS

ORIGIN

PURITY

PHASE KBr

CONCENTRATION

THICKNESS

DATE 26/9/79

OPERATOR Timothy

PERKIN-ELMER

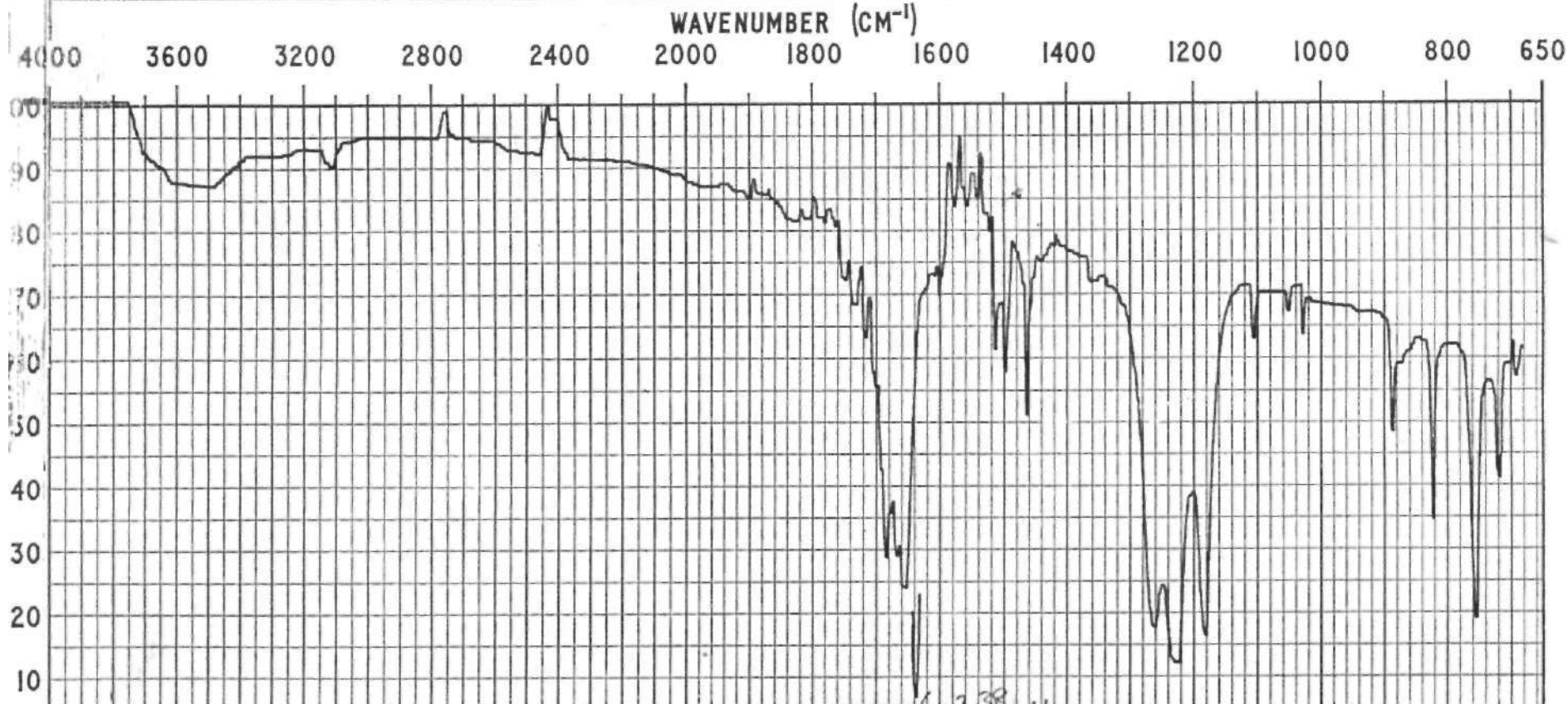
SPECTRUM NO.

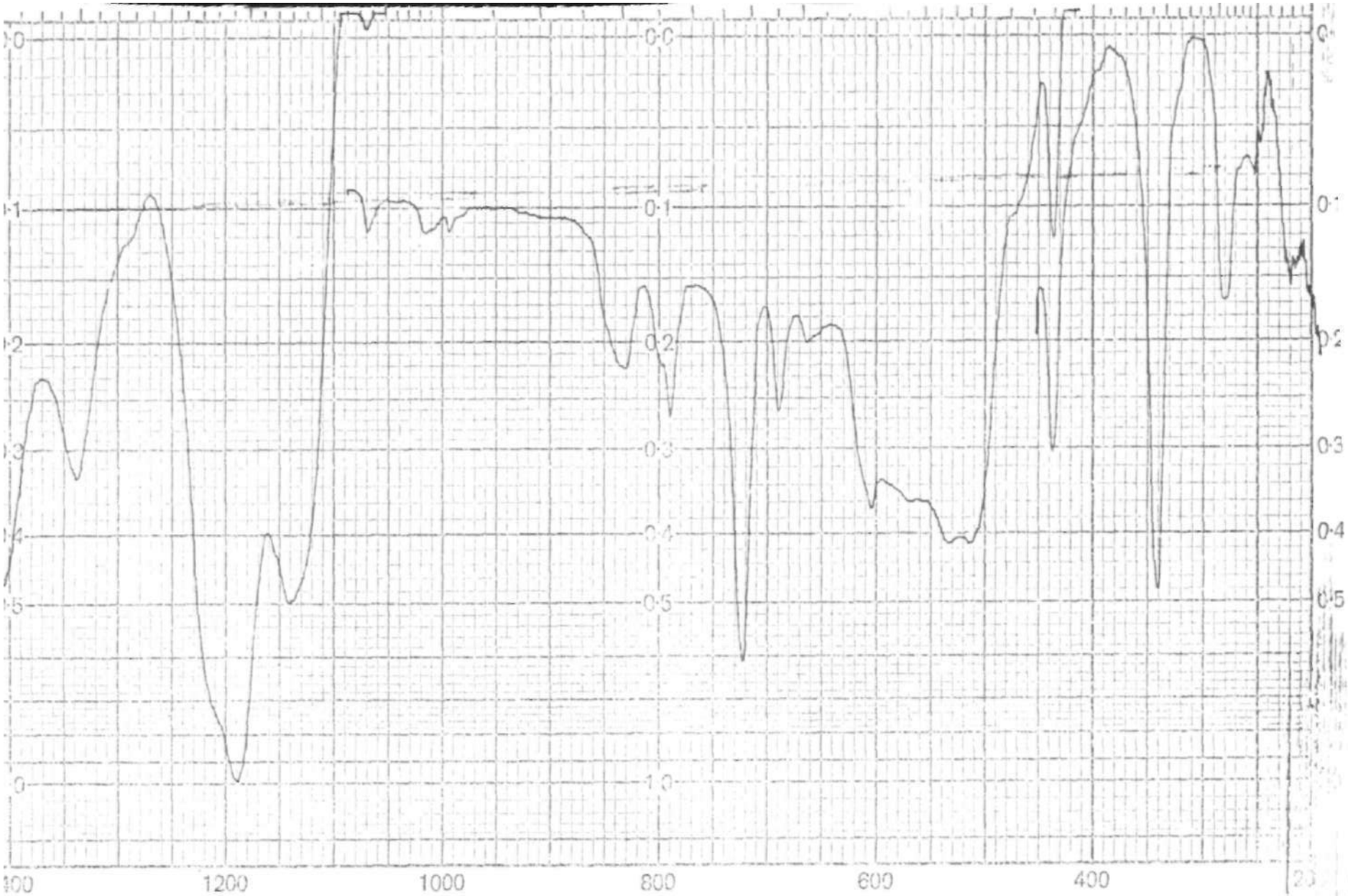
SAMPLE 1 $Ph_2Sn(O{\cdot}CO{\cdot}CF_3)_2$

SAMPLE 2

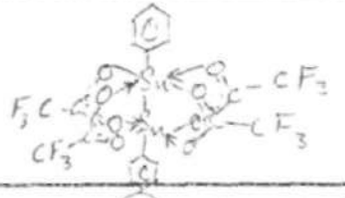
SAMPLE

SPECTRUM NO.





ample :



SCAN MODE 15 min
SLIT N TIME CONSTANT Auto

PERKIN ELMER
PART No. 5100 4366

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DATE 10/2/81

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$$\bar{\nu}_{A-X} = \frac{1}{2\pi C}\left(\frac{f_{A-X}}{\mu_{A-X}}\right)^{\frac{1}{2}}$$

where $\mu_{A-X} = \dfrac{M_A M_X}{M_A + M_X}$

f = force constant

μ = reduced mass.

Sn-Sn bonds in compounds are known[48,49] to have Raman shifts < 200cm^{-1}. No other type of bond, in an organotin compound, is known to have Raman shifts below 200cm^{-1}, for the Sn-Sn bond is about the weakest Raman active bond in an organotin compound having Sn as the only metal content.

On this basis, the Raman spectra of the isolated organotin products of the reaction of Ph_2SnCl_2 and $PhSnCl_3$ with $AgO.CO.CF_3$ were run, with the expectation that there would be bands < 200cm^{-1} if they contained any Sn-Sn bond. The bands shown by the spectra are as follows:

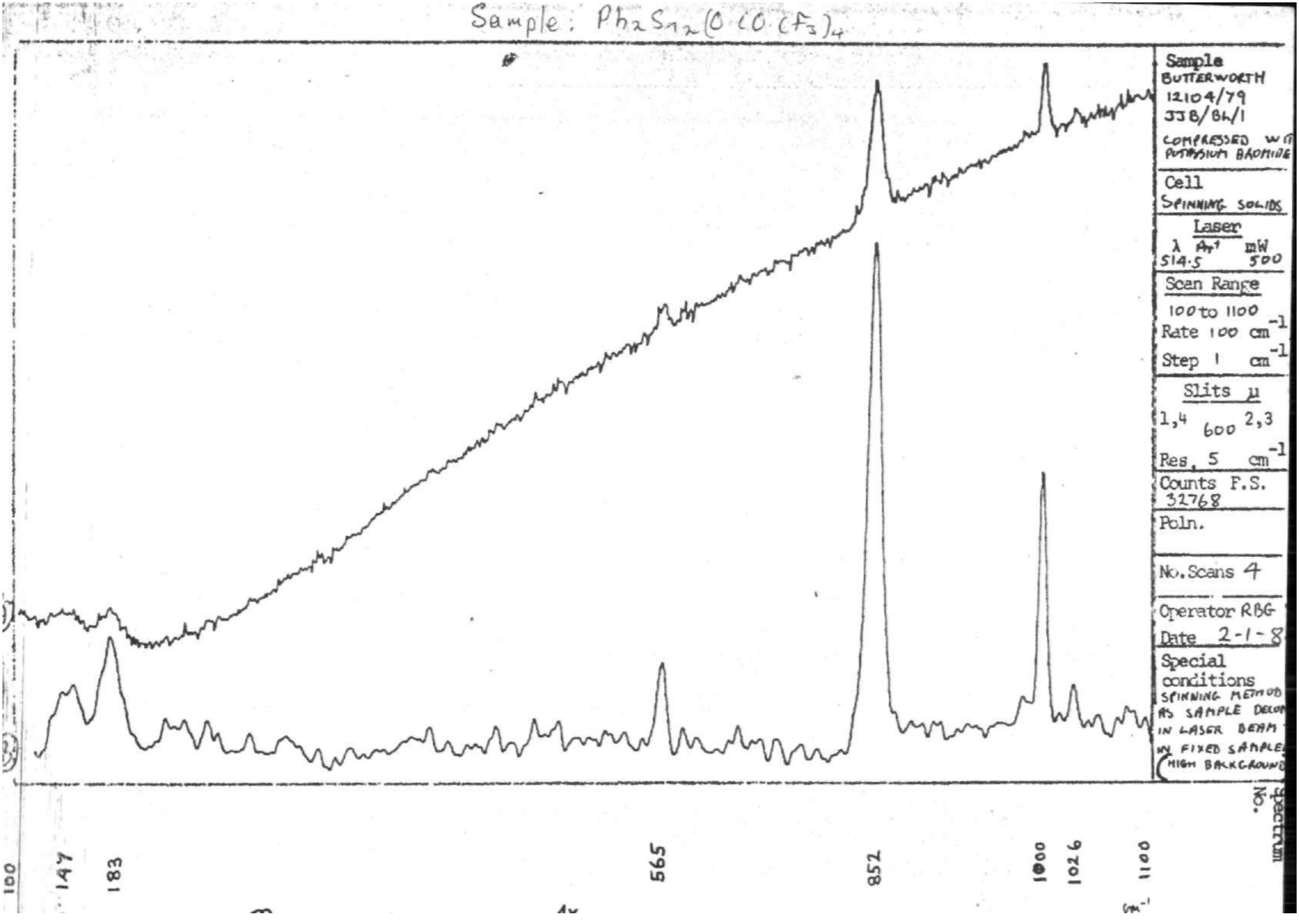
Table 13

Raman spectral Bands

$Ph_2Sn_2(O.CO.CF_3)_4$.

Raman Shift		Assignment
139 m	cm^{-1}	Sn-Sn (Symmetric stretch)
147 m	cm^{-1}	
183 m	cm^{-1}	
565 m	Cm^{-1}	
852 vs	cm^{-1}	
1000 s	cm^{-1}	
1026 w	cm^{-1}	

Sample: $Ph_2Sn_2(O\,CO\,CF_3)_4$



The product of the reaction of $PhSnCl_3$ with $AgO.CO.CF_3$ did not show any Raman activity between 100 - 1100cm^{-1}

iv. Mass Spectra.

Only the spectrum of the isolated organotin product of the reaction of Ph_2SnCl_2 with $AgO.CO.CF_3$ i.e $Ph_2Sn_2(O.CO.CF_3)_4$ could be run. The spectrum showed the following signals.

Table 14

$Ph_2Sn_2(O.CO.CF_3)_4$.

Mass	Fragment
77	$[C_6H_5]^+$
97	CF_3C^+O
120	Sn^+
197	$-Sn^+$
231	$F_3C.CO.O-Sn^+$
310	$PhSn^+O.CO.CF_3$
422	$PhSn^+(O.CO.CF_3)_2$
345	$(CF_3.CO.OSnO.CO.CF_3)^+$

Ultra-violet spectrum

Sn-Sn bonds in some compounds have been observed[7] to absorb energy in the u.v. region with λ_{max} between 270 - 280nm. A u.v. spectrum of $Ph_2Sn_2(O.CO.CF_3)_4$ in DMSO gave a u.v. absorption with λ_{max} of 273nm.

c. Chemistry of the Reaction

The reaction of Ph_3SnCl with $AgO.CO.CF_3$ appears to be no more than a nucleophilic substitution, feasible because of the polarity of the Sn - Cl bond, and the stability as well as the insolubility of AgCl in the medium of reaction.

$$Ph_3SnCl + AgO.CO.CF_3 \xrightarrow[\text{acetone}]{\text{dried}} Ph_3SnO.CO.CF_3 + AgCl\downarrow \quad .....lvii$$

LXXXV11 XX111

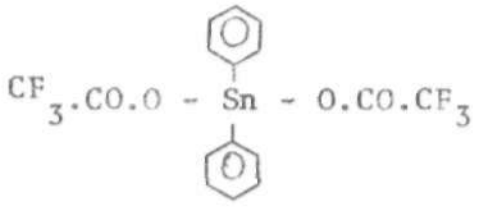
The polarity of the medium would enhance the polarization of the Sn-Cl bond, which would facilitate the removal of the halogen by the silver of $AgO.CO.CF_3$ which is more ionic than covalent.

The initial reaction of Ph_2SnCl_2 with $AgO.CO.CF_3$, in our view, is also a simple nucleophilic substitution reaction, feasible for reasons given above.

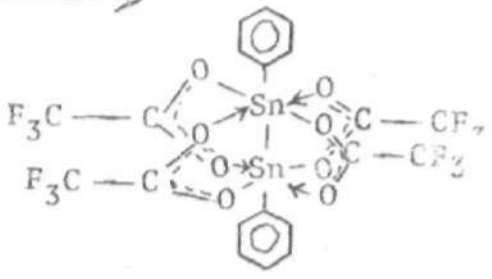
$$Ph_2SnCl_2 + 2AgO.CO.CF_3 \xrightarrow[\text{acetone}]{\text{dried}} Ph_2Sn(O.CO.CF_3)_2 + 2AgCl\downarrow \quad .....lviii$$

XV11 LXXXV111

The organotin product remained in the polar acetone medium as diphenyltin bistrifluoroacetate. But in a non polar medium, it proceeds to form, via homolytic fission, a binuclear product:



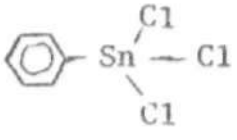
40-60 petrol



XC1

+ 2  lix

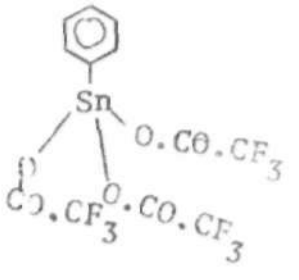
The reaction of $PhSnCl_3$ with $AgO.CO.CF_3$ is also, in our view, a nucleophilic substitution:



XC11

+ 3AgCl

dried
acetone



XC111

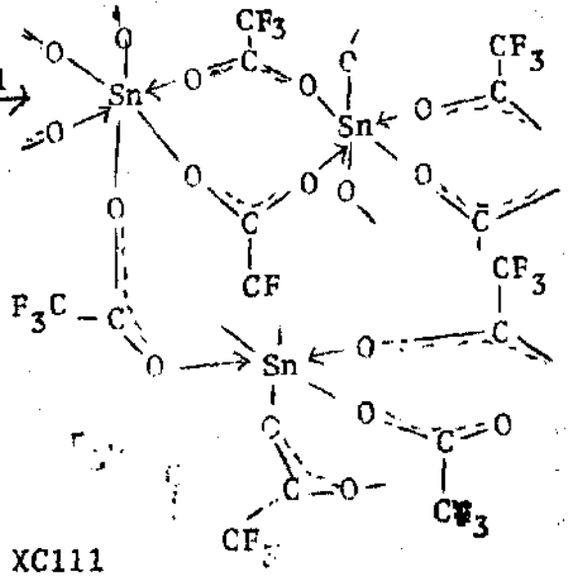
+ 3AgCl 1x

The organotin product would remain in acetone so long as there is no water. But with water present, hydrolysis, as suggested by Ford et al[26] for monoorganotin tricarboxylates, might occur:

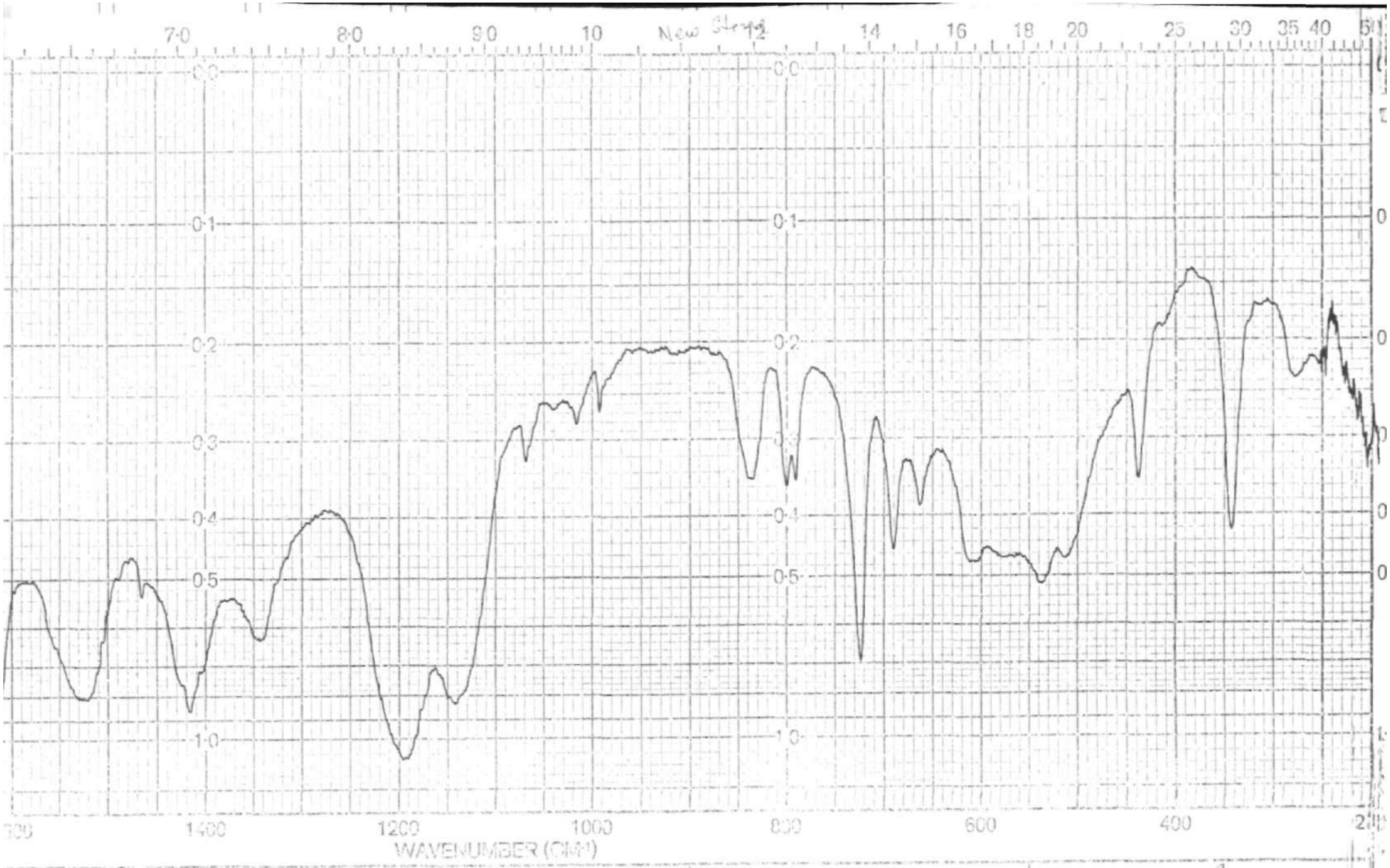
$$PhSn(O.CO.CF_3)_3 + H_2O \rightarrow \underset{XC1V}{PhSn(O)\ O.CO.CF_3} + 2CF_3.CO.OH$$

This might explain the hardening of the product of the organotin product of $PhSnCl_3$ and AgCl as explained earlier, when it was left crystallise. Unfortunately, the $PhSn(O)O.CO.CF_3$ would precipitate along with residual silver salts (AgCl and $AgO.CO.CF_3$) and make any purification very difficult if not virtually impossible. All efforts to purify the hardened product failed. It is possible that immediate extraction of the $PhSn(O.CO.CF_3)_3$ into petroleum spirit, a non-polar hydrophobic medium, could have prevented hydrolysis, while association of the product into a polymeric form occurred:

$$nPhSn(O.CO.CF_3)_3 \xrightarrow{Petrol}$$



XC111 ...lxii



REMARKS: Sample : $Ph_3Sn(O{\cdot}CO{\cdot}CF_3)_3$

Phase : CCl_4

SCAN MODE 15 min
SLIT N TIME CONSTANT Auto

PERKIN ELMER
PART No. 5100 4366

OPERATOR Bonire
DATE 10/2/81

REF No.

The suggested structure for the polymeric product obtained shows no plane of symmetry and thus most likely would be Raman inactive. Indeed, no Raman shift was observed in its spectrum between 100 - 1100cm^{-1}. The n.m.r. of the product showed only a benzene signal resulting perhaps from hydrolytic reactions in the deuterodimethyl sulphoxide which is so hydrophilic that it is hardly ever free of water. And the hydrolysis would be promoted by the heat which was required to dissolve the organotin in deuteroDMSO.

$$\underset{\text{moiety}}{PhSn(O.CO.CF_3)_3} + H_2O \xrightarrow{DMSO} PhSn(O)OCO.CF_3 + 2CF_3.CO.OH \quad \ldots lxiii$$

$$PhSn(O).O.CO.CF_3 + CF_3.CO.OH \rightarrow \underset{XCV}{\begin{array}{l} O.CO.CF_3 \\ | \\ Sn = O \\ | \\ O.CO.CF_3 \end{array}} + Ph\text{-}H \quad \ldots . lxiv$$

i. Diphenyltin bistrifluoroacetate.

The reaction of Ph_2SnCl_2 with $AgO.CO.CF_3$ gives AgCl and an organotin, which is obtainable only as an oil. All available methods were applied to obtain the "oil" in the purest possible form. These comprised redissolution of the oil in dry acetone, filtering, concentrating, and drying for a prolonged time in a dessicator. In its driest form, the oil was found to have a tin content of 21%. Further attempts to dry the oil made if solidify, and Sn analysis and spectroscopic properties of the solid were very similar to those of $Ph_2Sn(O.CO.CF_3)_4$.

An n.m.r. spectrum of the clean oil showed two multiplets at δ7.50 and δ7.85ppm, assignable to the meta- and para-protons of Sn-⬡ and the ortho- protons of Sn-⬡ respectively. Signals (singlets) also appeared at δ2.10ppm and δ9.30ppm, assignable to acetone and water, implying that in its 'driest' form, the oil still contained water and some acetone among other possible contaminants.

The oil, in aromatic hydrocarbon free 40-60 petrol as solvent, showed a sharp u.v. absorption at 222n.m. (λ_{max}). Corroborative u.v. measurements were carried out for the following compounds:

Table 15

The U.V. Absorption bands of some Phenyltin compounds

Compound	Solvent	U.V λmax
Ph_3SnOAc	40 - 60 Petrol	223 nm
Ph_3SnCl	40 - 60 Petrol	222 nm
Ph_2SnCl_2	40 - 60 Petrol	223 nm
Ph.CO.OH	40 - 60 Petrol	227 nm
"Oil" $Ph_2Sn(O.CO.CF_3)$	40-60 Petrol	222 nm

The corrollary that could be derived from this data is that the "oil" most likely contains a ⬡-Sn moiety, since Ph_3SnOAc, Ph_3SnCl, Ph_2SnCl_2, and Ph.CO.OH, none of which would be polymeric or intermolecularly associated in solution, all show their phenyl λ_{max} between 220 and 227nm.

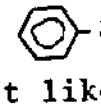
An infra red spectrum of the oil showed these bands:

Table 16

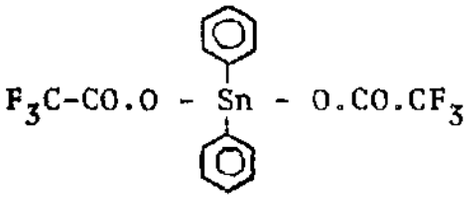
$Ph_2Sn(O.CO.CF_3)_2$

I.r. Band		Bond
$3400_{(s)}$	cm^{-1}	O - H water
3050 w	cm^{-1}	C - H stretch (aromatic)
1730 vs	cm^{-1}	CO.O.Ester stretch
1200 vs	cm^{-1}	C - F stretch
1080 m	cm^{-1}	Sn - Ph C - H aromatic deformation
1005 m		SnOC

There has been no sign of production of benzene in the formation of the "oil" from Ph_2SnCl_2, therefore it could be inferred that there are still two phenyl groups to one Sn in the "oil".

Now, the Sn content of Ph_2SnCl_2, the starting material, is 34.53%; the Sn content of the oil (the purest form obtained) was 21%, and the Sn content of pure $Ph_2Sn(O.CO.CF_3)_2$ is 23.80%. The Sn content of $Ph_2Sn_2(O.CO.CF_3)_4$ is 28.20%. However, $Ph_2Sn_2(O.CO.CF_3)_4$ is solid. I.r. spectroscopy has shown a signal for an ester -CO.O- group, C - F, Sn-Ph, and Sn-OC groups. N.m.r. shows the presence of -Sn in the oil. U.V. shows the presence of -Sn, most likely as a part of an uncoordinated or associated phenyltin carboxylate. AgCl was

produced as $AgO.CO.CF_3$ reacted with the Ph_2SnCl_2, and Lassaigne test did not indicate the presence of Cl to any important extent in the product. Benzene was not produced in the reaction leading to the formation of the oil. It could then be inferred, from this evidence, that the 'oil' was most probably $Ph_2Sn(O.CO.CF_3)_2$ i.e.



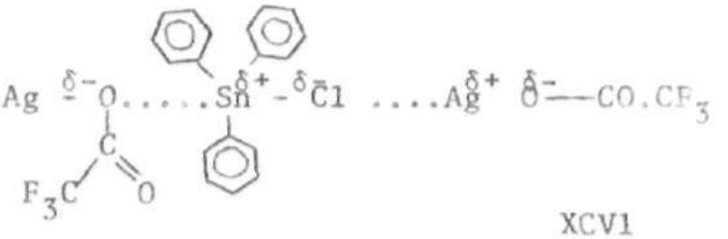
LXXXVIII

with probable trace contaminants like water and acetone, among possible others.

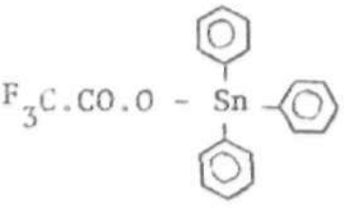
d. Suggested Mechanisms for the Reactions.

i. Reaction between Ph_3SnCl and $AgO.CO.CF_3$

This reaction could be a simple SN_2. reaction, which is thought feasible.

$Ph_3SnCl + AgO.CO.CF_3 \rightarrow$ 

XCV1



XXIII

$+ AgCl$

because of the electron withdrawing nature of the phenyl groups on Sn.

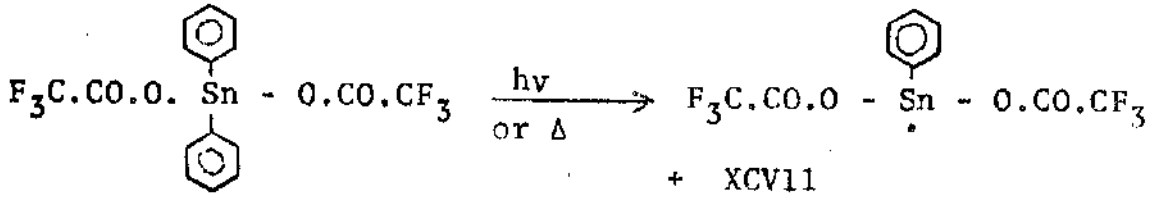
ii. Reaction between Ph_2SnCl_2 and $AgO.CO.CF_3$.

The first part of the reaction, the production of the diphenyltinbistrifluoroacetate oil, might be, like the one discussed above, a simple SN2 reaction:

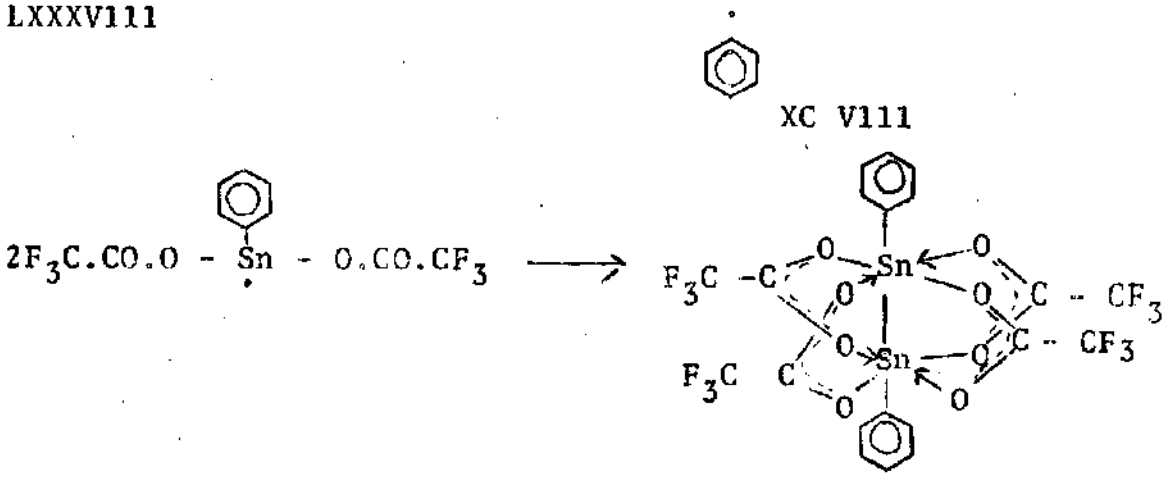
$Ph_2SnCl_2 + AgO.CO.CF_3 \rightarrow Ph_2Sn(O.CO.CF_3)_2$

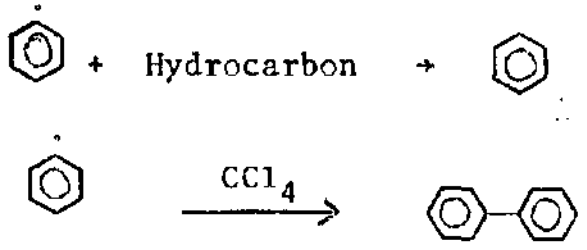
$+ 2AgCl$

However, further reaction of the diphenyltinbistrifluoroacetate in petrol is thought to occur thus:



LXXXV111





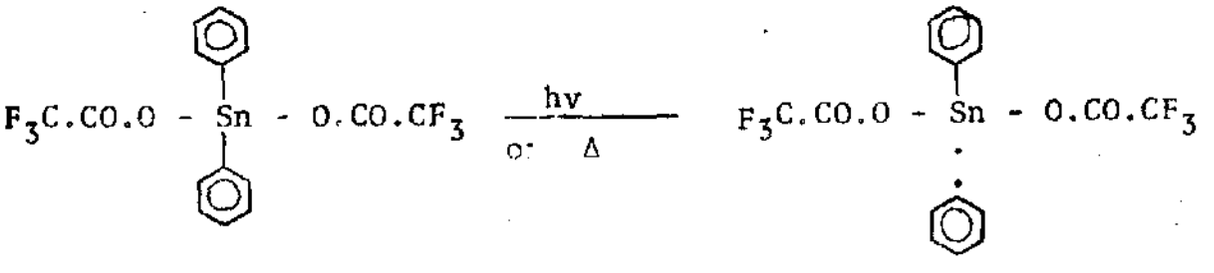
XC1X

To the best of our knowledge, this is a new reaction, although it cant be called a general reaction until it is widely tested, and this we could not do because of non-availability of the required reagents.

e. Proof of Mechanism.

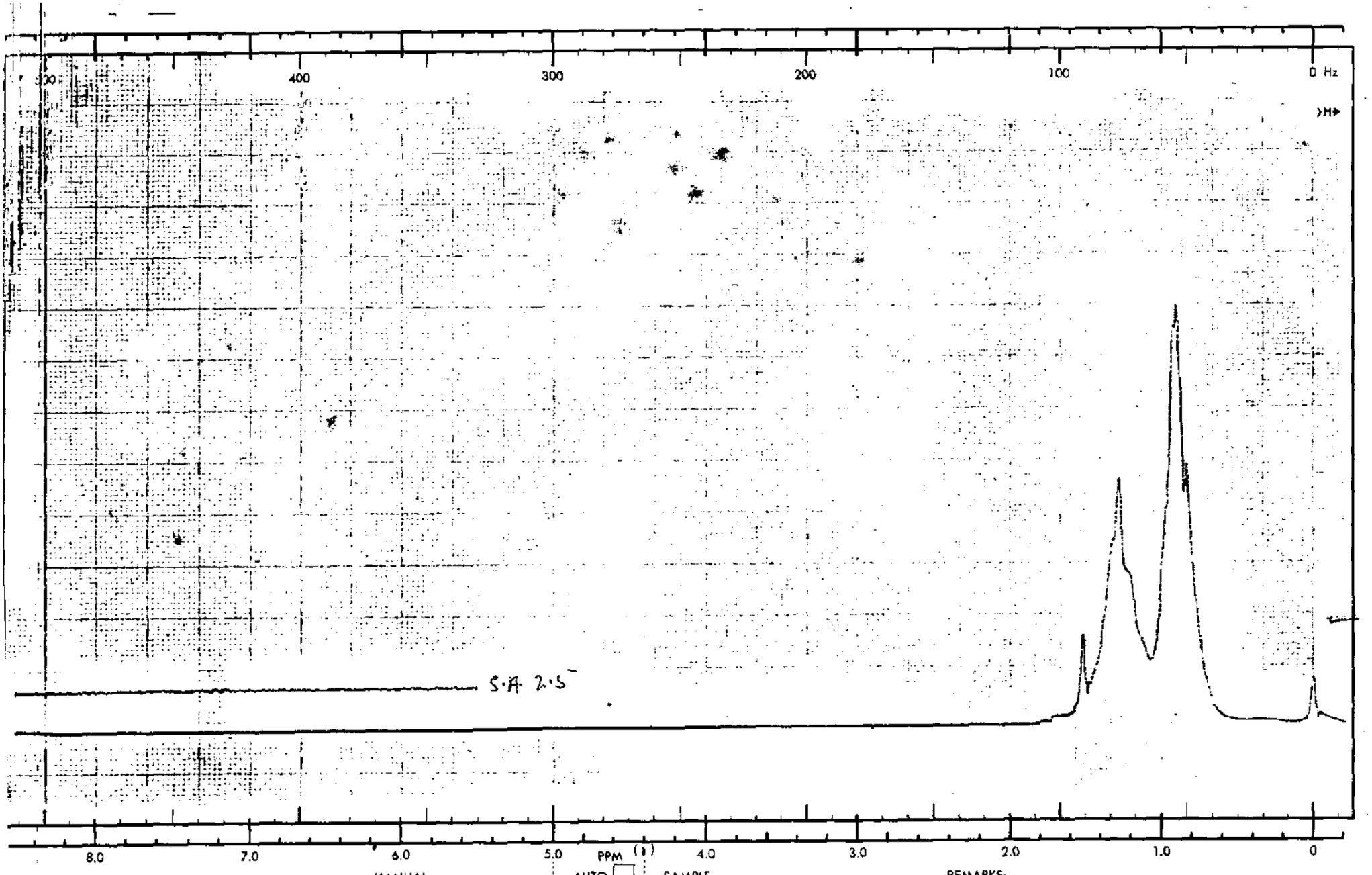
The formation of $Ph_2Sn_2(O.CO.CF_3)_4$ from $Ph_2Sn(O.CO.CF_3)_2$ in non-polar media, in our view, occurs by radical mechanism, for it is commonly known that radical reactions occur mainly in non-polar media where there are few or no ions to terminate or interfere with the reactions. The reaction yielding $Ph_2Sn(O.CO.CF_3)_2$, the oily intermediate, is carried out in acetone. The reaction does not proceed further until the 'oil' is boiled in a non-polar medium like petrol.

When a solution of the $Ph_2Sn(O.CO.CF_3)_2$ in petrol was kept in sunlight or under ultra-violet light, $Ph_2Sn_2(O.CO.CF_3)_4$ was produced. Heat and ultra-violet light are common initiators in radical reactions.



When a solution of diphenyltin bistrifluoroacetate in petrol was boiled with benzoquinone, a common radical scavenger, $Ph_2Sn_2(O.CO.CF_3)_4$ was not produced.

Boiling of diphenyltin bistrifluoroacetate in hydroxylic solvents yielded white amorphous powders, which tin analysis and infra-red spectroscopy showed to be not $Ph_2Sn_2(O.CO.CF_3)_4$, but products containing the -OH group, suggesting hydrolysis of



WEEP OFFSET (Hz): 0·00
PECTRUM AMPLITUDE: 0·4
ITEGRAL AMPLITUDE:
INNING RATE (RPS): 50

MANUAL
SWEEP TIME (SEC): 50 | 250
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500
FILTER: ✓1 | 2 | 3 | 4 | 5 | 6 | 7 | 8
RF POWER LEVEL: 0·1

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:

REMARKS:
#0·60° petrol (aromatic hydrocarbon free)

SOLVENT: CCl4

STOHLER ISOTOPE CHEMICALS
49 JONES RD., WALTHAM, MASS. 02154, U.S.A.
IM BAUMGARTEN CH 3044 INNERBERG, SWITZERLAND
P.O. BOX 1134, MONTREAL 101, CANADA

DATE: 23/6/78 OPERATOR:

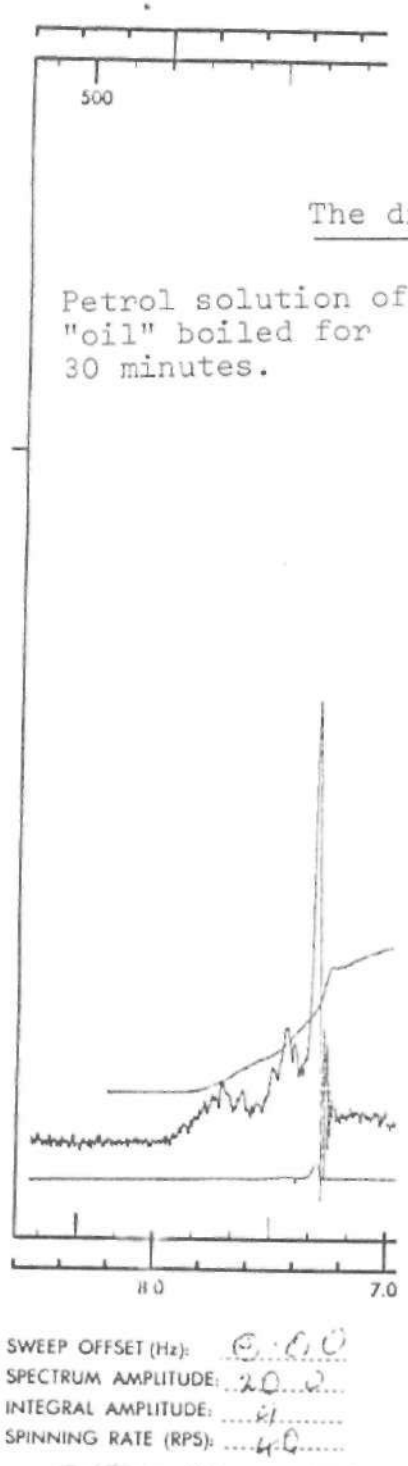
60 MHz NMR
SPECTRUM NO.

The disintegration of "oil" ($Ph_2Sn(O.CO.CF_3)_2$) in aromatic hydrocarbon-free 40 - 60 petrc



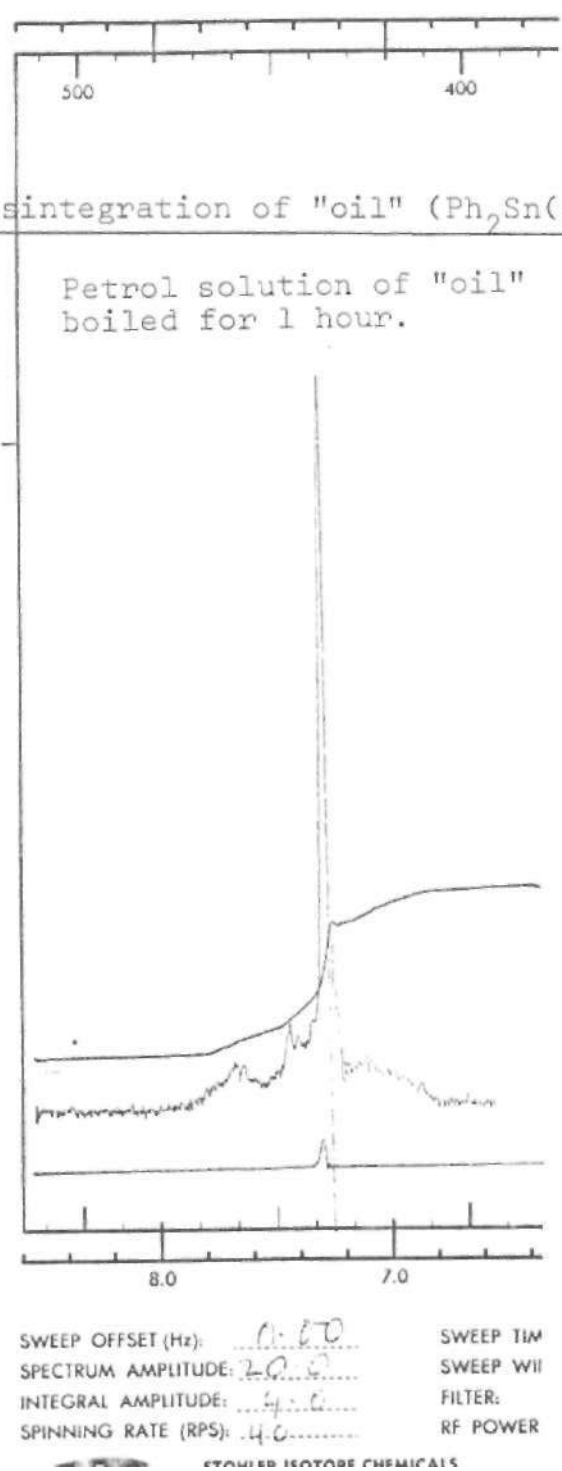
"Oil" in cold petrol (start)

SWEEP OFFSET (Hz): 0.00
SPECTRUM AMPLITUDE: 20
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 40



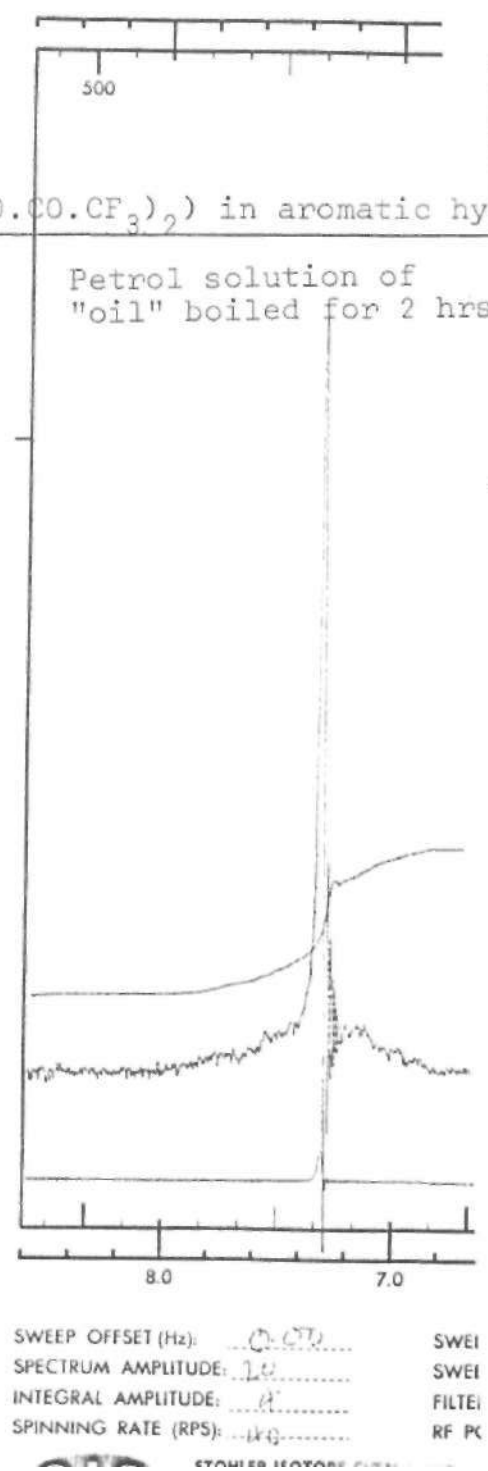
Petrol solution of "oil" boiled for 30 minutes.

SWEEP OFFSET (Hz): 0.00
SPECTRUM AMPLITUDE: 20.0
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 40



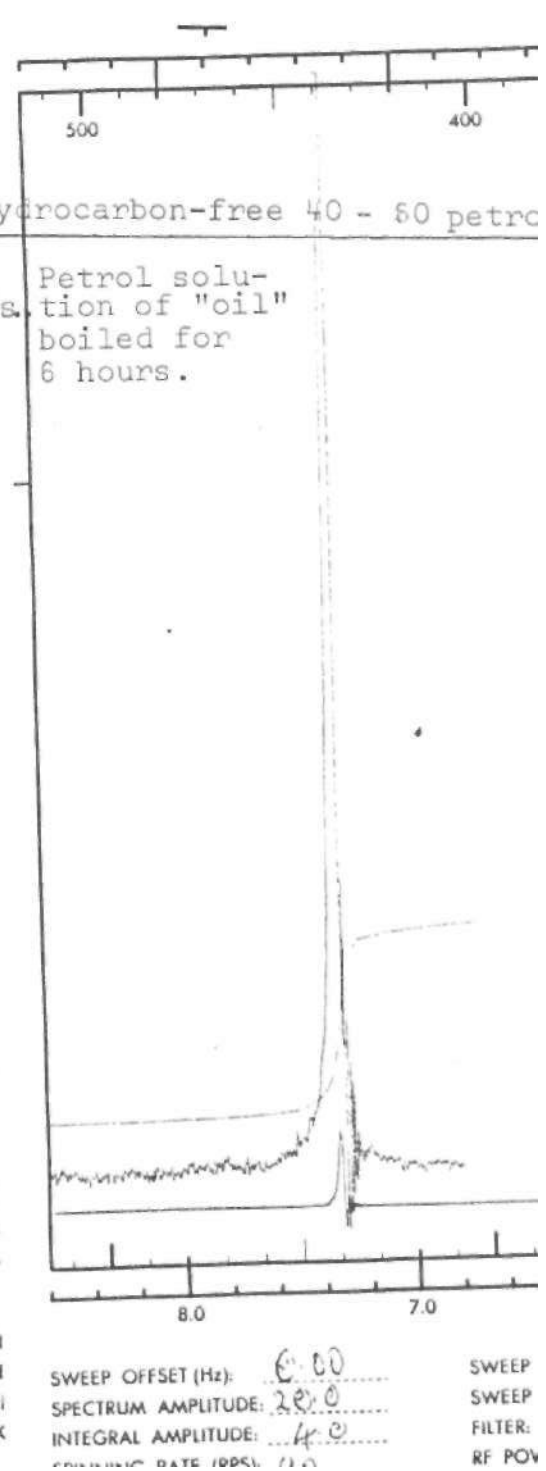
Petrol solution of "oil" boiled for 1 hour.

SWEEP OFFSET (Hz): 0.00
SPECTRUM AMPLITUDE: 20.0
INTEGRAL AMPLITUDE: 4.0
SPINNING RATE (RPS): 40
SWEEP TIM
SWEEP WI
FILTER:
RF POWER



Petrol solution of "oil" boiled for 2 hrs.

SWEEP OFFSET (Hz): 0.00
SPECTRUM AMPLITUDE: 20
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 40
SWEI
SWEI
FILTE
RF PO



Petrol solution of "oil" boiled for 6 hours.

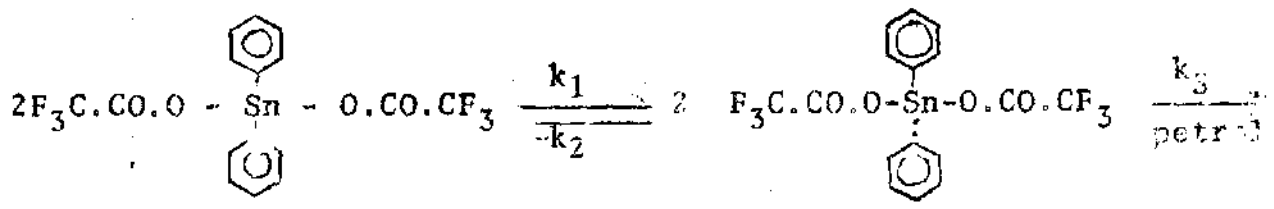
SWEEP OFFSET (Hz): 0.00
SPECTRUM AMPLITUDE: 20.0
INTEGRAL AMPLITUDE: 4.0
SWEEP
SWEEP
FILTER:
RF POW

the diphenyltin bistrifluoroacetate in hydroxylic solvents, rather than production of $Ph_2Sn_2(O.CO.CF_3)_4$.

A solution of the $Ph_2Sn(O.CO.CF_3)$ in benzene, when warmed, yielded $Ph_2Sn_2(O.CO.CF_3)_4$ and biphenyl, identified by Sn analysis, i.r. and n.m.r. spectroscopy, and thin layer chromatography.

A solution of the $Ph_2Sn(O.CO.CF_3)_2$ in CCl_4 also yielded $Ph_2Sn_2(O.CO.CF_3)_4$ and biphenyl on heating.

Periodical exposure of an aromatic hydrocarbon free 40-60 petrol solution of the $Ph_2Sn(O.CO.CF_3)_2$ to U.V. light at intervals of one hour, showed an exponential disappearance of $Ph_2Sn(O.CO.CF_3)_2$, which has a λ_{max} of 222nm.



$Ph_2Sn_2(O.CO.CF_3)_4$ +

+ 2 

If 'C' = concentration of $Ph_2Sn(O.CO.CF_3)_2$, 'e' the extinction coefficient, and 'l' the cell path length, by Beer-Lambert's law,

$$A = ecl$$

where A = absorbance of $Ph_2Sn(O.CO.CF_3)_2$

From the above equation then, by 1st orderrate law,

$$\log A = \log A_o + \frac{K_1 K_3}{2.303k_2} t$$

where A_o = initial concentration of $Ph_2Sn(O.CO.CF_3)_2$

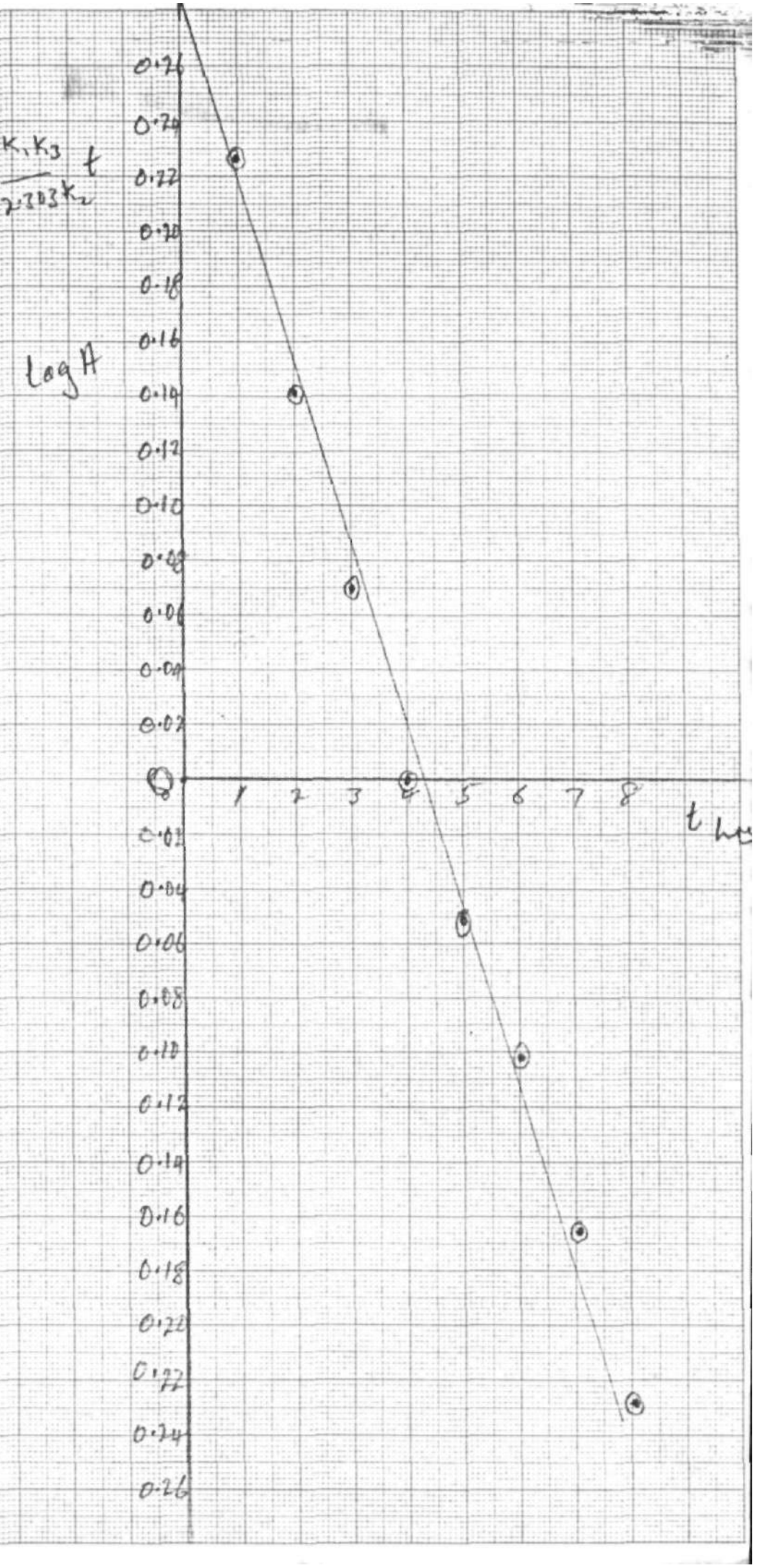
amd t = time in hours, in the process of disappearance of $Ph_2Sn(O.CO.CF_3)_2$ to form $Ph_2Sn_2(O.CO.CF_3)_4$

A plot of the absorbance at 222nm vs time t showed an exponential curve, while a plot of the logarithm of the absorbance, A, vs time, t, gave a straight line, suggesting that the "disappearance" of $Ph_2Sn(O.CO.CF_3)_2$ to form $Ph_2Sn_2(O.CO.CF_3)_4$ follows a first order rate law. (see graphs).

Thus, the production of $Ph_2Sn_2(O.CO.CF_3)_4$ from $Ph_2Sn(O.CO.CF_3)_2$ is strongly suggested to be by radical mechanism, for its occurrence, especially in an exponential manner, only in non-polar media; for the initiation of the reaction by sunlight, heat and u.v., and for its arrest by a radical scavenger.

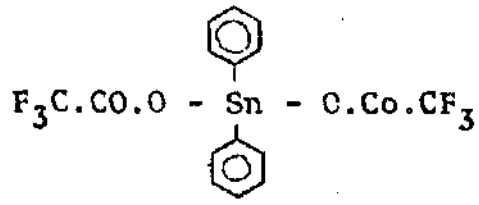
A potential use of diphenyltin bistrifluoroacetate then, would be as a radical initiator, since only mere warming in a non-polar medium would produce radical, some of which couple to form the insoluble $Ph_2Sn_2(O.CO.CF_3)_4$. It only has to be stored however, in a polar, non-aqueous and non-hydroxylic solvent; the solvent could be removed by evaporation when the $Ph_2Sn(O.CO.CF_3)_2$ is required for use.

$$\log A = \log A_0 + \frac{K_1 K_3}{2.303 K_2} t$$

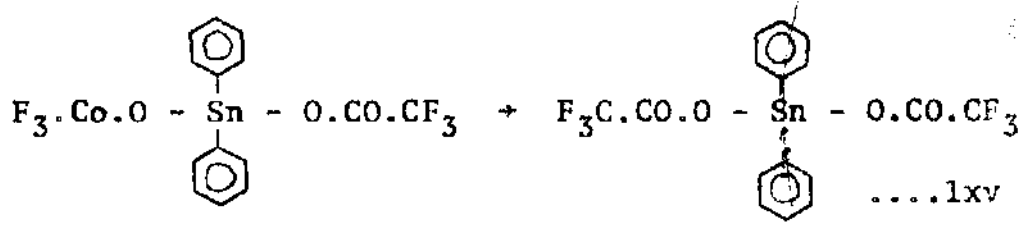


f. Driving force of reaction.

Looking at the structure of diphenyltin bistrifluoroacetate,



both the phenyls and trifluoroacetate groups attached to Sn are electron withdrawing. Ordinarily, Sn would be more "electropositive" than the phenyl group, and an Sn - Ph bond would therefore break heterolytically. But since the trifluoroacetate groups on Sn are electron withdrawing, it is possible that the effect makes Sn as electron affinitive as the phenyl attached to it. The Sn - Ph group, therefore, would perhaps rather break homolytically.

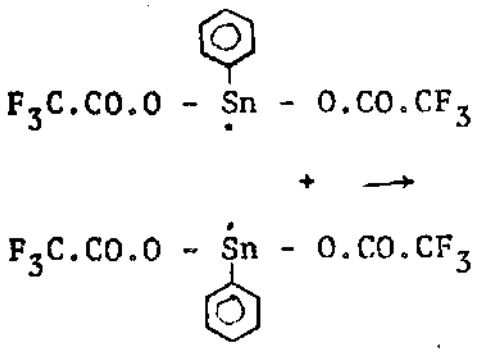


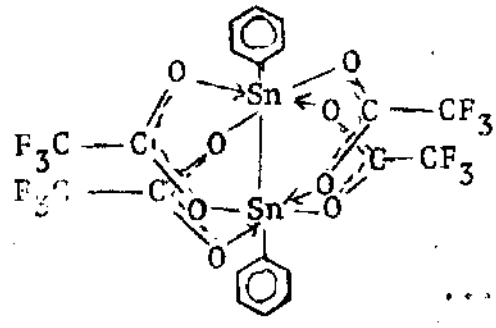
....lxv

Once the radicals are formed, the phenyltin bistrifluoroacetate moiety would cometogether in pairs, couple by bonding through their Sn, and also coordinate intramolecularly by means of their carboxylate groups, forming five membered and therefore

reasonably stable rings. The process gives Sn the stable hexacoordination. A highly sysmmetrical product $(Ph_2Sn_2O.CO.\dot{C}F_3)_4$ results, and highly symetrical compounds are commonly known to be high melting and insoluble in most organic solvents. Since the product precipitates from the solution then, the reaction is pushed forwards.

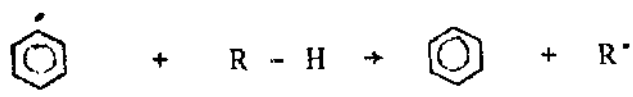
The phenyl radical most likely abstracts a hydrogen radical from the hydrocarbon to give benzene, but perhaps would rather couple to give biphenyl when the solvent is CCl_4, since perhaps more energy would be required to abstract a $Cl^{\cdot}$ from a CCl_4 which has its bonds polarized towards chlorine thereby making it difficult to break them homolytically.



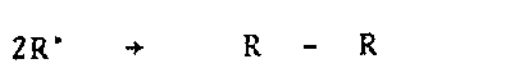


...lxvi

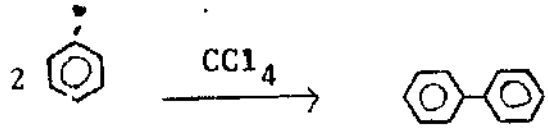
XCl



.....lxvii

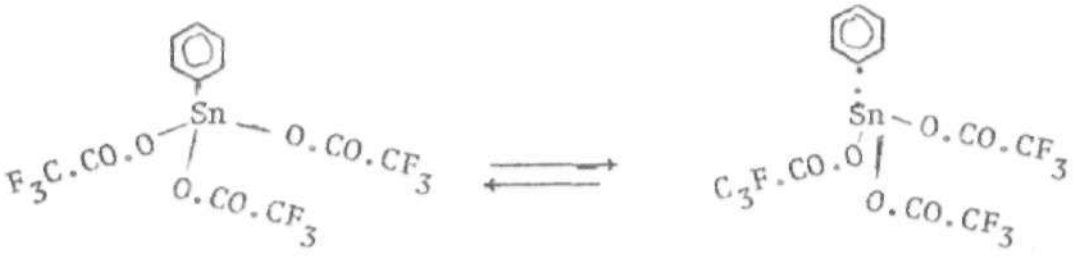


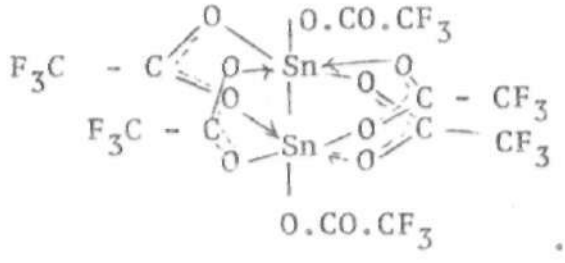
....lxix



....lxx

The mechanism of the reaction of $PhSnCl_3$ with $AgO.CO.CF_3$ is no clearer than earlier explained. It had however been thought that $PhSn(O.CO.CF_3)$, once formed, would also have its Sn - Ph bond breaking homolytically to give a product like $Sn_2(O.CO.CF_3)_6$, viz:





...lxxi

C

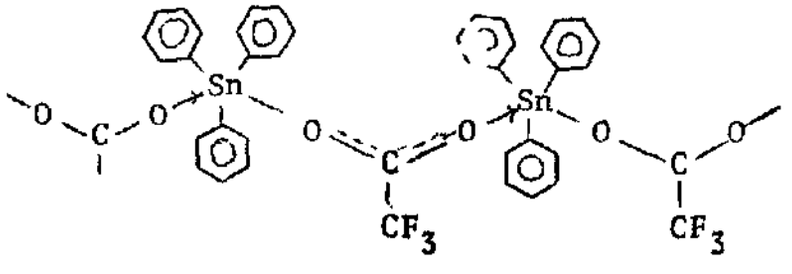
but the reaction did not show any production of benzene as earlier explained and the product contained the aromatic ring.

g. Proof of products and suggested products.

i. $Ph_3SnO.CO.CF_3$.

Triphenyltin trifluoroacetate has reportedly been prepared by Ford et al[26], from the reaction between triphenyltin hydroxide and trifluoroacetic acid - a method of preparation different from that used in this work. Ford et al found by Mössbauer and infrared spectroscopic techniques that $Ph_3SnO.CO.CF_3$ is a pentacoordinate polymer in the solid state, with O-C-O bridges between the tin atoms. The properties - elemental analysis, i.r. and n.m.r., spectra and melting point - of the $Ph_3SnO.CO.CF_3$ prepared by our method compare very well with those reported by Ford et al.

It would be inferred then, that the same $Ph_3SnO.CO.CF_3$, with same polymeric structure, has been obtained by our method of preparation



XX111

ii. $Ph_2Sn_2(O.CO.CF_3)_4$.

No compound having a molecular structure of $Ph_2Sn_2(O.CO.CF_3)_4$ has, to the best of our knowledge, been hitherto reported. We have the following reasons for suggesting the molecular formula and structure for the product.

The results of the elemental analysis of the product gave the following average values for four determinations: C,28.72 ± 0.30%; H, 1.65 ± 0.20%; Sn, 28.58 ± 0.40%. The empirical formula that agrees most closely with these values is $PhSn(O.CO.CF_3)_2$, which has a calculated assay of C,28.45%; H,1.20%; Sn, 28.13%. Fluorine analysis could not be successfully done; analysts reported undefined interferences in fluorine analytical estimation.

Sn is known to be either divalent or tetravalent in its uncoordinated compounds. Trivalent Sn has not been reported, and there is no ground to suppose, as yet, that it exists. For Sn to be tetravalent therefore, two units of the empirical formula must bind through their Sn. A binuclear molecule would result ($Ph_2Sn_2(O.CO.CF_3)_4$). If actually such a bond was formed, then there would be an Sn - Sn bond in each molecule, and the product would be Raman active below $200cm^{-1}$, for Sn - Sn stretches are known[48,49] to have Raman shifts $\leq 200cm^{-1}$. And indeed, a Raman spectrum of the product showed bands at 139, 147, and $183cm^{-1}$, which compare well with the Raman bands for Sn - Sn in other compounds having the Sn - Sn bond[48,49]. There however is not enough evidence to say which band is for which type of Sn - Sn mode of vibration, as complex quantum mechanical calculations are usually involved in such classifications.

Sn - Sn bonds are known to be easily broken by halogens[50]



lxxii

And the proposed product ($Ph_2Sn_2(O.CO.CF_3)_4$) decolourized a CCl_4 bromine solution when it was shaken with it and left to stand.

The product was found not to melt or decompose below 360°C. The mass spectrum did not show mass units equivalent to the molecular mass of 846, i.e. the molecular ion of $Ph_2Sn_2(O.CO.CF_3)_4$, but showed mass units at and around 423, which agrees with the mass of the $PhSn(O.CO.CF_3)_2$ moiety, a half of the suggested formula. This could be due to fission of the Sn-Sn bond due to the high temperature, and mode of operation, of mass spectroscopy, which invalues bombardment of the test product molecules to produce ions. Sn-Sn bonds would not be expected to be very strong; and actually, they are known[50] not to be strong.

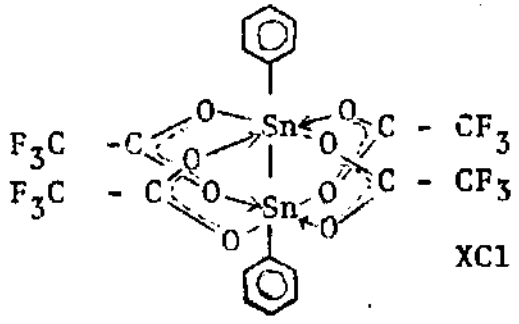
I.r showed the product to have, among other bands, an O.C.O band at 1640 cm^{-1}, known for 'bridging' carboxylate groups[26], and a band at 300cm^{-1}, known[8] for the Sn ← O coordinate bond.

N.m.r. showed aromatic signals similar to those expected for Sn-⬡ .

The compound was found to be insoluble in most organic

solvents except DMF, DMSO, and pyridine and its derivatives. Recrystallisation of the compound has not been possible to date, as once dissolved, it would not crystallise out of the solvent, even at high concentrations. The high melting point and the insolubility of the compound in most organic solvents suggest it to be either a polymer or a highly symmetrical simple molecule. But no polymeric formula could be written for $PhSn(O.CO.CF_3)_2$ except the "dimer", $Ph_2Sn_2(O.CO.CF_3)_4$, if the elemental analysis is to agree with the theoretical assay of the compound, and if a stable valency for the Sn is to be obtained.

From these evidences, we think therefore that the product has a molecular formula of $Ph_2Sn_2(O.CO.CF_3)_4$ and the following possible structure:



The structure shows a stable hexacoordination of the Sn moiety, and shows high symmetry, which would explain the high stability of the product to heat, and its insolubility in many organic solvents. Confirmation of this proposed

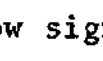
structure will have to await the result of X-ray diffraction studies

$Ph_3SnO.CO.CF_3$, has not been found to give any reaction in petrol or in any other non-polar medium, possibly because such a stable structure as $Ph_2Sn_2(O.CO.CF_3)_4$ cannot be produced from it in any straight forward reaction. Infact, $Ph_3SnO.CO.CF_3$ was recrystallised from petroleum spirit.

$PhSn(O.CO.CF_3)_3$.

Elemental analysis of this product gave results that agree well with calculated values for $PhSn(O.CO.CF_3)_3$.

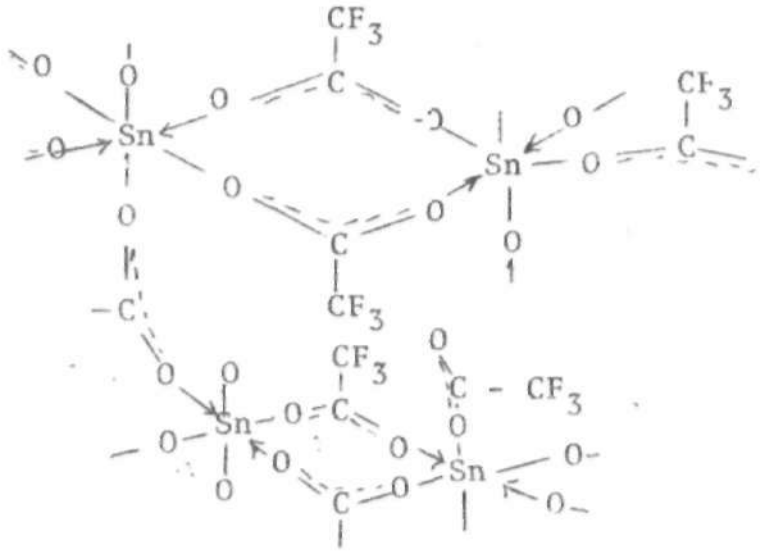
The Raman spectrum did not show any band below $200cm^{-1}$, suggesting a most probable absence of the Sn-Sn bond.

N.m.r. did not show signals for Sn  protons, but for benzene protons. The possible reason has earlier been explained.

I.r. shows, among other bands, the O-C-O. band around $1640cm^{-1}$, suggesting intermolecular linkage of the COO oxygens; and a band at $300cm^{-1}$ suggests the presence of the Sn ← O band. A band at $1005cm^{-1}$ has been assigned to the SnOC stretch. The intense C - F band was present at $1200cm^{-1}$, as well as the Sn - Ph deformation band at $1080cm^{-1}$.

The product did not melt below 360°, and dissolved with difficulty even in DMSO, suggesting that it might be polymeric.

Given the available evidence, therefore, $PhSn(O.CO.CF_3)_3$ is suggested as the formula of the monomer, for the product appears to be a polymer; and the polymer is suggested to be of the following network structure:



XC111

CONCLUSION

It has been found in this work that 3-acetyl and 4-acetyl, as well as 3-benzoyl and 4-benzoyl pyridines are strong enough Lewis bases to bind with most of the methyltin, phenyltin, and stannic chlorides to give, with the exception of trimethyltin chloride that forms 1:1 adducts, 1:2 Lewis acid: Lewis base adducts. Infrared spectroscopy has indicated that the Lewis bases bind through their N, in preference to their O atoms ($Eq^{ns}_{=}$ xvi - xxiv).

The p.m.r. spectra of the pyridine adducts of dimethyltin, methyltin, stannic, phenyltin and diphenyltin chlorides have been run - perhaps for the first time. P.m.r. spectroscopy has indicated unsubstituted pyridine to be a stronger Lewis base than the keto substituted pyridines.

The 2-benzoylpyridine adducts of methyltintrichloride, stannic chloride, and phenyltintrichloride have been synthesized. Elemental analysis and spectroscopy have shown them to be 1:1 adducts; the Lewis base acting as a bidenatate ligand)$Eq^{ns}_{=}$ xxvi - xxviii). 2-Pyridine carboxaldehyde too, although not a very stable Lewis base has been found to be capable of forming a stable isolable 1:1 adduct with phenyltin trichloride. Spectroscopy has shown it also to be a bidentate ligand, binding with its N and O atoms.

2-Acetylpyridine has been found to react with the phenyltin and stannic chlorides to give products, the structures of which are yet to be clearly understood. With the methyltin chlorides, 2-acetylpyridine reacts in a manner yet to be understood.

The J_{Sn-C-H} has been found to be a suitable parameter for determining the relative basicities of Lewis bases, especially of an aromatic Lewis base and its para-substituted derivatives. The binding strength of pyridine Lewis bases have been found to be near linearly related to the basicity values of the Lewis bases. The higher the basicity of the Lewis base, the higher its binding strength to a Lewis acid, it has been found that the increase in the J Sn-C-H value of a methyltin chloride in a given solution at a given temperature, as it complexes with a pyridine Lewis base, is almost directly proportional to the basicity of the Lewis base; departure from linearity existing only for the very weak Lewis bases. This implies that the relative basicities of Lewis bases, whose strengths might not be easily determinable by titration, could now be determined by this method. Methyltin adducts of such Lewis bases are prepared. Equimolar amounts of the adducts are dissolved in some suitable solvent, and the J Sn-C-H values for equal concentrations of the solutions at the same temperature are measured by taking their p.m.r. spectra. The basicity of the Lewis base is proportional to the increase in the J Sn-C-H value of the

adduct solution. This seemingly new method, is applicable only to Lewis bases which do not have substituents in positions such that they would sterically influence the Lewis base in adduct formation.

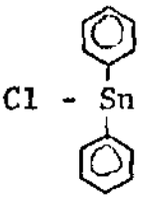
The synthesis of organotin carboxylate adducts, via nucleophilic substitution reactions of the organotin halide pyridine adducts, has been undertaken. Perhaps for the first time, some keto-substituted pyridine adducts of trimethyltin and dimethyltin trifluoroacetates have been prepared. They have been found to be 1:1 adducts. (Eq^{ns} xli, xlii).

The phenyltin chloride pyridine adducts have been found to react with silver trifluoroacetates to give, not phenyltin trifluoroacetate adducts, but products appearing to be trifluoroacetate salts of the Lewis bases. This led to the trial of the reaction between silver trifluoroacetate and the phenyltin chlorides.

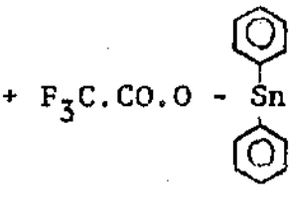
Triphenyltin trifluoroacetate has been prepared in better yield by a new, simple route:

$$Ph_3SnCl + AgO.CO.CF_3 \xrightarrow[\text{acetone}]{\text{dry}} AgCl\downarrow + Ph_3SnO.CO.CF_3$$

A potential radical initiator, especially in polymerization reactions, seems to have been discovered. Ph_2SnCl_2 has been found to react with $AgO.CO.CF_3$ in dried acetone to give an oil, $Ph_2Sn(O.CO.CF_3)_2$, storable in acetone, which on warming, produces radicals. This 'oil' has been found to undergo a reaction, seemingly new, in non-polar media to give what all available evidences have indicated to be a new binuclear compound, 1,2 - diphenyl - 1,1,2,2-tetrakis-trifluoroacetoxyditin.

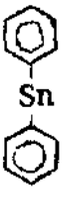


$$Cl - Sn - Cl + 2AgO.CO.CF_3 \xrightarrow[\text{acetone}]{\text{dry}} 2AgCl\downarrow$$



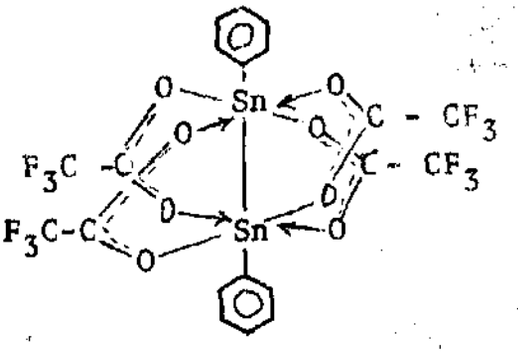
$$+ F_3C.CO.O - Sn - O.CO.CF_3$$

...1v



$$2CF_3.CO.O - Sn - O.CO.CF_3 \xrightarrow{\text{40-60 Petrol}}$$

LXXX111



xc1



$$+ 2$$

...1ix

The reaction is thought to occur by radical mechanism.

Phenyltin trichloride has been found to react with $AgO.CO.CF_3$ to produce what all available evidences have suggested to be $PhSn(O.CO.CF_3)_3$, which is thought to exist in the solid form as a polymer.

EXPERIMENTAL

The organotin and Lewis base chemicals used were either synthesized, or bought from Aldrich. All chemicals used were of high purity.

All gas evacuations were done using the Speedivac Rotary Pump that evacuates to as low a pressure as 60 Nm^{-2} (0.5 torr).

N.m.r. spectra were run with a varian T-60 spectrometer, at an operating temperature of about 38°C.

All melting points (uncorrected) were taken with the Gallenkamp Melting Point Apparatus. Temperatures were recorded in centigrades.

Elemental microanalyses for C, H, Cl, and N were carried out by the Scandianvian Microanalytical Laboratories.

Trimethyltin chloride - 4 - acetylpyridine.

Trimethyltin chloride (2.0g, 0.01M) in carbon tetrachloride (15ml) and 4-acetylpyridine (1.21g, 0.01M) in carbon tetrachloride (10ml) were mixed. The resulting clear yellow solution was cooled overnight. The resulting light brownish crystals were removed by filtration, washed with a little cold carbon tetrachloride, and dried in a dessicator. The product was recrystallised twice from carbon tetrachloride (2.17g, 67.60%). m.p 55 - 56°.

Elemental analysis:

Formula: $C_{10}H_{16}ClNOSn$

Calc. : C,37.40; H,4.99; N,4.37, Sn, 37.07%.

Found : C,37.69; H,5.00; N,4.43, Sn,37.25%.

n.m.r. : (CD_3COCD_3 + TMS).

δ0.61 (9H, S, 3 x CH_3)

δ2.65 (9H, S, CH_3.Co-)

δ7.90 (2H, d, pyridyl C3H and C5H)

δ9.10 (2H, d, pyridyl C2H and C6H)

i.r. (kBr and CsI disc)

3030 cm^{-1} (vw) C - H arom

1695 cm^{-1} (s) >C = O

1595 cm^{-1} (s) C = C arom. (Py)

790 cm^{-1} (m) Sn - Me (Rock)

Tin Analysis.

A small amount of the organotin compound was weight into a clean, dry crucible, to which was added about 1ml of $C.H_2SO_4$. The cruicible was placed on a clay tripod on a tripod stand and heated gently from the top with a burner flame. The mixture fumed. The heating was continued until all the liquid dried. The heating point on the crucible was then gradually lowered to the bottom of the crucible, and the heating continued for about one hour, during which all the carbonaceous content of the crucible burnt off, leaving behind a yellowish powder. The crucible was allowed to cool in a desiccator, and the powder was weighed as SnO_2. The Sn content of the organotin was then calculated.

Trimethyltin chloride-4-benzoylpyridine.

Trimethyltin chloride (2.0g, 0.01M) in carbon tetrachloride (15ml) and p-benzoylpyridine (1.84g, 0.01M) in carbon tetrachloride (20 ml) were mixed. The resulting clear yellow solution was cooled (at 25°C) for 48 hours. These were removed by filtration, washed with a little cold carbon tetrachloride, and dried in a desiccator for 48 hours. The product (3.20g) was recrystallised trice from carbon tetrachloride. m.p. 65 - 66°.

Elemental analysis:

Formula: $C_{15}H_{18}ClNOSn$

Calc. : C,47.10; H, 4.71; N, 3.66, Sn, 31.05%

Found: C,47.34; H,4.73; N,3.85; Sn, 31.50%

n.m.r. : (CCl_4 + TMS)

δ0.62 (9H, s, 3 x CH_3)

δ7.60 (5H, m, phenyl)

δ7.90 (2H, q, pyridyl C3H and C5H)

δ9.10 (2H, q, pyridyl C3H and C6H)

i.r. : (kBr and CsI discs)

3040 cm^{-1} (vw) C - H arom.

1660 cm^{-1} (s) C = O

1595 cm^{-1} (s) C = O arom. (Py)

790 cm^{-1} (m) Sn - Me (Rock)

Dimethyltindichloride-bis-4-acetylpyridine.

Dimethyltindichloride (2.21g, 0.01M) in dichloromethane (50 ml) and 4 - acetylpyridine (2.42g, 0.02M) also in dichloromethane (50 ml) were mixed. The resulting clear solution was left to stand for 24 hours. Light yellowish granular crystals precipitated out. These were filtered off, washed with dichloromethane (50 ml) and dried in vacuo (3.70g). The product was recrystallised three times from dried acetone. m.p. 117 - 118°.

Formula: $C_{16}H_{20}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc : C, 41.60; H, 4.36; N, 6.07; Sn, 25.70%

Found : C, 41.84; H, 4.45; N, 5.76; Sn, 25.79%

n.m.r.: ($CD_3.CO.CD_3$ + TMS)

δ1.20 (6H, s, 2 x CH_3);

δ2.63 (6H, s, 2 x $CO.CH_3$)

δ7.80 (4H, d, 2 x pyridyl C3H and C5H)

δ9.26 (4H, d, 2 x pyridyl C2H and C6H)

i.r. : (KBr and CsI discs)

3030 cm^{-1} (w) C - H arom.

1700 cm^{-1} (s) C = O

1595 cm^{-1} (s) C = C arom (Py)

795 cm^{-1} (m) Sn - Me (Rock)

Dimethyltindichloride-bis-3-acetylpyridine was similarly prepared from dimethyltindichloride (2.21g, 0.01M) and 3-acetylpyridine (2.42g, 0.02M). The product was recrystallised thrice from dried acetone.

Yield, 3.50g, 75.59%

m.p. 109 - 110°

Formula: $C_{16}\ H_{20}\ Cl_2\ N_2\ O_2\ Sn$.

Elemental Analysis:

Calc. : C,41.60; H,4.36; N,6.07; Sn,25.79%

Found : C,41.90; H,4.41; N,5.95; Sn,25.75%

n.m.r.: ($CD_3.CO.CD_3$ + TMS)

δ1.2 (6H, s, 2 x Sn - CH_3)

δ2.6 (6H, s, 2 x -$CO.CH_3$)

δ7.5 (2H, q, pyridyl 2 x C5H)

δ8.3 (2H, d, pyridyl 2 x C4H)

δ8.8 (2H, d, pyridyl 2 x C6H)

δ9.2 (2H, s, pyridyl 2 x C2H)

i.r.: (KBr and CsI discs)

3030 cm^{-1}	(w)	C - H arom.
1680 cm^{-1}	(s)	C = O
1585 cm^{-1}	(s)	C = C arom (Py)
795 cm^{-1}	(m)	Sn - Me Rock

Dimethyltindichloride bis-4-benzoylpyridine.

Dimethyltin dichloride (2.21g, 0.01M) in dichloromethane (50 ml) and 4-benzoylpyridine (3.68g, 0.02M) also in dichloromethane (50 ml) were mixed. The resulting clear yellow solution yielded light yellowish crystals on standing overnight at room temperature. The crystals were removed by filtration, washed with more cold solvent (100 ml), and dried in vacuo. (5.10g). The product was recrystallised three times from dried acetone.

m.p. 158 - 160°

Formula: $C_{26}H_{24}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,53.27; H,4.10; N,4.78; Sn,20.26%

Found: C,53.35; H,4.17; N,4.75; Sn,20.40%.

n.m.r.: (d-DMSO + TMS)

δ1.15 (6H, s, 2 x CH_3)

δ7.80 (14H, m, 2 x -CO.Ph + 2 x 2 pyridyl M-H)

δ9.00 (4H, q, 2 x 2 pyridyl O - H)

i.r.: (KBr and CsI discs)

3060 cm^{-1}	(w)	C - H arom.
1660 cm^{-1}	(s)	>C = O
1600 cm^{-1}	(s)	C = C arom.(Py)
790 cm^{-1}	(m)	Sn - Me (Rock)

Dimethyltindichloride bis-3-benzoylpyridine. was similarly prepared from dimethylti-dichloride (2.21g, 0.01M) and 3-benzoylpyridine (3.68g, 0.02M). The product (5.21g) was recrystallised twice from dried acetone.

m.p. 109 - 111°

Formula: $C_{26}H_{24}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,53.27; H,4.10; N,4.78; Sn,20.26%

Found: C,53.37; H,4.14; N,4.73; Sn,20.46%

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ1.30 ppm (6H, s, Sn - CH_3)

δ7.80 " (12H, m, 2 x 5 phenyl H + 2 x pyridyl C5H)

δ8.30 " (2H, h, 2 x pyridyl C4H)

δ9.10 " (2H, q, 2 x pyridyl C6H)

δ9.20 " (2H, d, 2 x pyridyl C2H)

i.r.: (KBr and CsI dis s)

3060 cm^{-1} (w) C - H arom

1660 cm^{-1} (s) C = O

1600 cm^{-1} (s) C = C arom. (Py)

795 cm^{-1} (m) Sn - Me (Rock)

Methyltintrichloride bis-4-acetylphyridine.

Recrystallised (from dichloromethane) methyltintrichloride (2.40g, 0.01M) in warm dichloromethane (30 ml) and 4 - acetylpyridine (2.42g, 0.02M) also in warm dichloromethane (30 ml) were mixed. A clear light yellowish solution was obtained. This brought forth light yellow flakes of crystals on standing at room temperature for an hour. The product was filtered off, washed a few times with dichloromethane, and dried in vacuo. (3.90g) The product was recrystallised twice from acetone. m.p. 138 - 140° decomp.

Formula: $C_{15}H_{17}Cl_3N_2O_2Sn$

Elemental Analysis:

Calc.: C,37.33; H,3.53; N,5.81; Sn,24.61

Found: C,36.92; H,3.59; N,5.65; Sn,24.80

n.m.r.; (d-DMSO + TMS)

1.05 ppm (3H, s, Sn - CH_3)

2.70 " (6H, s, -CO.CH_3)

8.00 " (4H, q, 2 x pyridyl C_3H and C5H)

9.00 " (4H, q, 2 x pyridyl C2H and C6H)

i.r.:KBr and CsI discs) 3040 cm^{-1} (w) C - H arom.

1700 cm^{-1} (s) C = O

1600 cm^{-1} (s) C = C arom (Py)

795 cm^{-1} (w) Sn - Me (Rock)

295 cm^{-1} (s) Sn - Cl

Methyltintrichloride bis-3-acetylpyridine was similarly prepared from recrystallised methyltin trichloride (2.40g, 0.01M) and 3-acetylpyridine (2.42g, 0.02M). Crystallisation of the product began almost immediately after the reactants were mixed. The product (4.10g) was washed five times with boiling dichloromethane (5 x 20 ml), and dried in vacuo.

m.p. 185 - 187° decomp.

Formula: $C_{15}H_{17}Cl_3N_2O_2Sn$.

Elemental Analysis:

Calc.: C,37.33; H,3.53; N,5.81; Sn,24.61

Found: C,37.10; H,3.61; N.5.70; Sn,24.87

n.m.r.: (d-DMSO + TMS)

1.05 ppm (3H, s, Sn - CH_3)

2.70 " (6H, s, -CO.CH_3)

7.70 " (2H, q, 2 x pyridyl C5H)

8.40 " (2H, h, 2 x pyridyl C4H)

9.00 " (2H, q, 2 x pyridyl C6H)

9.40 " (2H, d, 2 x pyridyl C2H)

i.r.: (KBr and CsI discs)

3050 cm^{-1}	(w)	C - H arom.
1665 cm^{-1}	(s)	C = O
1595 cm^{-1}	(s)	C = C arom. (Py)
795 cm^{-1}	(w)	Sn - Me (Rock)
300 cm^{-1}	(s)	Sn - Cl

Methyltintrichloride bis-4-benzoylpyridine.

Methyltintrichloride (2.40g, 0.01M) in warm dichloromethane (50 ml) and 4-benzoylpyridine (3.68g, 0.02M) also in warm dichloromethane (50 ml) were mixed. A clear greenish-yellow solution was obtained. This yielded, on standing overnight at room temperature, greenish-yellowish crystals. The product was filtered off, washed six times with boiling dichloromethane (6 x 20ml) and dried in vacuo. (4.95g, 81.41%)

m.p. 300 - 303°

Formula: $C_{25}H_{21}Cl_3N_2O_2Sn$

Elemental Analysis:

Calc.: C,49.41; H,3.62; N 4,1; Sn,19.58

Found: C,49.50; H,3.65; N,4.60; Sn,19.85

n.m.r.: (d-DMSO + TMS)

δ1.02 (3H, s, Sn - Me)

δ7.80 (14H, m, 2 x -CO-Ph + 2 x 2 pyridyl-M-H)

δ9.00 (4H, s, 2 x pyridyl - O - H)

i.r.: (KBr and CsI discs)

3040 cm^{-1}	(w)	C - H arom
1660 cm^{-1}	(s)	C = O
1600 cm^{-1}	(s)	C = C arom (Py)
795 cm^{-1}	(w)	Sn - Me (Rock)
292 cm^{-1}	(s)	Sn - Cl

Methyltintrichloride bis-3-benzoylpyridine was similarly prepared from methyltintrichloride (2.40g, 0.01M) and 3-benzoylpyridine (3.68g, 0.02M). The product yellowish granular crystals, was dried in vacuo. (5.0g, 82.24%).

m.p 163 - 164°

Formula: $C_{25}H_{21}Cl_3N_2O_2Sn$

Elemental Analysis:

Calc.: C,49.41; H,3.62; N,4.61; Sn,19.58

Found: C,49.52; H,3.66; N,5.68; Sn,19.82.

n.m.r.: (d-DMSO + TMS)

1.0 ppm (3H, s, Sn - CH_3)

7.8 " (12H, m, 2 x 5 phenyl H + 2 x pyridyl C5H)

8.2 " (2H, h, 2 x pyridyl C4H)

8.95 " (4H, q, 2 x pyridyl C2H + 2 x pyridyl C6H)

i.r.: (KBr and CsI discs)

3050 cm^{-1}	(w)	C - H arom.
1665 cm^{-1}	(s)	C = O
1595 cm^{-1}	(s)	C = C arom (Py)
795 cm^{-1}	(w)	Sn - Me Rock
300 cm^{-1}	(s)	Sn - Cl

Stannic Chloride bis-4-acetylpyridine

Stannic chloride (3.26g, 0.0125M, 1.4ml) in cold dichloromethane (100 ml) and 4-Acetylpyridine (3.0g, 0.025M) in cold dichloromethane (100 ml) were slowly mixed, with ice cooling. A clear yellow solution was obtained. On cooling overnight, this yielded light yellowish crystals. The product was filtered off, washed six times with warm dichloromethane (6 x 30 ml) and dried in vacuo (5.5g, 88%)

m.p. 173 - 175°

Formula: $C_{14}H_{14}Cl_4N_2O_2Sn$

Elemental Analysis:

Calc.: C,33.42; H,2.79; Cl,28.25; N,5.57; Sn,23.61%

Found: C,33.12; H,2.81; Cl,28.62; N,5.42; Sn,23.91%

n.m.r. (d.DMSO + TMS)

δ2.70 (6H, s, 2 x $CO.CH_3$)

δ8.0 (4H, q. 2 x 2 pyridyl- M-H)

δ9.0 (4H, q. 2 x 2 pyridyl - O-H)

i.r.: (KBr and CsI discs)

3060 cm^{-1}	(m)	C - H arom
1700 cm^{-1}	(s)	C = O
1610 cm^{-1}	(s)	C = C arom (Py)
335 cm^{-1}	(s)	Sn - Cl

Stannic Chloride bis-3-acetylpyridine was similarly prepared from stannic chloride (3.26g, 0.0125M, 1.40ml) and 3-acetyl-pyridine (3.0g, 0.025M). The product was dried in vacuo (5.70g, 91%)

m.p. 233 - 236°(decomp.)

Formula: $C_{14}H_{14}Cl_4N_2O_2Sn$

Elemental Analysis:

Calc.: C,33.42; H,2.79; Cl,28.25; N,5.57; Sn,23.61%

Found: C,33.02; H,2.86; Cl,28.57; N,5.43; Sn,23.98.

n.m.r.: (d-DMSO + TMS)

δ2.65 (6H, s, 2 x $-CO.CH_3$)

δ7.70 (2H, q, 2 x pyridyl C5H)

δ8.50 (2H, m, 2 x pyridyl C4H)

δ8.90 (2H, m, 2 x pyridyl C6H)

δ9.25 (2H, d, 2 x pyridyl C2H)

i.r.: (KBr and CsI discs)

3040 cm^{-1}	(m)	C - H arom. (Py)
1660 cm^{-1}	(s)	>C = O
1595 cm^{-1}	(s)	C = C
350 cm^{-1}	(s)	Sn - Cl

Tetrachlorotin bis-4-benzoylpyridine.

Stannic chloride (2.61g, 0.01M, 1.16ml) in dichloromethane (100 ml) and 4.benzoylpyridine (3.68g, 0.02M) in dichloromethane (100 ml) were slowly mixed, with ice cooling. A greenish yellowish solution was obtained. This was concentrated to 50mls and cooled overnight. Greenish yellow needles of crystals were yielded. The product was removed, washed five times with boiling dichloromethane, (5 x 30 ml) and dried in vacuo (4.9g, 77.9%)

m.p. 257 - 260° (decomp.)

Formula: $C_{24}H_{18}Cl_4N_2Sn$

Elemental Analysis:

Cals.: C,45.96; H.2.87; Cl,22.66; N,4.46; Sn,26.75.

Found: C,45.85; H,2.85; Cl,22.81; N,4.48; Sn,26.84.

n.m.r.: (d-DMSO + TMS)

δ7.90ppm (14H, m, 2 x -CO.Ph + 2 x 2 pyridyl-m-H)

δ9.02 " (4H, q, 2 x 2 pyridyl-O-H)

i.r. (KBr and CsI discs)

3070 cm^{-1}	(w)	C - H arom.
1665 cm^{-1}	(s)	C = O
1600 cm^{-1}	(s)	C = C arom. (Py)
335 cm^{-1}	(s)	Sn - Cl

Tetrachlorotin bis-3-benzoylpyridine was similarly prepared from stannic chloride (2.61g, 0.01M, 1.16ml) and 3-benzoylpyridine (3.68g, 0.02M). The reaction mixture required no concentration; overnight cooling yielded needles of greenish yellow crystals, which were removed by filtration, washed five times with boiling dichloromethane (5 x 30ml) and dried in vacuo (5.1g, 81%)

m.p. 239 - 242° (decomp.)

Formula: $C_{24}H_{18}Cl_4N_2O_2Sn$

Elemental Analysis:

Calc.: C,45.96; H,2.87; Cl,22.66; N,4.46; Sn,26.75.

Found: C,45.82; H,2.83; Cl,22.85; N,4.47; Sn,26.87.

i.r.: (KBr and CsI discs)

3060 cm^{-1} (w)	C - H arom.
1660 cm^{-1} (s)	C = O
1600 cm^{-1} (s)	C = C arom (Py)
345 cm^{-1} (s)	Sn - Cl

Phenyltintrichloride bis-4-Acetylpyridine.

Phenyltintrichloride (1.5g, 0.005M) in hot carbon tetrachloride (50 ml) and 4-Acetylpyridine (1.21g, 0.01M) also in hot CCl_4 (50ml) were mixed. A clear yellowish solution was obtained, which, on cooling to room temperature, yielded light yellow granular crystals. The mass of crystals was filtered off after cooling the reaction mixture at about 5°C for two hours, washed four times with hot CCl_4 (4 x 20ml) and once with cold CH_2Cl_2 (20ml), and dried in vacuo (2.1g, 77.2%)

m.p. 140 - 143° (decomp.)

Formula: $C_{20}H_{19}Cl_3N_2O_2Sn$

Elemental Analysis:

Calc.: C,44.10; H,3.49; N,5.15; Sn,21.81%

Found: C,44.24; H,3.64; N,4.89; Sn,22.10%

n.m.r.: (d-DMSO + TMS)

δ2.65 ppm (6H, s, 2 x $-CO.CH_3$)

7.40 " (3H, m, phenyl C3, 4,5H)

7.90 " (6H, m, phenyl C2, 6H + 2 x pyridyl C3,C5 H)

8.95 " (4H, q, 2 x pyridyl C2, C6 H)

i.r. (KBr and CsI discs)

3030 cm^{-1}	(w)	C - H arom.
1700 cm^{-1}	(s)	C = O
1595 cm^{-1}	(s)	C = C arom. (Py)
1060 cm^{-1}	(m)	Sn - Ph
300 cm^{-1}	(s)	Sn - Cl

Similarly prepared was Phenyltin trichloride bis-3-acetylpyridine from phenyltintrichloride (1.51g, 0.005M) and 3-acetylpyridine (1.21g, 0.01M). The product (granular crystals) was tried in vacuo (2.20g, 80.10%)

m.p. 133 - 135°

Formula: $C_{20}H_{19}Cl_3N_2O_2Sn$.

Elemental Analysis:

Calc.: C,44.10; H,3.49; N.5.15; Sn,21.81%

Found: C,44.15; H,3.55; N,4.97; Sn,22.05%

n.m.r.: (d-DMSO + TMS)

2.65 (6H, s, 2 x $CO.CH_3$)

7.60 (7H, m, phenyl H + 2 x pyridine C5H)

8.40 (2H, h, 2 x pyridyl C4H)

8.95 (2H, q, 2 x pyridyl C6H)

9.30 (2H, d, 2 x pyridyl C2H)

i.r. (KBr and CsI discs)

3030 cm^{-1} (w) C - H arom.

1680 cm^{-1} (s) C = O

1590 cm^{-1} (s) C = C arom. (Py)

1060 cm^{-1} (w) Sn - Ph

325 cm^{-1} (s) Sn - Cl

Phenyltin trichloride bis-4-benzoylpyridine.

Phenyltin trichloride (1.51g, 0.005M) in warm dichloromethane (30 ml) and 4-benzoylpyridine (1.84g, 0.01M) also in warm dichloromethane (30 ml) were mixed. A clear solution was obtained. This yielded greenish yellowish granular crystals on standing at room temperature. The mixture was cooled at about 5°C for two hours, and the product was then filtered off, washed four times with boiling CH_2Cl_2 (4 x 20ml) and dried in vacuo. (2.85g, 85.07%)

m.p. 255 - 257° (decomp.)

Formula: $C_{30}H_{23}Cl_3N_2O_2Sn$.

Elemental Analysis:

Calc.: C,53.88; H,3.44; N,4.19, Sn,17.76%

Found: C,53.95; H,3.52; N,4.08; Sn,18.10%

n.m.r.: (d$_6$-DMSO + TMS)

δ7.70 ppm (19H, m, Sn-Phenyl 5H + 2xCO-Phenyl 5H + 2 x 2 phyridyl C3H and C5H)

δ9.00 ppm (4H, q, 2 x 2 pyridyl C2H and C6H)

i.r.: (KBr and CsI discs)

3030 cm^{-1}	(w)	C - H arom.
1665 cm^{-1}	(s)	C = O
1595 cm^{-1}	(s)	C = C arom. (Py)
1065 cm^{-1}	(m)	Sn - Ph
300 cm^{-1}	(s)	Sn - Cl

Prepared in a similar way was phenyltin trichloride-3-benzoylpyridine from phenyltin trichloride (1.51g, 0.005M) and 3-benzoylpyridine (1.84g, 0.01M). The product was dried in vacuo. (2.90g, 86.57%).

m.p.: 95 - 97°

Formula: $C_{30}H_{23}Cl_3N_2O_2Sn$

Elemental Analysis:

Calc.: C,53.88; H,3.44; N,4.19; Sn,17.76%

Found: C,53.96; H,3.60; N,4.21; Sn,18.05%

n.m.r.: (d-DMSO + TMS)

δ7.75 (17H, m, Sn-phenyl 5H + 2x -CO.phenyl 5H + 2x pyridyl C5H)

δ8.20 (2H, h, 2 x pyridyl C4H)

δ9.00 (4H, q, 2 x pyridyl C6H + 2x pyridyl C2H)

i.r.: (KBr and CsI discs)

3030 cm^{-1}	(w)	C - H arom.
1660 cm^{-1}	(s)	C = O
1590 cm^{-1}	(s)	C = C arom. (Py)
1060 cm^{-1}	(w)	Sn - Ph
325 cm^{-1}	(s)	Sn - Cl

Diphenyltindichloride bis-4-acetylpyridine.

Diphenyltindichloride (1.72g, 0.005M) in CH_2Cl_2 (30ml) and 4-acetylpyridine (1.21g, 0.01M) in CH_2Cl_2 (30 ml) were mixed. A clear yellowish solution was obtained, which yielded light yellow flakes of crystals on cooling overnight. The mass of crystals was filtered off, washed with CH_2Cl_2 (50 ml) and dried in vacuo. (2.10g). The product was recrystallised twice from acetone.

m.p. 94 - 96°

Formula: $C_{26}H_{24}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,53.27; H,4.10; N,4.78; Sn,20.26%

Found: C,53.01; H,4.05; N,4.68; Sn,20.48%

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ2.60 ppm (6H, s, 2 x $-CO.CH_3$)

δ7.35 " (6H, m, 2 x Sn-Phenyl C3,4,5H)

δ7.80 " (8H, m, 2 x Sn-phenyl C2, 6H + 2 x pyridyl C3,5H)

δ8.75 " (4H, q, 2 x pyridyl C2,6H)

i.r.: (KBr and CsI discs)

3045 cm^{-1}	(w)	C - H arom.
1700 cm^{-1}	(s)	C = O
1600 cm^{-1}	(s)	C = C arom (Py)
1065 cm^{-1}	(m)	Sn - Ph
270 cm^{-1}	(s)	Sn - Cl

Diphenyltindichloride bis-3-acetylpyridine was prepared in a similar way from diphenyltindichloride (1.72g, 0.005M) and 3-acetylpyridine (1.21g, 0.01M). The product was dried in vacuo (2.07g); it was recrystallised twice from acetone.

m.p. 62 - 64°

Formula: $C_{26}H_{24}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,53.27; H,410; N,4.78; Sn,20.26%

Found: C,52.98; H,4.14; N,4.70; Sn,20.51%

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ2.60 (6H, s, 2 x $-CO.CH_3$)

δ7.40 (10H, m, 2 x Sn-Pyenyl 5H)

δ7.90 (2H, m, 2 x pyridyl C5H)

δ8.35 (2H, h, 2 x pyridyl C4H)

δ8.80 (2H, q, 2 x pyridyl C6H)

δ9.10 (2H, d, 2 x Pyridyl C2H)

i.r. (KBr and CsI discs)

3030 cm^{-1}	(w)	C - H arom.
1680 cm^{-1}	(s)	C = O
1600 cm^{-1}	(s)	C = C arom (Py)
1065 cm^{-1}	(w)	Sn - Ph
280 cm^{-1}	(s)	Sn - Cl

Diphenyltindichloride bis-4-benzoylpyridine.

Diphenyltindichloride (1.72g, 0.005M) in warm CH_2Cl_2 (50 ml) and 4-benzoylpyridine (1.84g, 0.01M) also in warm CH_2Cl_2 (50ml) were mixed. A clear greenish yellow solution was obtained. This yielded flakes of greenish yellowish crystals on cooling overnight. The mass of crystals was removed, washed twice with CH_2Cl_2 (2 x 25ml), and dried in vacuo (2.80g). The product was recrystallised thrice from acetone.

m.p. 118 - 120°

Formula: $C_{36}H_{28}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,60.87; H,3.95; N,3.95; Sn,16.72%

Found: C,60.56; H,4.04; N,3.89; Sn,16.94%

n.m.r.: ($CD_3.Co.CD_3$ + TMS)

δ7.70 ppm (24H, m, 2 x Sn-phenyl 5H,
+ 2 x -CO.phenyl 5H
+ 2 x pyridyl C3,5H)

δ9.05 ppm (4H, q, 2 x pyridyl C2,6H)

i.r.: (KBr and CsI discs)

3040 cm^{-1}	(w)	C - H arom.
1660 cm^{-1}	(s)	C = O
1590 cm^{-1}	(s)	C = C arom. (Py)
1065 cm^{-1}	(m)	Sn - Ph
270 cm^{-1}	(s)	Sn - Cl

Diphenyltindichloride bis-3-benzoylpyridine was similarly prepared from diphenyltindichloride (1.72g, 0.005M) and 3.benzoylpyridine (1.84g, 0.01M). The product was dried in vacuo. (2.65g) and then recrystallised three times from acetone.

m.p. 115 - 117°

Formula: $C_{36}H_{28}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,60.87; H,3.95; N,3.95; Sn,16.72%

Found: C,60.64; H,3.98: N,3.90; Sn,16.85%

n.m.r.: ($CD_3.CO.CD_3$ + TMS)

δ7.80 (22H, m, 2 x Sn-phenyl 5H + 2x -CO phenyl 5H + 2x pyridyl C5H)

δ8.40 (2H, h, 2 x pyridyl C4H)

δ9.00 (4H, m, 2 x pyridyl C2, 6H)

i.r.: (KBr and CsI discs)

3040 cm^{-1}	(w)	C - H arom.
1660 cm^{-1}	(s)	>C = O
1590 cm^{-1}	(s)	C = C arom. (Py)
1075 cm^{-1}	(m)	Sn - Ph
275 cm^{-1}	(s)	Sn - Cl

Methyltintrichloride 2-benzoylpyridine.

Methyltin trichloride (2.40g, 0.01M) in dichloromethane (40ml) and 2-benzoylpyridine (3.68g, 0.03M) also in dichloromethane (40ml) were mixed. The resulting yellowish solution was boiled for five minutes and left to stand overnight. Bright greenish yellow crystals were formed. The product was filtered off, washed three times with boiling dichloromethane, and dried in vacuo. (3.50g, 82.3%)

m.p., 182 - 183°

Formula: $C_{13}H_{12}Cl_3NOSn$

Elemental Analysis:

Calc.: C,36.86; H,2.84; N,3.31; Sn,28.01%

Found: C,36.85; H,2.88; N,3.27; Sn,28.35%

n.m.r.: (d-DMSO + TMS)

δ1.0 ppm (3H, s, $Sn-CH_3$)

δ7.7 " (4H, m, Ph.CO.C3,4,5H + pyridyl C4H)

δ8.1 ppm (4H, m, Ph-CO.C2,6H + pyridyl C3, 5H)

i.r.: (KBr and CsI discs)

3060 cm^{-1}	(w)	C - H arom
1605 cm^{-1}	(s)	C = O coordinated
1590 cm^{-1}	(s)	C = C arom. (Py)
795 cm^{-1}	(w)	Sn - Me

Tetrachlorotin 2-benzoylpyridine.

Stannic chloride (2.61g, 0.01M, 1.16ml) in cold dichloromethane (100ml) and 2 benzoylpyridine (3.68g, 0.02M) also in cold dichloromethane (100ml) were mixed with ice cooling. A clear yellow solution was obtained. This was concentrated to 50ml, and cooled overnight. Greenish yellow crystals were formed. The mass of crystals was removed by filtration, washed four times with warm dichloromethane (4 x 30ml), and dried in vacuo (4.0g, 89.90%).

m.p. 271 - 273° (decomp.)

Elemental Analysis:

Formula: $C_{12}H_9Cl_4NOSn$

Calc.: C,32.46; H,2.03; Cl,32.01; N,3.16; Sn,26.75%

Found: C,32.57; H,2.10; Cl,32.32; N,3.06; Sn,26.80%

n.m.r. (d-DMSO + TMS)

δ7.65 ppm (4H, m, phenyl 3,4,5H + pyridyl 4H)

δ8.10 " (4H, m, phenyl 2,5H + pyridyl 3,5H)

δ8.95 " (1H, d, pyridyl 6H)

i.r. (KBr and CsI discs)

3060 cm^{-1} (w) C - H arom

1600 cm^{-1} (s) >C = O coordinated

1600 cm^{-1} (s) C = C arom. (Py)

325 cm^{-1} (s) Sn - Cl

Phenyltintrichloride -2-benzoylpyridine.

Phenyltintrichloride (3.02g, 0.01M) in warm dichloromethane (30ml) and 2-benzoylpyridine (3.68g, 0.02M) also in warm dichloromethane (30ml) were mixed. A clear yellowish solution was obtained. This yielded light yellowish crystals on cooling. The mass of crystals was filtered off, washed four times with warm dichloromethane (4 x 20ml), and dried in vacuo (3.75g, 77.2% calculated for 1:1 adduct).

m.p. 209 - 211° (decomp.)

Elemental Analysis:

Formula, $C_{18}H_{14}Cl_3NOSn$

Calc.: C,44.52; H,2.89; Cl,2.91; N,2.89; Sn,24.46%

Found: C,44.29; H,2.79; N,2.83; Sn,24.78%

n.m.r.: (d-DMSO + TMS)

δ7.4 ppm (3H, m, Sn - Ph 3,4,5CH)

δ7.8 " (5H, m, Sn-Ph 2,6 CH + Ph-CO.3,4,5CH).

δ8.1 " (5H, m, Ph-CO.2,6,CH + pyridyl 3,4,5 CH)

δ8.95 " (1H, d, pyridyl C6H)

i.r. (KBr and CsI discs)

3100 cm^{-1} (w) C - H arom.

1610 cm^{-1} (s) C = O coordinated

1595 cm^{-1} (s) C = C arom. (py)

1065 cm^{-1} (w) Sn.Ph

320 cm^{-1} (s) Sn - Cl

Reaction of dimethyltindichloride with 2-Acetylpyridine.

Dimethyltindichloride (2.21g, 0.01M) in cold dichloromethane (50ml) and 2-acetylpyridine (2.42g, 0.01M) also in cold dischloromethane (50ml) were mixed. The clear solution obtained was left to stand at room temperature for two days. A mass of colourless crystals was deposited. This was removed, washed with dichloromethane (50ml) and dried in vacuo. (2.56g). The product was recrystallised twice from acetonitrile. m.p. 185° decomp.

Elemental Analysis:

Calc.: for $Me_2SnCl_2.(2\text{-Ac.Py})_2$:

C,41.60; H,2.36; N,6.07; Sn,25.75%

FOUND: C,27.33; H,3.48; N,3.17; Sn,39.8%

n.m.r. (d.DMSO + TMS)

δ1.13 ppm (s, Sn - CH_3)

δ2.10 " s

δ2.40 " s

δ2.70 " s, -CO - CH_3

δ8.00 ppm m broad. Pyridyl?

i.r. KBr and CsI discs.

3075 cm^{-1} (m) C - H arom.

1640 cm^{-1} (s) >C = O coordinated?

1600 cm^{-1} (s) C = C arom. (Py)

795 cm^{-1} (s) Sn - Me

Reaction of Methyltintrichloride with 2-Acetylpyridine.

Methyltintrichloride (2.40g, 0.01M) in warm dichloromethane (50ml) and 2-Acetyl Py (2.42g, 0.02M) also in warm dichloromethane (50ml) were mixed. A clear yellowish solution was obtained. This gradually yielded a yellowish mass of crystals when left to stand for two days at room temperature. The mass of crystals was filtered off, crushed, and washed six times with boiling dichloromethane (6 x 30ml) and dried in vacuo. (3.5g) m.p., 195° (decomp.)

Elemental Analysis:

Formula: $C_{15}H_{17}Cl_3N_2O_2Sn$

Calc.: C, 37.33; H, 3.53; N, 5.81; Sn, 24.61%

Found: C, 36.68; H, 3.23; N, 5.55; Sn, 24.90%

n.m.r.: (d-DMSO + TMS)

δ1.00 ppm (3H, s, Sn-CH_3)

δ2.70 " (6H, s, 2x -CO.CH_3)

δ7.80 " (2H, q, 2x pyridyl C4H)

δ8.15 " (4H, m, x pyridyl C3,5H)

δ8.90 " (2H, d, 2 x pyridyl C6H)

i.r. (KBr and CsI discs)

3050 cm^{-1}	(w)	C - H arom.
1630 cm^{-1}	(s)	C = O coordinated?
1600 cm^{-1}	(s)	C = C arom. (Py)
280 cm^{-1}	(s)	Sn - Cl

Tetrachlorotin bis-2-acetylpyridine.

Stannic chloride (3.26g, 1.4ml, 0.0125M) in cold dichloromethane (100ml) and 2.acetylpyridine (3.0g, 0.025M) also in cold dichloromethane (100ml) were mixed, with stirring. A clear yellow solution was obtained. This was cooled overnight. A light yellow mass of crystals separated out. This was filtered off, washed four times with dichloromethane (4 x 30ml), and dried in vacuo. (5.00g, 79.90%)

m.p. 253 - 255° (decomp.)

Elemental Analysis:

Formula: $C_{14}H_{14}Cl_4N_2O_2Sn$

Calc: C,33.42; H,2.79; Cl,28.25; N,5.57; Sn,23.61%

Found: C,32.91; H,2.87; Cl,28.41; N,5.36; Sn,23.80%

n.m.r.: (d-DMSO + TMS)

δ1.95 (s)

δ2.40 (s)

δ2.70 (s, $-CO.CH_3$)

δ3.00 (s)

δ5.80 (s)

δ7.00 (s)

δ8.00 (m)

i.r.: (KBr and CsI discs)

3450 cm^{-1}	(m)	O - H
3100 cm^{-1}	(w)	C - H arom.
1620 cm^{-1}	(s)	C = O coordinated?
1600 cm^{-1}	(s)	C = C arom (Py)
325 cm^{-1}	(s)	Sn - Cl

Phenyltintrichloride bis-2-Acetylpyridine.

Phenyltintrichloride (3.02g, 0.01M) in dichloromethane (50ml) and 2-acetylpyridine (2.42g, 0.02M) also in dichloromethane (50ml) were mixed. A clear yellowish solution was obtained. The solution was boiled for five minutes and left to stand for a day. Dirty white crystals were formed. The mixture was cooled for a six hours, and the crystals were filtered off, washed with dichloromethane, and dried in vacuo. (4.1g, 75.37%).

m.p., 189 - 191° decomp.

Elemental Analysis:

Formula: $C_{20}H_{19}Cl_3N_2O_2Sn$

Calc.: C,44.10; H,3.49; Cl,19.57; N,5-15; Sn,21.81%

Found: C,43.72; H,3.63 N,5.09; Sn,22.05%

n.m.r.: (d;DMSO + TMS)

δ2.6 ppm (6H, s, 2 x CH_3.CO-)

δ7.4 ppm (3H, m, Sn-Ph C3,4,5H)

δ8.0 ppm (8H, m, Sn-Ph C2,6H, + 2 x pyridyl C3,4,5H)

δ9.0 ppm (2H, m, 2 x pyridyl C6H)

i.r. (KBr and CsI discs)

3450 cm^{-1}	(m)	O - H
3100 cm^{-1}	(m)	C - H arom
1610 cm^{-1}	(m)	C = O coordinated?
1600 cm^{-1}		C = C arom. (Py)
1060 cm^{-1}		Sn - Ph

Diphenyltindichloride bis-2-acetylpyridine.

Diphenyltindichloride (3.44g, 0.01M) in carbon tetrachloride (50ml) and 2-Acetylpyridine (2.42g, 0.02M) also in carbon tetrachloride (30ml) were mixed at room temperature. A light yellowish solution was obtained, which turned turbid on standing. A clustered mass of yellow crystals was obtained on cooling overnight. This was filtered off, washed with CCl_4 (50ml), and dried *in vacuo* (4.1g). The product was recrystallised twice from a 1:1 mixture of toluene and diisopropyl ether.

m.p. 125 - 127°

Formula: $C_{26}H_{24}Cl_2N_2O_2Sn$

Elemental Analysis:

Calc.: C,53.27; H,4.10; N,4.78; Sn,20.26%

Found: C,53.06; H,3.97; N,4.39; Sn,20.46%

n.m.r. (d-DMSO + TMS)

δ2.20 ppm (6H, s, 2x $-CO-CH_3$)

δ7.40 " (10H, m 2x Sn-Ph C3,4,5H + 2x pyridyl C4,5H)

δ8.10 " (8H, m, 2 x Sn-Ph C2,6H + 2x pyridyl C3,6H)

i.r. (KBr and CsI discs).

3500 cm^{-1} (w) O - H (broad)?

3050 cm^{-1} (w) C - H arom.

1630 cm^{-1} (s) C = O coordinated?

Reaction of Methyltin trichloride with 2-Pyridine carboxaldehyde.

Methyltin trichloride (1.20g, 0.005M) in dichloromethane (40ml) and 2-Pyridine carboxaldehyde (1.07g, 0.01M) also in dichloromethane (40ml) were mixed at room temperature. A dirty brown mass of crystals separated out. After leaving to stand overnight, the mass of crystals was filtered off, washed five times with boiling dichloromethane, (5 x 30ml) and dried in vacuo (1.80g)

m.p. 112 - 115°

Elemental Analysis.

Calc. for $C_7H_8Cl_3NOSn$:

C,24.19; H,2.30; Cl,30.67; N,4.03; Sn,34.18%

Found: C,31.26; H,2.91; Cl,27.37; N,5.54; Sn,32.50%

n.m.r.: (d-DMSO + TMS)

δ1.00 ppm (s, $Sn-CH_3$)

δ1.10 " (d)

δ2.10 " (s)

δ5.85 " (s)

δ7.00-9.00 ppm (m)

δ10.20 ppm (s, $-C\overset{O}{\underset{H}{=}}$)

i.r. KBr and CsI discs.

3050 cm^{-1} (w) C - H arom.

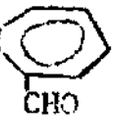
1710 - 1600 cm^{-1} (s) C = O ?

300 cm^{-1} (vs) Sn - Cl

Tetrachlorotin-2-pyridine carboxaldehyde.

Stannic chloride (2.61g, 1.16ml, 0.01M) in dichloromethane (100ml) and 2-pyridinecarboxaldehyde (2.14g, 0.02M) also in dichloromethane (100ml) were mixed with ice cooling. A dirty white paste was obtained. After allowing to stand at room temperature for two hours, the paste was filtered off, washed six times with warm dichloromethane (6 x 30ml) and dried in vacuo. (3.5g), m.p. 83 - 85°

Elemental Analysis:

For $SnCl_4.2$

($C_{12}H_{10}Cl_4N_2O_2Sn$)

Calc.: C,30.34; H,2.11; Cl,29.92; N,5.90; Sn,25.00%

Found: C,24.79; H,2.42; Cl,32.44; N,4.79; Sn,27.50%

i.r. (KBr and CsI discs)

3100 cm^{-1}	(w)	C - H arom.
1680 cm^{-1}	(s)	C = O
1600 cm^{-1}	(s)	C = C arom. (Py)
320 cm^{-1}	(s)	Sn - Cl

Phenyltintrichloride-2-pyridine carboxaldehyde.

Phenyltin trichloride (1.51g, 0.005M) in warm dichloromethane (30ml) and 2-pyridine carboxaldehyde (1.07, 0.01M) also in warm dichloromethane (30ml) were mixed. A brownish paste was precipitated. The mixture was allowed to stand at room temperature for two hours; the paste was then filtered off, washed five times with boiling dichloromethane, (5 x 25ml) and dried in vacuo. (1.5g, yield, 73.17%)

m.p., 150 - 152° decomp.

Elemental Analysis:

Formula: $C_{12}H_{10}Cl_3NOSn$

Calc.: C,35.19; H,2.44; Cl,26.03; N,3.42; Sn,29.00%

Found: C,34.88; H,2.60; Cl,26.82; N,3.48; Sn,29.40%

n.m.r.: (d-DMSO + TMS)

δ7.4 ppm (3H, m, Sn-Ph C3,4,5H)

δ7.9 " (3H, m, Sn-Ph C2,6H + pyridyl C4H)

δ8.1 " (2H, m, pyridyl C3, 5H)

δ8.7 " (1H, d, pyridyl C6H)

δ9.8 " (1H, s, -CHO)

i.r.: (KBr and CsI discs)

3100 cm^{-1}	(w)	C - H arom.
1630 cm^{-1}	(s)	C = O coordinated
1595 cm^{-1}	(s)	C = C arom. (Py)
1065 cm^{-1}	(w)	Sn - Ph
320 cm^{-1}	(s)	Sn - Cl

Reaction of Diphenyltin dichloride with 2-Pyridine carboxaldehyde

Diphenyltin dichloride (1.72g, 0.005M) in cold dichloromethane (40ml) and 2-phyridine carboxaldehyde (1.07g, 0.01M) also in cold dichloromethane (40ml) were mixed. A pink, clear solution was obtained. This yielded only a think oil on standing and then cooling at about 0°C overnight. All efforts to get the oil to solidify failed.

Wher dimethyltindichloride (1.11g, 0.005M) in dichloromethane (40ml) was mixed with 2-pyridinecarboxaldehyde, (1.07g, 0.01M) also in dichloromethane (40ml), a brown wax was obtained. All efforts to purify the wax further, failed.

Pyridine adducts of Methyltin, Phenyltin, and stannic Chlorides.

The adducts, except $Me_3SnCl.Py$, were prepared by mixing dichloromethane solutions of stoichiometric amounts of organotin or stannic chloride and pyridine, (ratio 1:2 Lewis Acid to Lewis base), at room temperature. Each reagent was dissolved in 100ml of dichloromethane; 0.01M Lewis acid was used for each preparation. The products came out as precipitates, which were filtered off, washed with more solvent, and dried in vacuo.

$Me_3SnCl.Py$ was similarly prepared from trimethyltin chloride, pyridine, and 40 - 60 petrol as solvent.

$Me_3SnCl.Py$.

m.p. 39 - 40° (Lit[2]. 40 - 41°)

n.m.r. (CCl_4 + TMS)

δ0.62 ppm (9H, s, 3x Sn-Me)
δ7.30 " (2H, m, 2 x pyridine -m-H)
δ7.60 " (1H, m, pyridine- p -H)
δ8.50 " (2H, d, 2 x pyridine-O-H)

i.r. (KBr disc)

3050 cm^{-1}	(vw)	C - H arom.
1600 cm^{-1}	(s)	C = C arom. (Py)
795 cm^{-1}	(m)	Sn - Me (Rock)

$Me_2SnCl_2.2Py$.

m.p. 162 - 163° (Lit.[2] 163°)

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ1.25 ppm (6H, s, 2x Sn - Ch_3)

δ7.50 ppm C 6H, m, 2x pyridine C3,4,5H)

δ8.90 " (4H, 2x pyridine C2, 6H)

i.r. (KBr disc)

3050cm^{-1}	(w)	C - H arom.
1600 cm^{-1}	(s)	C = C arom. (Py)
795 cm^{-1}	(m)	Sn - Me

$MeSnCl_3.2Py$.

Non fusible < 360° (Lit.[27]: non fusible < 360°)

n.m.r. (d-DMSO + TMS)

δ1.10 ppm (3H, s, Sn-Ch_3)

δ7.50 " (6H, m, 2x pyridine C3,4,5H)

δ8.90 " (4H, m, 2x pyridine C2, 6H)

i.r. (KBr and CsI discs

3050 cm^{-1}	(w)	C - H arom.
1600 cm^{-1}	(s)	C = C arom. (Py)
795 cm^{-1}	(w)	Sn - Me (Rock)
290 cm^{-1}	(s)	Sn - Cl

$SnCl_4.2Py$.

m.p. Not melting < 360° (lit.[10] non melting)

i.r. (KBr and CsI discs)

3050 cm^{-1} (w)	C - H arom.
1605 cm^{-1} (s)	C = C arom. (Py)
330 cm^{-1} (s)	Sn - Cl

$Ph_2SnCl_2.2Py$.

m.p. 148° (lit.[2] Unstable)

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ7.45 ppm and 7.80 ppm (m, difficult to assign because of interference of pyridine and phenyl signals)

δ8.85 ppm (4H, m, 2x pyridine C2, 6H)

i.r. KBr and CsI discs)

3040 cm^{-1}	(w)	C - H arom.
1600 cm^{-1}	(s)	C = C arom. (Py)
1065 cm^{-1}	(m)	Sn - Ph
250 cm^{-1}	(s)	Sn - Cl

$PhSnCl_3.2Py$.

m.p. > 360° (lit.[27] not melting)

n.m.r. (d-DMSO + TMS)

δ7.70 ppm (11H, m, Sn-Phenyl, + 2x pyridine C3,4,5H)

δ8.90 " (4H, q, 2x pyridine C2, 6H)

i.r. (KBr and CsI discs)

3050 cm^{-1}	(w)	C - H arom.
1605 cm^{-1}	(s)	C = C arom. (Py)
1060 cm^{-1}	(m)	Sn - Py
285 cm^{-1}	(s)	Sn - Cl

Nuclear Magnetic Resonance study of the Sn-C-H couplying constants of Pyridine and some substituted pyridine adducts of methyltin chlorides.

Abbreviations:

4-Me.Py	:	4-Picoline
4-Vi.Py	:	4-Vinylpyridine
Py	:	Pyridine
4-Be.Py	:	4-Benzoylpyridine
4-Ac.Py	:	4-Acetylpyridine
3-Be.Py	:	3-Benzoylpyridine
3-Ac.Py	:	3-Acetylpyridine.

0.10M solutions of the following adducts were made in nitrobenzene. 0.50ml of each solution was measured into an n.m.r. tube containing a drop of tetramethyl silane, and the n.m.r. spectra taken. The J Sn-C-H value for each adduct was noted. (see table 17)

TABLE 17

J Sn-C-H values for 0.1M solutions of some methyltin chloride pyridine adduct

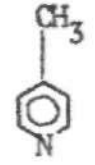
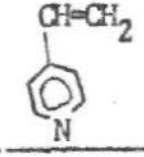
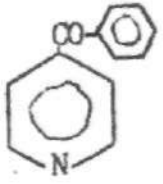
Compound	wt/ml	Molar Conc.	J^{119}Sn-C-H c.p.s	J^{117}Sn-C-H c.p.s.
$Me_3SnCl.4\text{-}Me.Py$	0.0290g	0.10	65.0	62.5
$Me_3SnCl.Vi.Py$	0.03050	0.10	64.0	61.5
$Me_3SnCl.Py$	0.0280	0.10	63.0	60.5
$Me_3SnCl.4\text{-}Be.Py$	0.0380	0.10	62.3	60.0
$Me_3SnCl.4\text{-}Ac.Py$	0.0320	0.10	62.0	59.5
Me_3SnCl	0.0200	0.10	61.3	59.0
$Me_2SnCl_2.(4\text{-}Me.Py)_2$	0.0406	0.10	96.0	92.0
$Me_2SnCl_2.(4\text{-}Vi.Py)_2$	0.0428	0.10	92.0	88.0
$Me_2SnCl_2.2Py$	0.0380	0.10	88.0	84.0
$Me_2SnCl_2.(4\text{-}Be.Py)_2$	0.0590	0.10	82.0	78.0
$Me_2SnCl_2.(4\text{-}Ac.Py)_2$	0.0460	0.10	81.0	77.5
Me_2SnCl_2	0.0220	0.10	75.5	72.5
$MeSnCl_3.(4\text{-}Be.Py)_2$	0.0305	0.05	123.6	116.8
$MeSnCl_3.4\text{-}Ac.Py$	0.0240	0.05	121.0	114.0
$MeSnCl_3$	0.0240	0.05	109.0	104.0
$MeSnCl_3.(4\text{-}Me.Py)_2$	Insol.	Insol.	-	-
$MeSnCl_3.(4\text{-}Vi.Py)_2$	Insol.	Insol.	-	-
$MeSnCl_3.2Py$	Insol.	Insol.	-	-
$Me_2SnCl_2.(3\text{-}Be.Py)_2$	0.0590	0.10	81.0	77.0
$Me_2SnCl_2(3\text{-}Ac.Py)_2$	0.0460	0.10	81.5	78.0
$MeSnCl_3.(3\text{-}Be.Py)_2$	0.0305	0.05	121.0	114.0
$MeSnCl_3.(3\text{-}Ac.Py_2$	0.0240	0.05	120.0	113.0

Determination of the strength of Pyridine and some para-substituted pyridines.

Using 20% v/v aqueous ethanol as solvent, 25ml of 0.10M solutions of pyridine and the following substituted pyridines were prepared. Against each solution was titrated 0.10M HCl, using the pH meter as a monitor. The amounts of acid used were plotted against the corresponding ph values.

TABLE 18

Titre and pH values in the determination of base strength of some pyridines.

Base	wt of base in 25ml of its 20% EtOH soln	Molar Conc.	Vol. of acid at end point.	pH of mixture at end point	pKa=pH of mixture at half neutral^{n}	pK_B of Base
	g 0.23	0.10	ml. 24.60	3.10	5.64	8.36
	0.26	0.10	24.80	3.10	5.13	8.87
	0.20	0.10	24.40	3.00	4.83	9.17
	0.46	0.10	23.00	1.94	2.51	11.49
	0.30	0.10	24.00	2.00	3.04	10.96

Reaction of Pyridine and substituted pyridine adducts of Methyltin and Phenyltin chlorides with silver Trifluoroacetate:

Preparation of dry acetone.

Commercial acetone (AnalaR, 1.50L) was boiled under reflux with p-toluene sulphonic acid (3g.) for forty five minutes. The acetone was then distilled into clean dry bottle and stoppered.

Trimethyltin trifluoroacetate-4-Acetylpyridine.

Trimethyltinchloride-4-acetylpyridine (1.60g; 0.005M) in dry acetone (30ml) and silver trifluoroacetate (1.10g, 0.005M) also in dry acetone (30ml) were mixed. A white precipitate of silver chloride was formed. The mixture was boiled under reflux on a water bath for ten minutes in the dark. The precipitate coagulated, and was filtered off. The filtrate was concentrated until a brown viscous oil was left. This solidified on cooling, and was scraped off and dried in mild vacuum (1.80g). The product was recrystallised three times from carbon tetrachloride.

m.p. 91 - 92°

Elemental Analysis:

Formula: $C_{12}H_{16}F_3NO_3Sn$.

Calc.: C,36.21; H,4.02; N,3.52; Sn,29.84%

FOUND: C,35.85; H,3.92; N,3.49; Sn,29.91%

n.m.r. (CCl_4 + TMS)

δ0.7 ppm (9H, s, 3x CH_3)

δ2.6 " (3H, s, -$CO.CH_3$)

δ7.8 " (2H, d, pyridyl C3,5H)

δ8.6 " (2H, d, pyridyl C2, 6H)

i.r. (KBr and CsI discs)

3050 cm^{-1} (w)		C - H arom.
1710-1650 cm^{-1}	(s)	C = O, OCO
1600 cm^{-1} (m)		C = C arom. (Py)
1410 cm^{-1} (m)		C - O
1200 cm^{-1} (s)		C - F
795 cm^{-1} (s)		Sn - Me (Rock)
300 cm^{-1} (m)		Sn ← O

Trimethyltin trifluoroacetate-4-benzoylpyridine.

Trimethyltin chloride-4-benzoylpyridine (1.91g, 0.005M) in dry acetone (50ml) and silver trifluoroacetate (1.11g, 0.005M) also in dry acetone (50ml) were mixed. A white precipitate was formed. The mixture was boiled under reflux for ten minutes in the dark. The precipitate coagulated, and was filtered off. The filtrate was concentrated by evaporation. Light yellowish crystals separated out in the process. The mass of crystals was removed and dried in mild vacuum. (2.0g). The product was recrystallised three times from carbon tetrachloride. m.p., 80-81°

Elemental Analysis:

Formula: $C_{17}H_{18}F_3NO_3Sn$

Calc.: C,44.38; H,3.91; N,3.04; Sn,25.81%

Found: C,43.87; H,3.96; N,3.06; Sn,25.95%

n.m.r. ($CB_3.CO.CD_3$ + TMS)

δ0.7 ppm (9H, s, 3 x Sn - CH_3)
δ7.9 " (7H, m, -CO.Ph + pyridyl C3,5H)
δ9.0 " (2H, d, pyridyl C2,6H)

i.r. (KBr and CsI discs)

3030 cm^{-1}	(w)	C - H arom.
1710 - 1650 cm^{-1}	(s)	C = O, OCO
1600 cm^{-1}	(m)	C = C arom. (Py)
1410 cm^{-1}	(m)	C - O
1200 cm^{-1}	(s)	C - F
790 cm^{-1}	(s)	Sn - Me
305 cm^{-1}	(m)	Sn ← O

Dimethyltin bistrifluoroacetate-4-acetylpyridine.

Dimethyltindichloride bis-4-acetylpyridine (2.32g, 0.005M) in hot, dry acetone (50ml) and silver trifluoroacetate (2.21g, 0.01M) also in hot, dry acetone were mixed. A white precipitate of silver chloride was formed. The mixture was boiled under reflux for ten minutes in the dark. The precipitate coagulated, and was filtered off. The filtrate was evaporated until a thick brownish oil was left. This yielded yellowish crystals on cooling. The mass of crystals was removed and dried in vacuo. (2.05g). The product was recrystallised three times from toluene.

m.p. 88 - 89°

Elemental analysis:

Formula: $C_{13}H_{13}F_6NO_5Sn$

Calc.: C,31.47; H,2.62; N,2.82; Sn,23.94%

Found: C,31.50; H,2.81; N,2.73; Sn,24.10%

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ1.03 (6H, s, 2 x Sn-CH_3)

δ2.75 (3H, s, -CO CH_3)

δ7.6 (s, OH from H_2O).

δ8.3 (2H, d. pyridyl C3,5H)

δ9.1 (2H, d, pyridyl C2, 6H)

Mass spec.:

120 (Sn^+); 121 $(C_7H_7NO)^+$; 135 $(SnMe)^+$;

139 $(SnF)^+$; 361 $(MeSn(O.CO-CF_3)_2)^+$;

496 $(Me_2Sn(O.CO.CF_3)_2.L)^+$; 873$\{(Me_2Sn(O.CO.CF_3)_2\}_2.L^+$

i.r. (KBr and CsI discs)

3100 cm^{-1} (w)	C - H arom.
1720 cm^{-1} (s)	C = O, OCO
1585 cm^{-1} (m)	C = C arom. (Py)
1410 cm^{-1} (m)	C - O
1200 cm^{-1} (s)	C - F
795 cm^{-1} (m)	Sn - Me
300 cm^{-1} (m)	Sn ← O

Reactions of dimethyltindichloride bis-3-acetylpyridine with silver trifluoroacetate yielded dimethyltinbistrifluoroacetate (m.p. 241 - 243°, lit.[28] 240 - 243°)

Dimethyltin bistrifluoroacetate bis-4-benzoylpyridine.

Dimethyltindichloride (2.21g, 0.01M) and 4-benzoyl pyridine (3.68g, 0.02M) were both dissolved in dry acetone (50ml each). The two solutions were mixed. To the clear greenish yellow solution was added silver trifluoroacetate (4.42g, 0.02M) in dry acetone (100ml). A white ppt was formed, which was coagulated by boiling the mixture under reflux in the dark for ten minutes. The precipitate was filtered off. The filtrate was concentrated, by evaporation, to about 15ml. A mass of yellowish crystals separated out on standing. This was removed, and dried in vacuo. (5.70g). The product was recrystallised four times from toluene.

m.p. 86 - 88°

Elemental Analysis: Calc. for $C_{18}H_{15}F_6NO_5Sn$

Calc.: C,38.73; H,2.69; N,2.51; Sn,21.28%

Found: C,38.91; 2.72; 2.60; 21.80%

n.m.r. (d-DMSO + TMS)

0.92 ppm (6H, s, 2x Sn-CH_3)

7.80 " (7H,m, CO - Ph + 2x pyridyl m_H)

8.96 " (2H, q, 2x pyridyl-O-H)

i.r.: (KBr and CsI discs)

3100 cm^{-1}	(w)	C - H arom
1720-1620 cm^{-1}	(s)	C = O, O.CO
1600 cm^{-1}	(m)	C = C arom., (Py)
1410 cm^{-1}	(m)	C - O
1200 cm^{-1}	(s)	C - F
795 cm^{-1}	(m)	Sn - Me (Rock)
300 cm^{-1}	(m)	Sn + O

Reactions of dimethyltindichloride bis-3-benzoylpyridine with silver trifluoroacetate under similar conditions, gave a mixture, which yielded after three recrytallisations in toluene, dimethyltinbistrifluoroacetate (m.p. 239 - 242°, lit.[28] 240 - 243° decomp.).

Reaction of dimethyltindichloride bis-pyridine with silver Trifluoroacetate.

Dimethyltindichloride bis-pyridine (3.79g, 0.01M) in dried acetone (150ml) and silver trifluoroacetate (4.42g, 0.02M) also in dried acetone (50ml) were mixed. A white precipitate of silver chloride was formed. This was coagulated by boiling the mixture under reflux for ten minutes, and then removed by filtration. The filtrate was concentrated until a near colourless oil was left. This was left to stand overnight in a dessicator. A mass of colourless crystals was formed. This was removed and dried in a desiccator (4.10g). The crude product was recrystallised twice from toluene. It was then dried in mild vacuum for four days. (m.p., 42 - 44°). It, however, retained a strong pyridine smell, and gradually hardened to a solid melting at 240 - 243°C

Elemental Analysis:

Calc. for $C_{11}H_{11}F_6NO_4Sn$:
C,29.14; H,2.43; N,3.09; Sn,26.20%
Found: C,33.77%; H,2.92; N,4.63; Sn,25.50%

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ1.00 ppm (s, Sn-CH_3)
δ8.00 " (t, pyridyl-M.H)
δ8.45 " (d, pyridyl-p-H)
δ9.00 " (d, pyridyl-O-H)
δ10.30 " (s, H_2O)

Reaction of Diphenyltindichloride bis-4-acetylpyridine with silver trifluoroacetate.

Diphenyltindichloride bis-4-acetylpyridine (2.93g, 0.005M) in dried acetone (100ml) and silver trifluoroacetate (2.21g, 0.01M) also in dried acetone (50ml) were mixed in a 250 ml round bottomed flask. A white precipitate was formed. The mixture was refluxed on a water bath for twenty minutes in the dark. The silver chloride precipitate was filtered off; and the filtrate was concentrated by evaporation until a brown viscous oil was left. The oil was left to stand overnight. Brownish crystals were formed. The mass removed, washed with a little toluene, and dried in vacuo (1.28g). The product was recrystallised thrice from toluene.

m.p. 118 - 120°

Elemental Analysis:

Calc. for $ph_2Sn(O.CO.CF_3)_2$ bis-4-Acetyl Py:

C,48.60%; H,3.24; N,3.78; %

Found_ C,42.69; H,3.12; N,6.02; %

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ2.60 (s, $-CO.CH_3$)

δ7.85 (s, pyridyl C3,5H)

δ8.80 (d, pyridyl C2,6H)

Petroleum Spirit (free of aromatic hydrocarbons)

Commercial 40 - 60 petroleum spirit, (AnalaR, 2½L) and concentrated sulphuric acid (1¼L) were mixed in a 5L conical flask and stirred magnetically at room temperature for 20h. The petrol was decanted into a clean, dry 4L conical flask and treated with sodium carbonate (10g) to decompose any acid in the petrol, which was then dried over anhydrous sodium sulphate. The supernatant was filtered and distilled.

Triphenyltin trifluoroacetate.

Triphenyltin chloride (3.85g, 0.01M) in dried acetone (50ml) and silver trifluoroacetate (2.21g, 0.01M) also in dried acetone (50ml) were mixed. A white precipitate of silver chloride was formed. The mixture was boiled under reflux for ten minutes to coagulate the precipitate, which was then filtered off. The filtrate was evaporated to dryness; a white powder was obtained. This was removed and dried in vacuo (3.6g). The product was recrystallised three times from 40 - 60 petrol. m.p. 120 - 122, lit.[26] 121 - 123°

Elemental Analysis:

Formula: $C_{20}H_{15}F_3O_2Sn$

Calc.: C,51.87; H,3.24; Sn,25.65%

Found: C,51.84; H,3.40; Sn,25.61%

n.m.r.: ($CD_3.CO.CD_3$ + TMS)

7.4 (9H, m, 3x Sn-Ph C3,4,5H)

7.8 (6H, m, 3 x Sn - Ph C2,6H)

i.r. (KBr and CsI discs)

3050 cm^{-1}	(w)		C - H arom.
1640 cm^{-1}	(vs)	(broad)	OCO assym.
1440 cm^{-1}	(m)		OCO sym.
1220 cm^{-1}	(vs)	(Broad)	C - F
1075 cm^{-1}	(m)		Sn - Ph deform.
990 cm^{-1}	(m)		SnOC
300 cm^{-1}	(s)		Sn + O

1,2-Diphenyl-1,1,2,2 - tetrakistrifluoroacetoxyditin.

Diphenyltindichloride (3.44g, 0.01M) and silver trifluoroacetate (5.53g, 0.025M) each in 50ml of dried acetone, were mixed. A white precipitate was formed. This was coagulated through boiling for 10mins, and removed by filtration. The filtrate was gently evaporated until a colourless viscous oil was left. This was extracted into cold purified petroleum spirit (40 - 60°, 100ml); the mixture was filtered. The filtrate was warmed in a round bottomed flask (250ml) connected to a condenser, on a heating mentle. The mixture gradually turned milky as it boiled; the boiling was continued for two days. A white mass of tiny crystals, as revealed by the microscope, was gradually deposited. The white powdery mass was filtered off with a sintered glass funnel, washed with dried acetone (50ml) and five times with petroleum spirit (5 x 30ml) (aromatic Hydrocarbon free, 40 - 60°), and dried in vacuo. (2.5g, (59.4%) The product did not melt or decompose below 360°.

Elemental Analysis:

Formula: $C_{20}H_{10}F_{12}O_8Sn$.

Calc.: C,28.45; H,1.19; Sn,28.13%

Found: C,28.07; H,1.63; Sn,28.60%

n.m.r. (d-DMSO + TMS)

δ7.45 (6H, m, 2x Sn-Ph (3,4,5H)

δ7.7 (4H, m, 2x Sn-Ph C2, 6H)

i.r.: (KBr and CsI discs.)

3030 cm^{-1} (vw)	C - H arom.
1610 cm^{-1} (s)	OCO assym.
1430 cm^{-1} (m)	OCO sym.
1200 cm^{-1} (vs)	C - F
1075 cm^{-1} (w)	Sn - Py deform.
995 cm^{-1} (m)	SnOC
300cm^{-1} (m)	Sn + O

Raman (KBr)

139 cm^{-1} (m)	
147 cm^{-1} (m)	
183 cm^{-1} (m)	Sn - Sn sym. stretch
565 cm^{-1} (m)	
852 cm^{-1} (vs)	
1000 cm^{-1} (s)	
1026 cm^{-1} (w)	

Proof of production of benzene along with $Ph_2Sn_2(O.CO.CF_3)_4$ in the reaction of Ph_2SnCl_2 with $AgO.CO.CF_3$: Preparation of m-dinitrobenzene.

The petroleum spirit filtrate obtained in the preparation of $Ph_2Sn_2(O.CO.CF_3)_4$ was distilled. To the distillate was added 8ml of 1:1 mixture of conc. H_2SO_4 and conc. HNO_3, with ice cooling. The mixture was then carefully heated to boiling, and pured into an excess of cold distilled water (70ml). A yellowish aqueous layer was obtained. This was separated and cooled. Yellow crystalline threads were obtained. The crystals were separated by filtration, and dried in vacuo (0.185g). The product was recrystallised three times from petrol (40 - 60°). m.p. 87-88°, lit, 90°

Formula: $C_6H_4N_2O_4$

Elemental Analysis:

Calc.: C,42.86; H,2.38; N,16.67%

Found: C,42.85; H,2.51; N,16.54%

n.m.r. (CCl_4 + TMS)

7.7 ppm ($_1H$, t, C_5H)
8.5 " (2H, d, C4,6H)
9.0 " (1H, s, C3H)

i.r.: (KBr disc)

3100 cm^{-1} (w)	C - H arom.
1605 cm^{-1} (s)	C = C arom.
1560 - 1500, 1350cm^{-1} (s)	C - nO_2 arom.

Study of the reaction of Diphenyltin dichloride and Silver trifluoroacetate.

Diphenyltin dichloride (1.72g, 0.005M) and silver trifluoroacetate (2.21g, 0.01M) each in dry acetone (50ml) were mixed. A white precipitate was formed. The mixture was boiled under reflux for ten minutes to coagulate the precipitate, which was then filtered off. The filtrate was concentrated to about 5mls, and further dried for twenty four hours in a vacuum desiccator. A brown viscous oil was obtained (2.60g). This, for convenience, will subsequently be referred to as the "Oil".

n.m.r. (clean sample + TMS)

δ7.50 ppm (6H, m, 2x Sn-Ph C3,4,5H)

δ7.85 " (4H, m, 2x Sn.Ph C2,6H)

δ2.10 " (s, $CH_3.CO.CH_3$)

δ9.30 " (s, OH of water)

i.r. O - H (water 3400 cm^{-1} (m)

C - H (aromatic) 3050 cm^{-1} (m)

C = O 1720 cm^{-1} (vs)

C - F 1200 cm^{-1} (vs)

u.v. λ_{max} 224nm (40 60 petrol solvent)

i) Tin content of the "Oil".

Into a clean dry silica crucible was pipetted 0.20g of the "oil". To this was added concentrated sulphuric acid (1.50ml). The crucible was heated on a clay tripod with a burner flame, first at the sides until all the excess acid had evaporated, and then more strongly at the bottom until all the carbonaceous matter had burned off, leaving a yellow residue. The crucible was further heated for thirty minutes and then allowed to cool in a desiccator. The residue was weighed as stannic oxide (0.044g)

0.20g of "Oil" yielded 0.044g SnO_2

$\therefore$ Tin content of the "oil"

$$= \frac{118.67 \times 0.044 \times 100}{150.67 \times 0.20} \%$$

$$= 17.24\%$$

The "oil" was further dried for another day; its tin content rose to 20.92%. After another twelve hours of drying, the "oil" solidified; the tin content of the solid was found to be 26.75%. The solid was washed in carbon tetrachloride and dried in vacuo. Its tin content rose to 27.50%. The spectra of the solid were as for $Ph_2Sn_2(O.CO.CF_3)$.

ii) "Oil under U.V.

0.2g of the "oil" was dissolved in purified petrol ($40-60^{o}$, 100ml). The solution absorbed in the U.V., giving a sharp band with a λ_{max} 224nm. The absorbance (A_1) of the solution was measured at intervals of one hour, with the solution in u.v. path only at times of measurement.

The experiment was repeated with the solution constantly in the path of U.V., to give absorbance values of A_2 at intervals of one hour.

The volume of the solution was kept constant in each case by filling the cell with fresh purified petrol at times of measurement.

Table 19

U.v absorbance values in the disintegration of "Oil"

Time(h)	A_1	A_2	A_3	$\frac{1}{A_1}$	$\frac{1}{A_2}$	$\frac{1}{A_3}$
0	1.69	1.54	1.56	0.59	0.65	0.60
1	1.39	1.37	1.67	0.71	0.73	0.60
2	1.18	1.09	1.62	0.85	0.92	0.62
3	1.00	0.83	1.62	0.10	1.20	0.62
4	0.88	0.66	1.56	1.14	1.52	0.64
5	0.78	0.50	1.49	1.28	2.00	0.67
6	0.68	0.34	1.46	1.47	2.94	0.68
7	0.59	0.23	1.44	1.67	4.35	0.69
8	0.55	0.16	1.43	1.82	6.25	0.70

A control experiment was performed by running the spectra of fresh aliquots of the stock solutions at intervals of one hour (A_3).

Results:

TABLE 19 (CONTD)

A_1	log A_1	A_2	log A_2
1.69	0.2279	1.54	0.1875
1.39	0.1430	1.37	0.1367
1.18	0.0719	1.09	0.0374
1.00	0.0000	0.83	-0.0809
0.88	-0.0555	0.66	-0.1804
0.78	-0.1079	0.50	-0.3010
0.68	-0.1675	0.34	-0.4685
0.59	-0.2291	0.23	-0.6383
0.55	-0.2596	0.16	-0.7959

The u.v. spectral monitoring of the break down of $Ph_2Sn(O.CO.CF_3)_2$ (oil) in purified 40-60 petrol showed a smooth exponential decrease of the absorbance A_1 of the $Ph_2Sn(O.CO.CF_3)$ with time t, where the unv. radiation served as just the initiator of the reaction, and a rather steep decrease of the absorbance A_2 with time t where the u.v. radiation started off and also took part in the subsequent reaction.

A graph of log A_1 us t showed a straight line, as expected for:

$$\log A_1 = \log A_1 + \frac{k_1 k_3}{2.303 k_2} t$$

derived for the reaction:

$$Ph_2Sn(O.CO.CF_3)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} PhSn(O.CO.CF_3)$$

"oil"

$$PhSn(O.CO.CF_3) \xrightarrow{k_3} Ph_2Sn_2(O.CO.CF_3)_4$$

iii) Effect of sunlight on the "oil" ($Ph_2Sn(O.CO.CF_3)_2$)

0.5ml of the "oil" was pipetted and dissolved in purified petroleum spirit (40 - 60°, 50ml). A clear solution was obtained. The solution was left in sunlight for one hour. A white paste was precipitated. The mixture was left standing in the sun for another two hours: the precipitate was then filtered off, washed with petrol (40 - 60) and dried in vacuo. (0.08g).

n.m.r. and i.r. spectra of the solid were as for 1,2-diphenyl-1,1,2,2-tetrakistrifluoroacetoxyditin.

iv) The "oil" ($Ph_2Sn(O.CO.CF_3)_2$) in acetone.

0.5 ml of the "oil" was pipetted into dry acetone (50ml). A clear solution was obtained. The solution, even after several hours (14 hr) of boiling, (under reflux) did not show any sign of producing a precipitate.

n.m.r. showed that there was no reaction during the boiling.

v) Spectroscopic study of the reaction of diphenyltindichloride with silver trifluoroacetate.

Diphenyltin dichloride was recrystallised from dichloromethane and dried in vacuo. m.p. 42 - 44°.

n.m.r. ($CD_3.CO.CD_3$ + TMS)

δ7.50 ppm (6H, m, 2x Sn-Ph C3,4,5H)

δ7.90 " (4H, m, 2x Sn-Ph C2,6H)

To 3.44g (0.01M) of the recrystallised diphenyltindichloride in dried acetone (60ml) was added silver trifluoroacetate (4.42g, 0.02M) in dried acetone (60ml). The mixture was boiled for ten minutes to coagulate the precipitate formed which was then removed by filtration. The filtrate was concentrated to about five or six ml.

N.m.r. of the clean oil (ref. TMS) showed a small singlet at 7.30 ppm (probably benzene), a multiplet at δ7.50 ppm (6H, 2x Sn-Ph C3,4,5H), another multiplet at δ7.85ppm (4H, 2x Sn - Ph C2,6H), and a small singlet at δ9.15 ppm (water). A large singlet at δ2.00 ppm indicated the presence of acetone (solvent).

The "oil" was extracted into purified petroleum spirit (40 - 60°, 50ml). The n.m.r. spectrum (ref. TMS) of the cold solution showed a small singlet at δ7.30ppm (benzene), a multiplet at δ7.40 ppm (6H, 2x Sn-Ph C3,4,5H) and another multiplet at δ7.70ppm (4H, 2x Sn-Ph C2, 6H) as well as

as solvent signals between zero and 2ppm.

The solution was carefully warmed, under a long reflux column, to boiling. It turned turbid. The boiling was continued for thirty minutes. n.m.r. (ref. TMS) showed an increase in the intensity of the signal (singlet) at δ7.30 along with a decrease in the intensity of the signals at δ7.40 and δ7.70 ppm.

The boiling was continued for fourteen hours, n.m.r. spectrum showed a large increase in the intensity of the signal at δ7.30, and a large decrease in the intensity of the signals at δ7.40 and δ7.70ppm.

The mixture was distilled, the distillate was made up to 50mls with fresh 40-60 petrol, and the n.m.r. spectrum (ref. TMS) was run. The solvent signals showed between 0 and 2 ppm. In addition, an intense singlet at δ7.30 was observed (benzene produced in the reaction).

Action of bromine on 1,2-diphenyl-1,1,2,2, tetrakistrifluoroacetoxyditin.

A little (about 0.1g) 1,2-diphenyl-1,1,2,2-tetrakistrifluoroacetoxyditin was shaken up with a dilute solution of bromine in carbon tetrachloride (5ml). The orange colour faded and the mixture turned colourless overnight.

A control set of bromine in carbon tetrachloride did not show any colour change during the same period of time.

Action of Radical scavengers on "oil".

A solution of 2ml of "oil" was made in 100ml of purified petroleum spirit. The solution was divided into four portions.

The first portion was left at room temperature for four hours. It remained clear.

The second portion was warmed to boiling and refluxed for four hours on a water bath. A white paste, which spectroscopy and elemental analysis later showed to be $Ph_2Sn_2(O.CO.CF_3)_4$, was precipitated.

The third portion was warmed to boiling, and as the precipitation of the white paste started, about ½g of benzoquinone was added. The precipitation stopped, and did not reoccur even after boiling for two hours.

To the forth portion was added about ½g of benzoquinone. The mixture was then warmed to boiling. It turned turbid, and then began to clear again, with a simulataneous deposit of a brown slurry at the bottom of the flask. No white paste was produced even after boiling under reflux for two hours.

"Oil" in benzene.

The "oil" (1ml) in benzene (50ml) was boiled under reflux for eight hours. A white paste was deposited. The mixture was evaporated to dryness. A dirty white powder was left. This was shaken with carbon tetrachloride (20ml). The mixture was filtered, and the filtrate evaporated to dryness. A dirty white paste was left. An n.m.r. spectrum of this (CCl_4 + TMS) was compared will with that of biphenyl (δ7.4ppm, multiplet). TLC of the residue showed it to have the same r.f. as biphenyl.

Boiling of the "oil" in carbon tetrachloride gave similar results.

Reaction of Phenyltin trichloride with Silver trifluoroacetate.

Phenyltintrichloride (1.51g, 0.005M) in dried acetone (50ml) and silver trifluoroacetate (9.95g, 0.015M) also in dried acetone (100ml) were mixed. A white precipitate was obtained. The mixture was boiled under reflux for ten minutes and then left to stand at room temperature for three hours. The precipitate settled and was filtered off. A yellowish filtrate was obtained. This was concentrated by evaporation until a brown, thick oil was obtained. But the thick oil soon hardened to a virtually unpurifiable brown solid.

The experiment was therefore repeated and the oil was partly extracted into purified 40 - 60 petrol (200ml). The extract was boiled under reflux to see if it would follow the pattern of behaviour of $Ph_2Sn(O.CO.CF_3)_2$ in petrol. A white precipitate was, indeed, deposited as the extract boiled, but the production of the precipitate was over in about thirty minutes, and n.m.r. spectroscopic monitoring did not show the production of any benzene.

The white deposit was obtained from the mixture by filtration. It was washed five times with more petrol, (5 x 20ml) and dried in vacuo.

(1.20g) m.p., > 360°

Elemental Analysis:

Calculated for $PhSn(O.CO.CF_3)_3$

Calc.: C,26.93; H,0.94; Sn,22.19%

Found: C,27.04; H,1.08; Sn,22.80%

N.m.r.: (d-DMSO + TMS)

δ 7.3 (s, benzene)

I.r.: (KBr and CsI discs)

3060 cm^{-1}	(vw)	C - H arom.
1640 cm^{-1}	(vs)	OCO asym.
1440 cm^{-1}	(m)	OCO sym.
1200 cm^{-1}	(vs)	C - F
1080 cm^{-1}	(w)	Sn-Ph arom (C-H deform.)
1005 cm^{-1}	(m)	SnOC stretch
300 cm^{-1}	(s)	Sn + O

REFERENCES:

1. Poller, R.C., J. Organometal Chem., 1965, 3, 321.
2. Poller, R.C., The Chemistry of Organotin Compds, 1970, 185.
3. Pearson, R.G.,; J. American Chem. Soc., 1963, 85, 3553.
4. Poller, R.C.: The Chemistry of Organotin Compds., 1970, 186.
5. Tse-Lok Ho; Chemical Reviews, 1975, 75, 1
6. Karantassis, T. and Basileiddos, K.; Compt. Rend., 1937, 205, 460; CA 31, 8505
7. Neumann, P.W.: The Organic Chemist of Tin. 1970, 214.
8. Poller, R.C.: The Chemistry of Organotin Compounds. 1970, 199.
9. Beattie, I.R.; Mcquillan, G.P.; Rule, L.; and Webster, M.: J. Chem. Soc., 1963, 1514
10. Beattie, I.R. and Mcquillan, G.P.: ibid.,1963, 1519.
11. Hulme, R.: ibid., 1963, 1524
12. Bolles, T.F. and Drago, R.S.: J. Amer. Chem. Soc., 1966, 88, 5730.
13. Petrosyan, V.S., Yashina, N.S., and Reutov, O.A.: Adv. in Oranometal. Chem. 1976, 14, 63
14. Plytzanopoulos, M.; Pneumatikakis, G.; Hadjiliadis, N; Katakis, D; and Papadoupoulos, V.: Chimika Chronika, New Series, 1979, 8, 109.
15. Plytzanopoulos, M., and Pneumaticakis, G.: Chimika Chronica, New Series, 1979, 8, 281.

16. Plytzanopoulos, M.; Pneumaticakis, G; Hadjiliadis, N.; and Katakis, D.: J. Inorg. nucl. Chem., 1977, 39, 965

17. Poller, R.C.; The Organic Chemistry of tin compounds, 1970, 221

18. Petrosyan, V.S.; Yashina, N.S.; Bakhmutov, V.I.; Permin, A.B.; and Reutov, O.A.: J. Oranometal Chem., 1974, 72, 71.

18a. Tanaka, T.: Inorg. Chim. Acta, 1967, 1, 217

19. Poller, R.C.: The Chemistry of Organotin Compounds, 1970, 59.

20. Anderson, H. H., and Vasta, J.A.: J. Org. Chem. 1954, 19, 1300.

21. Eaborn, C.: J. Chem. Soc.: 1950, 3077

22. Poller, R.C.; The Chemistry of Organotin Compounds 1970, 173.

23. Saitow, A.; Rochow, E.G.; and Seyferth, D.: J. Org. Chem., 1958, 23, 116; CA. 52, 18195.

24. Anderson, H.H.: Inorg, Chem., 1962, 1, 647; C.A., 57, 9868

25. Brandes, Dietmar: J. Organometal. Chem., 1977, 136, 25

26. Ford, B.F.E. and Sams, J. R. J. Organometal. Chem., 1971, 31, 47

27. Dub, Michael (Ed.): Organometallic Compounds. Vol. II Compds of Ge, Sn, and Pb.; Pub. Springer-Verlag New York Inc, 1967, p. 330.

28. Dub, Michael (Ed.): ibid., 1967, 443

29. Jain, Sumer C. (Def. Res. Lab. (Mater.), Kanpur, India). Labdev. Part A, 1970, 8(4), 169-73(Eng); C.A., 1971, 74, 1195161.

30. Van den Berghe, E.V. and Van der Kelen, G.P.: J. Organometal. Chem., 1966, 6, 515

31. Van den Berghe, E.V. and Van der Kelen, G.P.: ibid., 1968, 11, 479.

32. Jackman, L.M. and Sternhell, S: Applications of Nuclear Magnetic Resonance In Organic Chemistry. Pub. Pergamon, 1969, 5, 61.

33. Van den Berghe, E.V. and Van der Kelen, G.P.: Bull. Soc. Chim. Belges, 1965, 74, 479.

34. Ortego, Dale J.; Waters, D.D.; Steele, C.S.: J. Inorg. Nucl. Chem., 1974, 36, 751

35. Kriegsmann, H., and Ulbricht, K., Z. Anorganic. Allg. Chem., 1964, 328, 90

36. Cummins, R.A., and Evans, J. V., Spectroahim. Acta. 1965, 21, 1016.

37. Yingst, R.E., and Douglas, B.E.: Inorg. Chem., 1964, 3, 1177.

38. Gill, N.S; Nuttal, R.H.: Scaife, D.E; and Sharp, D.W.A.: J. Inorg. Nucl. Chem., 1961, 18, 79

39. Mitchell, P.C.H.: ibid., 1961, 21, 382

40. Ponov., A.I., Marshall, J.C.; Stute, F.B., and Person, W.B.; J. Am. Chem. Soc., 1961, 83, 3586

41. Brittain, E.F.H.; Georg, W.O.; and Wells, C.H.J.: Introduction to Molecular Spectroscopy, Pub. Academic Press, 1970, 145.

42. Ramsey, N.F.: Phys. Rev., 1953, 91, 303.

43. Karplus, M. and Anderson, D.H.: J. Chem. Phys.: 1959, 30, 6

44. Holmes, J.R. and Kaesz, H.D.: J. Amer. Chem. Soc., 1961, 83, 3903

45. Bent, H.A.: Chem. Rev., 1961, 61, 275.

46. Vanden Berghe, E.V., and Van der Kelen, G.P.:
J. Organometal. Chem., 1968, 11, 479

47. Krans, C.A. and Greer, W.N.:
J. Amer. Chem. Soc.1923, 45, 294

48. Brown, M.P.; Cartmel, E; Fowles, G.W.A:
J. Chem. Soc. 1960, 506.

49. Bulliner, P.A.; Quicksall, C.P.; Spiro, T.G.:
Inorg. Chem., 1971, 10, 13

50. Poller, R.C.: The Chemistry of Organotin Compounds.
1970, 145.

51. Graddon, D.P., and Rana, B.A.
J. Organometal. Chem., 1977, 136, 19

52. Stone, F.G.A., West, R.: Advances in Organometal
Chemistry. 1976, 14, 85