SYNTHETIC, SPECTRAL AND FUNGICIDAL ASPECTS OF SOME ORGANOTIN COMPOUNDS

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D E D I C A T I O N

To my Grannie

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

I am immensely grateful to God Almighty for giving me the courage to pursue this work to a successful end, despite many heartbreaking difficulties.

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To the friends whose names I have not mentioned 'merci beaucoup' for your moral support.

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A B S T R A C T

3- and 4-acetylpyridine adducts of dimethyltindichloride and diphenyltindichloride are synthesized. 2-Acetylpyridine reacts with dimethyltin- and diphenyltindichlorides to give not adducts, but some other compounds yet to he identified. The l4--acetylpyridine adduct of trimethyltinchloride is also reported.

Dimethyltiribistrifluoroacetate-U-acetylpyridine and trimethyltin trifluoroacetate-U-acetylpyridine, the first compounds of their type, have also been made.

Infrared, nuclear magnetic resonance, and mass spectral studies of the new compounds have been carried out.

In an effort to examine the possible use of these, and other, organotin compounds for the control of yam rot, their activity against yam rot fungi has "been studied. The results show many of the compounds to be active fungicides.

C O N T E N T S

	Page
INTRODUCTION	
The Project	1
Literature Survey:	
The Tin Element	3
Nomenclature	4
Fission of the Sn-C bond	5
Preparation of Organotin Halides	7
Organotin Halides as Lewis Acids	10
Reaction of Organotin Halides	13
Spectral Studies	17
Effects of some Organotin Compounds on yam rot	19
RESULTS AND DISCUSSIONS	
Synthesis of Organotin Halide Adducts ..	25
Reaction of 2-acetylpyridine with dimethyltindichloride and diphenyltin dichloride	33
4-Acetylpyridine Adducts of dimethyltin bistrifluoroacetate and trimethyltin trifluoroacetate	36

	Page
Reaction of Silver trifluoroacetate with dimethyltin dichloride bis-3-acetylpyridine	40
Infrared studies of the Organotin Compounds	46
Nuclear Magnetic Resonance Spectral Studies of the Organotin Compounds	65
Mass Spectral Studies of the Organotin Compounds	84
Effects of Organotin Compounds on Yam rot-causing Fungi	90
Natural and Local ways of Reserving Yams ..	91
Growth of the Fungi on PDA Treated with Organotin Compounds	92
Growth of Fungi on Slices of Yam Treated with Organotin Compounds	93
Comparison of the Inhibitive Ability of the Organotin Compounds	95
Suggested Preferential use of the Organotin Compounds in Protecting Yams Against Rot	97
Toxicity of the Organotin Compounds ..	97
Weathering and Degeneration of Organotin Compounds	98
Suggestions on Methods of Manufacture ..	99
EXPERIMENTAL	101
REFERENCES	125

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

THE PROJECT

Adduct formation is one of the possible reactions that can occur between a Lewis acid and a Lewis base. If the Lewis acid is sufficiently basic, then the chance of its forming an adduct with a Lewis base depends on the relative availability of the electron pair on the Lewis base. Since an acetyl group is electron-withdrawing, an acetylpyridine would presumably be a weaker Lewis base than pyridine. Pyridine adducts of organotin halides have been known, but would the acetylpyridines be strong enough Lewis bases to form similar adducts? Attempts have been made to synthesize acetylpyridine adducts of some organotin halides, some of which were made in the laboratory.

The tin atom is either penta - or hexaco-ordinated in most of its adducts. As such, adducts of organotin halides would be expected to be stable and perhaps unreactive especially in cases where tetravalent tin atom would exhibit penta- or hexaco-ordination in an intermediate while reacting with a nucleophile. The second part of this work has been

devoted to an examination of the pattern of reactivity of the adducts of organotin halides and a determination of the products of their reactions.

Of the ten isotopes of tin there are three in which the nuclear spin quantum number $I = \frac{1}{2}$, of these the abundance of the ^{115}Sn isotope (0.34%) is so low that n.m.r. measurements involving this nucleus are rarely possible hence the nuclei which are significant in magnetic resonance measurements are those of the ^{117}Sn (7.54% abundance) and ^{119}Sn (8.62% abundance) isotopes. By observing the Sn-C-H coupling constant and using a heteronuclear double resonance technique it is possible to obtain, indirectly, ^{119}Sn chemical shift values [1]. Proton magnetic resonance measurements have been made [1]. involving the hydrogen atoms 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. Tin-proton coupling constants for some pyridine adduct of methyl and phenyltin halides have been established [1]. Efforts have been made to study the effect of the acetyl group in the acetylpyridine adducts on these coupling constants.

The Sn-C stretching frequencies of organotin compounds are known to be low [1]. Acetylpyridines, being weaker electron donors than pyridine, would be expected to give

less stable adducts with organotin compounds. Would the acetyl group substitution on pyridine in the acetyl-pyridine adducts alter the Sn-C stretching frequencies as compared with the Sn-C stretching frequencies of the corresponding pyridine adducts? The i.r. spectra of the novel acetylpyridine adducts have been examined.

Yam rot, a fungal disease, has been a menace to farmers. Some organotin compounds are known to possess fungicidal activity, but would they be strong enough fungicides to prevent the growth of yam rot fungi? In an attempt to find a potential fungicide against yam rot, a number of organotin compounds have been tested for relative fungicidal activity on yam rot fungi.

Literature Survey

The Tin Element

Tin is a white, light metal which retains its lustre on exposure to air and moisture. A member of Group IV, it has an atomic number of 50, an atomic weight of 118.69, and the following isotopic composition:

Isotope	112	114	115	116	117	118	119	120	122	124
% Abundance	1	0.68	0.34	14.4	7.54	24.1	8.62	32.5	4.7	5.9

As a group IV element, the valence shell of the tin atom in the ground state has an outer shell electronic configuration

$5s^2$, $5p^2$

Tin is present in its compounds in the oxidation state of either 2 or 4. All members of group IV show tetraco-ordination, which is possible by sp^3 hybridisation. Down the group, metallic character appears and increases as the outer s subshell electron pair become partially inert. Thus tin exhibits a valency of two when only the 5p electrons are involved in bonding, and a valency of four when a 5s electron is transferred to an empty 5p orbital, thereby forming an sp^3 hybridisation. The tetravalent tin atom is capable, and does form sp^3-sp^3 bonds with carbon and compounds of carbon, thereby forming organometallic compounds known as organotins e.g. tetramethyltin, $(CH_3)_4Sn$. Tetravalent tin also forms covalent bonds with the halogens as seen in stannic chloride ($SnCl_4$); with the non-metals of Group VI as seen in trimethyltin oxide. $Me_3SnOSnMe_3$; and generally with most other non metals. Compounds containing Sn-Metal bonds are also known[2,3] as seen in hexaethyldistannane[2] ($Et_3SnSnEt_3$) and tetrakis (triphenylstannyl) germane[4], $(Ph_3Sn)_4$ Ge.

Nomenclature[5,6]

Clear designation of organotin compounds is almost always possible on the basis of Rule 48 of the nomenclature of organic compounds of the International Union of Pure

and Applied Chemistry:

"Organometallic compounds will be designated by the names of the organic radicals united to the metal which they contain, followed by the name of the metal ..... However, if the metal is united in a complex manner, it may be considered as a substituent". Thus the compound $(C_3H_7)_4Sn$ is called tetrapropyltin, Me_3SnCl is trimethyltinchloride, $Ar_3SnO.CO.R$ is a triaryltin carboxylate. No rule of nomenclature, however, is elevated into an inviolable principle when there are other simpler, clearer designations. Thus $Ar_3Sn\text{-}SnAr_3$ is hexaarylditin, $R_3Sn\text{-}Sn(R_2)\text{-}SnR_3$ is an octaalkyltritin. Adducts of organotin compounds are designated by naming systematically the parent organotin compound followed by Lewis base e.g.



$Me_2SnCl_2 \cdot (\quad CO.Me)_2$

is dimethyltindichloride bis-4-acetylpyridine.

Fission of the Sn-C bond

The rate of any reaction involving breaking of an Sn-C would very much dependent on the ease with which the Sn-C bond breaks. Most important among the factors that determine the ease of the breaking of the Sn-C bond is the strength of the bond. Among the group IV elements, the C-M (where M is C, Si, Ge, Sn or Pb) bond strength

decreases down the group as the atomic radii of the elements increase, and as the tendency for covalent bonding decreases due to increase in metallic character.

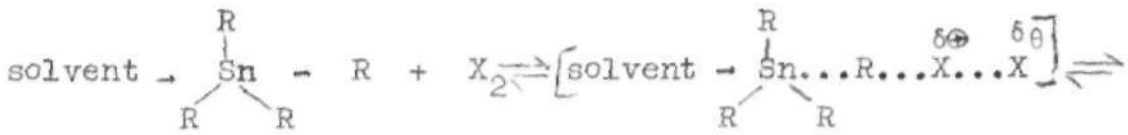
In a reaction of the type

$$\text{Sn-C} + \text{A-B} \rightarrow \text{Sn-A} + \text{C-B}$$

where A-B could be halogen, mineral acid, carboxylic acid, thiol, phenol, alcohol, metallic or non-metallic halide, alkali, alkali metal e.t.c., the breaking of the Sn-C bond could also be determined by nature of the R group containing the C[7,8]. From studies of the cleavage reactions of unsymmetrical compounds, such as the R_3SnR^1 or $R_2SnR^1_2$ types, sequences have been obtained showing the relative ease with which groups are cleaved from tin[7], e.g. $R=$ O-tolyl > p-tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > isobutyl > butyl > isoamyl > amyl > hexyl > heptyl > octyl.

The nature of the medium of reaction could also affect the rate of a reaction involving scission of the Sn-C bond. Nucleophilic assistance is rendered by co-ordination of the solvent to the tin atom thereby weakening the strength of the Sn-C bonds viz.

$$R_4Sn + \text{solvent} \rightleftharpoons \text{solvent} \rightarrow SnR_4 \quad .. \quad .. \quad .. \quad (1, 2)$$



$$R_3SnX.\ solvent + RX \quad .. \quad .. \quad (1, 3)$$

where X is a halogen[9, 10 11].

Preparation of Organotin Halides

Most straight forward and efficient is the method of comproportionation discovered by K. A. Kocheshkov[12,13,14]. It consists of heating together tetra organotins and stannic halides in stoichiometric amounts to give mono-, di-, and/or trihalides as the sole end products, depending on the proportion of the starting materials used viz.

$$3R_4Sn + SnCl_4 \rightarrow 4R_3SnCl \quad .. \quad .. \quad (1, 4)$$

$$R_4Sn + SnCl_4 \rightarrow 2R_2SnCl_2 \quad .. \quad .. \quad (1, 5)$$

$$R_4Sn + 3SnCl_4 \rightarrow 4RSnCl_3 \quad .. \quad .. \quad (1, 6)$$

The mechanism of comproportionation is not clear, but it could be based on the theory of redistribution whereby the ligands on the tin of an organotin and a stannic halide when heated together, redistribute themselves on the tin atoms to give more stable organotin halides. It is possible that the reactions might go via formation of radicals, viz:

$$R_4Sn \rightleftharpoons [R_3Sn^{\circ} + {}^{\circ}R]$$

$$SnX_4 \rightleftharpoons [{}^{\circ}SnX_3 + {}^{\circ}X]$$

$\xrightarrow{\Delta}$ $R_3SnX + RSnX_3$ .. (1, 7)

The initial formation of R_3SnX and $RSnX_3$ has been confirmed by E.V. vanden Berghe and G. P. Van der Kelen[15] who followed the process of formation of organotin halides from tetra organotins and stannic halides by route of comproportionation by means of nuclear magnetic resonance spectroscopy and found that the reactions (1, 4 and 1, 5) above occur in the followings steps.

$$R_4Sn + SnX_4 \rightarrow R_3SnX + RSnX_3 \quad .. \quad .. \quad (1, 8)$$

$$R_3SnX + RSnX_3 \rightarrow 2R_2SnX_2 \quad .. \quad .. \quad .. \quad (1, 9)$$

$$2R_4Sn + 2R_2SnX_2 \rightarrow 4R_3SnX \quad .. \quad .. \quad .. \quad (1, 10)$$

~~$R_4Sn + SnX_4 \rightarrow R_3SnX + RSnX_3$ .. .. (1, 11)~~

~~$R_3SnX + RSnX_3 \rightarrow 2R_2SnX_2$ .. .. .. (1, 12)~~

By reasoning in the same line, reaction 1, 6 could be said to occur thus

$$R_4Sn + SnX_4 \rightarrow R_3SnX + RSnX_3 \quad .. \quad .. \quad (1, 13)$$

$$R_3SnX + 2SnX_4 \rightarrow 3RSnX_3 \quad .. \quad .. \quad .. \quad (1, 14)$$

The organotins and stannic halide when mixed in stoichiometric amounts, produce the sole expected product only

when the reaction mixture has been heated above 120°[15].

Some organotin halides have been prepared by single-step synthesis using alkyl halides and metallic tin[16]. Most of the reactions however are catalytic, viz.

$$2EtI + Sn \xrightarrow{\text{sunlight}} Et_2SnI_2 \quad .. \quad .. \quad (1, 15)$$

$$2EtI + Sn \xrightarrow[\Delta]{} Et_2SnI_2 \quad .. \quad .. \quad (1, 16)$$

The yield could be high as in the preparation of dimethyltindichloride from iodomethane and tin[17], or low as in the preparation of bis-p-halobenzyltindihalide from p-halobenzyl halide and tin[18]. All these reactions are slow compared with those of comproportionation.

Alkylation of stannic halides by Grignard reagents and trialkyl aluminium has been proved effective in the preparation of organotin halides[19].

$$2RMgX + SnCl_4 \rightarrow R_2SnCl_2 + 2MgXCl \quad .. \quad .. \quad .. \quad (1, 17)$$

$$2R_3Al + SnCl_4 \rightarrow 3R_2SnCl_2 + 2AlCl_3 \quad .. \quad .. \quad .. \quad (1, 18)$$

$$R_3Al + SnCl_4 + R'_2O \xrightarrow{-/50^\circ C} R_3SnCl + R'_2O.AlCl_3{}^{20} \quad .. \quad (1, 19)$$

Alkyltin trihalides have been prepared from alkali stannite and alkyl halide via the alkylstannonic acid[21]

$$RSn(O)OH + 3HCl \rightarrow RSnCl_3 + 2H_2O \quad .. \quad .. \quad .. \quad (1, 20)$$

Tetraorganotins are cleaved by halogens, giving triorganotin halides and diorganotindihalides. Chlorine is more reactive than bromine which is more reactive than

iodine. The halogens are best used in solution

$$R_4Sn + X_2 \rightarrow R_3SnX + RX \quad .. \; .. \; (1, 21)$$

$$R_3SnX + X_2 \rightarrow R_2SnX_2 + RX \quad .. \; .. \; (1, 22)$$

Organotin Halides as Lewis Acids

Tetravalent tin atom, like other elements in group IV, exhibits sp^3 hybridisation. Expansion of its co-ordination number above four is therefore not possible unless the 5d orbitals are made use of. Tin has been found to differ from the lighter metals of its group by being able to make use of its 5d orbitals, as the energy of these orbitals is sufficiently low, to expand its co-ordination number [22, 23]. The tendency to form co-ordination compounds with Lewis bases is therefore exhibited in some tin compounds. This tendency increases with decrease of electron density around the central tin atom in the compound, and electron density around the central tin atom is determined by the ligands attached to the tin. An electron withdrawing group bound to tin would enhance formation of adducts as it makes the tin more susceptible to nucleophilic attack, while an electron-donating group produces the reverse effect. Thus while no co-ordination compounds of tetramethyl tin are known as yet, adducts of stannic chloride are common.

Organotin halides are known for the readiness with which they form adducts with Lewis Bases[23]. The stability of the adduct however depends on the donor strength of the Lewis Base. A strongly electron-donating ligand is more likely to form an adduct with an organotin halide than a weakly electron-donating one. Also, a small ligand is more likely to gain access to the tin atom of an organotin halide than a large ligand. The size of the groups joined to the tetravalent tin also determines the accessibility of the tin atom to the attacking Lewis Base. Because of the small sizes of the CH_3 radical and the halogen atoms as well as the high electron-negativity exhibited by the halogens, methyltin halides very readily form adducts with suitable ligands.

On the basis of the Principle of Hard and Soft Acids and Bases[24], tin is a hard acid. However, the presence of electron-donating organic groups confers some softness on it[25]. Thus tin IV, generally accepted as a class A acceptor[26], sometimes shows in some of its compounds characteristics of class B acceptors towards certain ligands[27]. It has been found that methyltin halides form more stable adducts with oxygen or nitrogen donors than it does with the corresponding sulphur or phosphorus compounds[28]. The most commonly used ligands for preparing adducts, thus,

are those with donor atoms of the first period, especially oxygen and nitrogen[23].

Adducts of Organotin Mono-, di-, and Trihalides

Organotin trihalides are known to form stable complexes with various donors, except in cases where the donors are weak[30, 31]. 1:2 complexes are usually formed with monodentate ligands[30], with few exceptions like the reaction of some substituted anilines with some aryltin trichlorides where 1:1 adducts result[32].

Organotin dihalides usually form stable 1:2 adducts with monodentate donors[30]. It has been found however that some diaryltin dihalides give unstable 1:4 adducts with pyridine[33]. Bidentate donors give 1:1 adducts with organotin dihalides. A few adducts of dialkyltin diacetates have been reported.

Unlike organotin di- and trihalides, triorganotin halides form 1:1 adducts with monodentate donors.[34] Other trialkyl- or triaryltin compound form 1:2 adducts, as seen in $Me_3SnX.\ 2NH_3$ ($X = NO_3,\ ClO_4$)[35].

Pyridine adducts of Organotin Halides

Since the presence of electron-donating organic groups on tetravalent tin atom (classed a hard acid) confers it some softness on the basis of Hard and Soft Acids and Bases Principle [24, 30, 36], most organotin halides bind well with

pyridine, classed a borderline base under the same principle[36]. Pyridine forms 1:2 adducts with methyltin trihalides, 1:2 with dihalides and 1:1 with monohalides[30].

$$MeSnX_3 + 2Py \rightarrow MeSnX_3Py_2 \quad .. \quad .. \quad .. \quad (1, 23)$$

$$Me_2SnX_2 + 2Py \rightarrow Me_2SnX_2.Py_2 \quad .. \quad .. \quad (1, 24)$$

$$Me_3SnX + Py \rightarrow Me_3SnX.Py \quad .. \quad .. \quad .. \quad (1, 25)$$

where X = Cl, Br, or I.

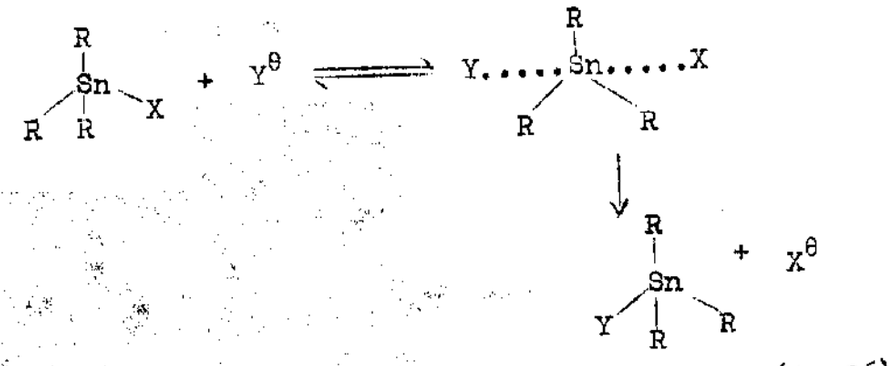
Pyridine adducts of diphenyltin dihalides are known though they are unstable[33]; that of phenyltintrichloride is also known.

Pyridine complexes of organotin halides have been widely used for characterisation of the organotin halides and in studies of co-ordination chemistry[37].

Reactions of Organotin Halides

Poller[38] has stressed the ease with which the halogens of organotin halides can be replaced by a variety of nucleophiles in preparative work. 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 to 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 SN2 fashion



.. (1, 26)

For these reasons, organotin halides have been found to be good starting materials in the preparation of other organotin compounds[38]. Anderson et al[39] have drawn up a "conversion series" for the interconversion of triethyltin compounds:

$(Et_3Sn)_2S \rightarrow Et_3SnI \rightarrow Et_3SnBr \rightarrow Et_3Sn(CN) \rightarrow Et_3Sn(NCS) \rightarrow Et_3SnCl \rightarrow (Et_3Sn)_2O \rightarrow Et_3Sn(NCO) \rightarrow Et_3SnO.CO.CH_3 \rightarrow Et_3SnF.$

According to the findings of Anderson[39], using the appropriate nucleophilic reagent, any of the compounds in the series could be converted to any other on to its right, but none to the left.

A similar series has been drawn by Eaborn[40] for some triorganosilicon compounds:

$R_3SiI \rightarrow (R_3Si)_2S \rightarrow R_3SiBr \rightarrow R_3SiNC \rightarrow R_3SiCl \rightarrow R_3SiNCS \rightarrow R_3SiNCO$.

Eaborn[40] 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 psuedohalogen 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.

$$RnSnX_{4-n} + {}_{4-n}Y^{\theta} \rightarrow RnSnY_{4-n} + {}_{4-n}X^{\theta}$$

would occur if Y^{θ} has a higher affinity for Sn than X^{θ}. This has been proved experimentally by Anderson[39] in drawing out his conversion series for some organotin compounds.

In interconverting organotin halides and pseudohalides, silver salts are most often used, as they are in interconversion reactions of organosilicon halides and pseudohalides. It could be inferred from Eaborn's explanation of his interconversion reactions of organosilicon halides and pseudohalides[40] that the rate determining step in the interaction of a tin compound $\equiv SnX$, 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 separation of anions from tin.

Although reactions of organotin halides have been intensively studied, hardly has anything been reported on reactions of their adducts. A most important problem encountered in attempts to make organotin halides adducts react is their insolubility in many organic solvents, and their hydrolysis in aqueous media. Although Anderson et al[39] have used pastes of silver salts in their interconversion reactions, at least the organotin compound starting materials were in solution. Fortunately however, acetylpyridine adducts of methyltin- and phenyltin chlorides are fairly soluble in a few organic solvents. Their reaction with silver trifluoroacetate, which is also soluble in many organic solvents would be interesting since the resulting silver chloride would be insoluble in the media, thereby pushing the reaction to near completion. A few of these reactions have been studied.

Infra red, Mass and Nuclear Magnetic Spectral Studies of Acetylpyridine Adducts of Dimethyl-, trimethyl-, diphenyl tin halides and trifluoroacetates

Infra red- and nuclear magnetic resonance spectroscopy have often been used in structural studies of organotin compounds[41, 42, 43, 44]. However, except the ν(Sn-H) mode, nearly all fundamental stretching vibrations involving the tin atom[41] occur at i.r. frequencies below 650cm^{-1}, The structural and infra red spectral studies of pyridine complexes of methyltin halides have been made[45]. Apart from the fact that the acetyl group on acetylpyridine accounts for about a third of the weight of the molecule, it is an electron withdrawing group which would have some effect on the Sn-N and perhaps on Sn-C stretching vibrations of acetylpyridine complexes of methyl- and phenyltin halides. The Sn-C frequencies in the novel dimethyltin-bistrifluoroacetate-4-acetylpyridine should be strong and high as the trifluoroacetate group is strongly electron-withdrawing and would be expected, as postulated by Clark, Davies and Puddephatt[46], to increase the effective nuclear charge on tin. Though the Sn-N stretching frequencies come very low ($\lesssim$200cm^{-1})[45] and therefore instruments for measurements are not easy to come by,

efforts have been made to study the Sn-C bonds to examine the effect of the acetyl group of acetylpyridine adducts.

Three naturally occurring tin nuclides have magnetic moments a ^{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 ones (^{115}Sn 0.34%, ^{117}Sn 7.54%, ^{119}Sn 8.62%)[1]. 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[1]. The chemical shift of the methyl protons of methyltin halides also is proportional to the electron density on the tin atom[47]. Nuclear magnetic resonance study of pyridine adduct with dimethyltindichloride had been to no avail as the complex is insoluble in any solvent in all proportions[48]. Although it has been found[49] that the protons of a phenyl group attached to tin (in phenyltin halides) show chemical shifts of T 2.7ppm, n.m.r. spectra of phenyltin halide adducts with pyridine or any derivative of pyridine have not been reported. Efforts have been made to study the n.m.r. spectra of

the novel acetylpyridine adducts of dimethyltindichloride, trimethyltinchloride, and diphenyltindichloride. Spectra of the trifluoroacetate products of some of these adducts, the first of their kind, have also been examined.

Mass spectroscopy has been known as a most important means of determining the structure as well as molecular weights of compounds. Apart from these uses, it could also throw some light on the strength of the Sn-N bonds in the organotin halide and trifluoroacetate acetylpyridine adducts. Mass spectra of some of the compounds have been run and examined.

Effects of some Organotin Compounds on Yam Rot

Yam rot has always been a menace to the successful growing and storage of the important crop and staple foodstuff in many parts of West Africa. Although local farmers have attempted various ways to combat this fungus disease, none has proved successful. In an attempt to find a suitable fungicide to remedy yam rot, a number of organotin compounds have been tested for fungicidal activity on yams. Some of them have proved very active, and could eventually be used to prevent yam rot if found physiologically safe.

Yam, the 'King' of root crops, is a most important staple food in West Africa, and is known and eaten in

many parts of the world. It is also an important source of wealth for the farmers. Roughly of the shape of a capsule, it has high carbohydrate content. As a year-round staple food in many tropical countries, the tubers are usually stored for later use after the harvesting season.

Seed yams are prepared by slicing the big healthy u tubers into smaller pieces, which are usually stored either in shallow pits or under sheets of large leaves and palmfronds until the planting season.

A most serious problem encountered in preserving yam is rot known to be caused by a number of fungi[50, 51]. Said a farmer during an interview: "As much as eighty percent of the year's harvest of yams could be lost through rotting, when serious". Seeds of some species of yam cannot be prepared at all at certain times of the year when rot is most rampant. Interview of some yam farmers has revealed that yams are most susceptible to rot during the hot and humid months of February through April, and since this is the season for preparing seed yams to be planted in March or April, rot has always been a problem for farmers. It has also been revealed that any yam injured during harvesting in the months of February through April, the period for harvesting most of the preceeding year's yams, is almost sure to rot.

And the rot is infectious.

The local farmer knows two types of yam rot: the brown and totally destructive rot which is more rampant, and the white and smelly rot which is partially destructive as the residue of the yam infected by this rot is still consumable in some other form. The former type of rot is very infectious and would infect any yam through an injury at any time of the year, while the latter type occurs only when the stored yams are subjected to excessive heat.

Adeniji[51] has identified the fungi responsible for yam rot as Aspergillus niger Aspergillus tamarii, Botryodiplodia theobromae, Clasdosporium herbarum, Cylindrocarpon radicicola, Fusarium sp., Penicillium oxalicum, and Rhizopus nigricans. By examining cultures of fungi made by inoculating potato-dextrose agar (PDA) and yam-dextrose agar (YDA) with slices of rotten yam, the fungi were confirmed. Most prominent of the fungi causing white rot is Fusarium sp., while a black, fast growing still unidentified fungus is an active agent of brown rot.

Spores of the fungi that attack yam are air-borne, and when these settle on a newly cut surface of yam, germination of the spores followed by consequent growth of the fungi occurs. Once growth has started, the hyphae

penetrate the yam tissue, feeding on and destroying the tissue as they grow. From observation, it seems that the infecting fungi grow only on the newly cut tissue. Exposure of the cut surface of the tuber to the air for a few hours leads to evaporation of water from the cut surface. The surface dries up and a hard coat develops. Fungi hyphae or spores do not grow on this coat. Once a cut or injured yam develops this coal, it is free from the attack of fungi. It is before the development of this protective tissue that fungi attack yams and cause rot. The February, April period is the most suitable season in terms of temperature and humidity for the mass bearing of the spores (inference from interview of farmers and Adeniji's report[50, 51]).

A prospective fungicide to prevent yam rot would be something to prevent growth of fungi on a cut or injured surface of a tuber until the protective coat is formed.

Organotin Compounds as Fungicides

Unlike mercury, copper, cadmium and zinc, metallic tin does not possess any fungicidal activity[53]. Many organic compounds of tin are however known to be fungicidal [53, 54, 55]. Tri-n-butyltin oxide has been used to combat the rice blast disease caused by Piricularies oryzae[56]; triphenyltin acetate is being used in combating fungus diseases of potatoes and sugar beet[57].

Fungicidal activity of organotin compounds is dependent upon the extent of alkylation of the tin atom, being at a maximum in compounds with 3 Sn-C bonds[55]. Tri-aryltin compounds are preferred as fungicides to trialkyltin compounds, as the former have a lower phytotoxicity[55, 58].

Organotin fungicides have the added advantage of being amenable to degradation by weathering and sunlight to give inorganic tin so that, unlike the copper and mercury fungicides, they do not leave toxic residues in the soil[59, 60, 61].

In finding a potential fungicide against yam rot, the following compounds have been tested for effectiveness in inhibiting growth of rot-causing fungi both on Yam-Detrose Agar (YDA) as well as potato-dextrose agar (PDA) in petri-dishes and slices of healthy yam inoculated with the fungi:

Triphenyltin acetate, triphenyltin oxide, triphenyltin acetate, triphenyltin oxide, triphenyltin chloride, tri-n-butyltin oxide and a series of new compounds, viz:

dimethyltindichlrodie bis-4-acetylpyridine,

dimethyltindichloride bis-3-acetylpyridine,

trimethyltinchloride -4-acetylpyridine,

diphenyltin dichloride -3-acetylpyridine,

diphenyltindichloride -4-acetylpyridine,

dimethyltin bistrifluoroacetate -4-acetylpyridine,

dimethyltin bistrifluoroacetate

and trimethyltin trifluoroacetate-4-acetylpyridine.

Since most of these compounds would not even disperse in water, aqueous 'Tween 80, a detergent, has been used as an emulsifier for the compounds.

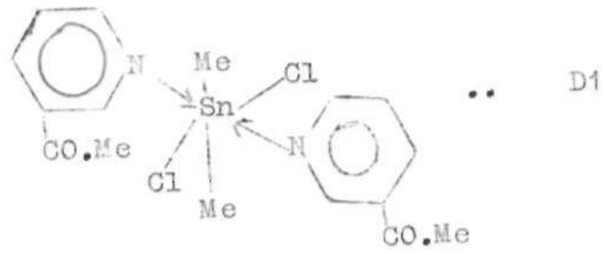
RESULTS AND DISCUSSIONS

Methods of Synthesis of Organotin Halide Adducts

Organotin halide adducts are usually prepared by mixing solutions of the organotin halide and the Lewis base in an inert solvent. Beattie et al[44] have prepared the pyridine adduct of dimethyltindichloride in benzene and of trimethyltin chloride in light petroleum. In preparing an organotin halide adduct, a suitable solvent is chosen such that it interferes as little as possible in the reaction, and does not hold much of the product in solution at the end of the reaction Neutral solvents are preferred as they only weakly solvate the reactants and do not interfere much in the reaction. 3-and 4-acetylpyridine (IC) reacted with dimethyltindichloride (Ia) to give 1:2 adducts, dimethyltindichloride bis-3-acetylpyridine (I) and dimethyltindichloride bis-4-acetylpyridine (II) respectively.

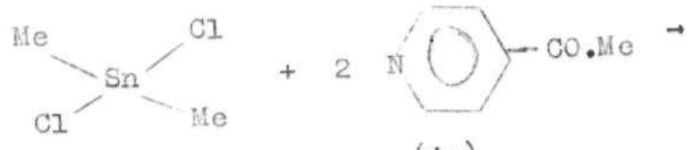


(1a) (1b)

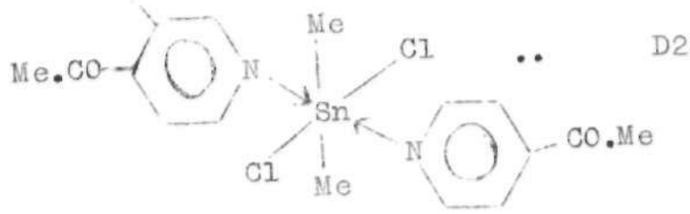


.. D1

(I)



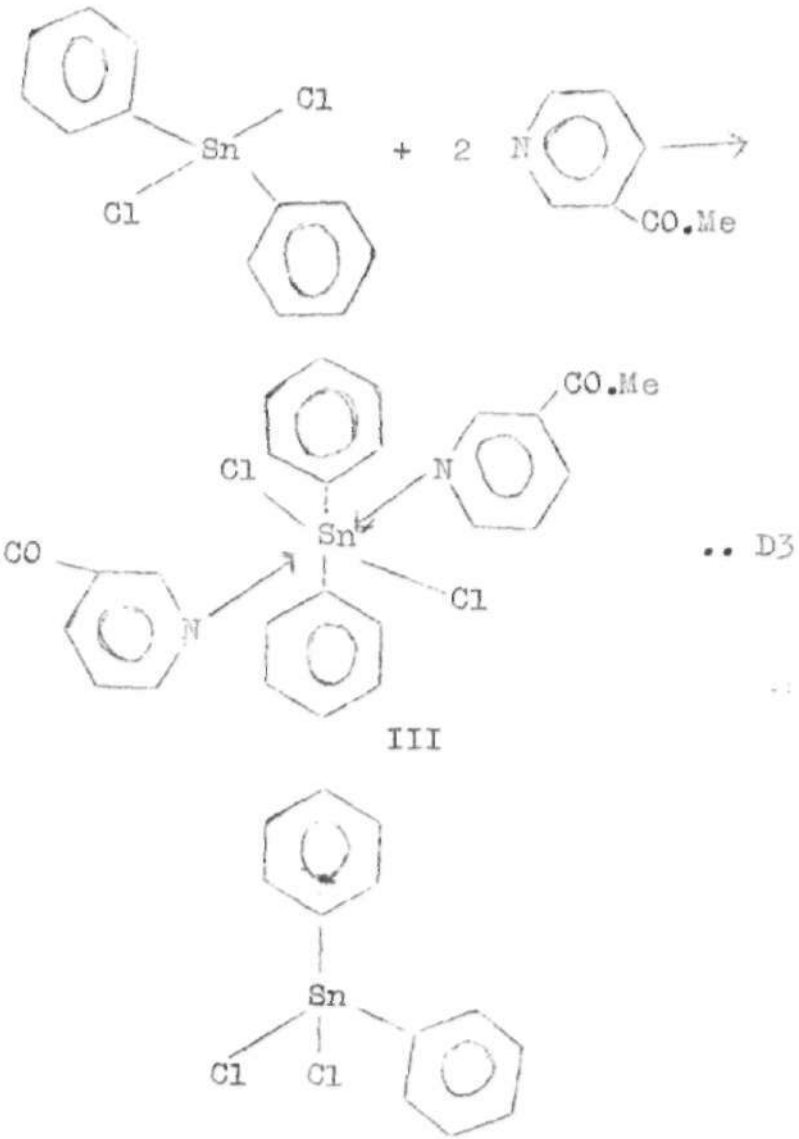
(1c)



.. D2

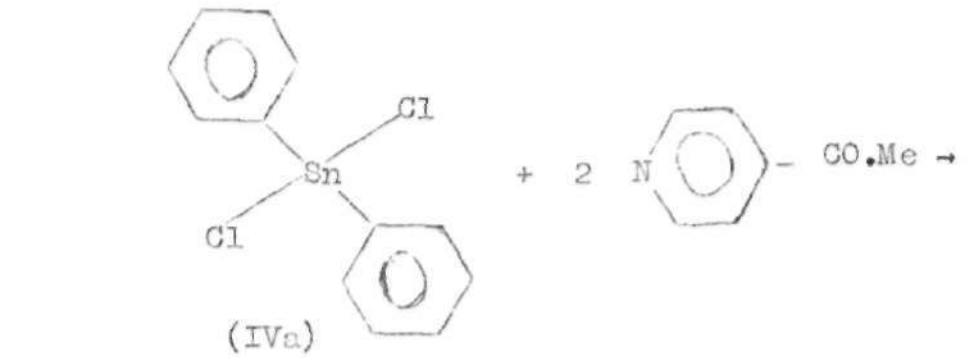
II

With diphenyltin dichloride (IVa), 1:2 adducts were also obtained: diphenyltindichloride bis-3-acetylpyridine (III) and diphenyltindichloride bis-4-acetylpyridine (IV)

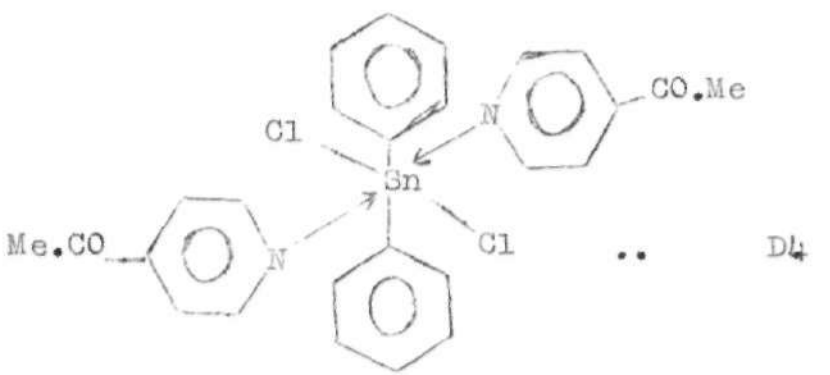


.. D3

III



(IVa)

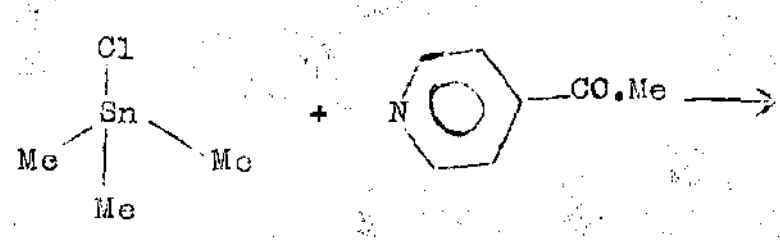


.. D4

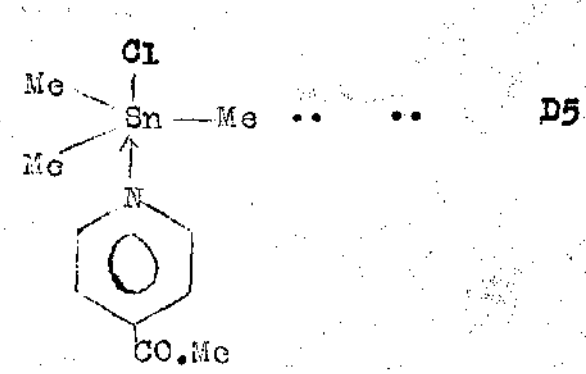
(IV)

The adducts III and IV were quite stable, unlike the pyridine adduct of diphenyltin dichloride which Kocheshi et al[5] had found to be **an unstable** 1:4 adduct. The stability of the adducts is not surprising as steric factors would make it difficult for the central tin atom to exhibit a co-ordination number greater than six with a base like acetylpyridine as the ligand.

Trimethyltinchloride (Va) formed a 1:1 adduct with 4-acetylpyridine, giving trimethyltinchloride-4-acetyl-pyridine (V)



(Va)

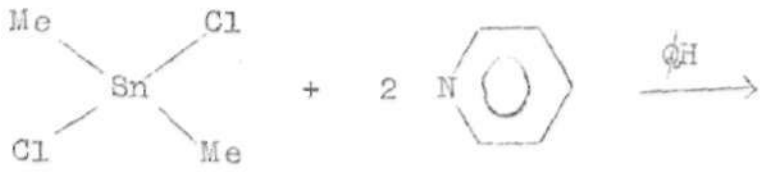


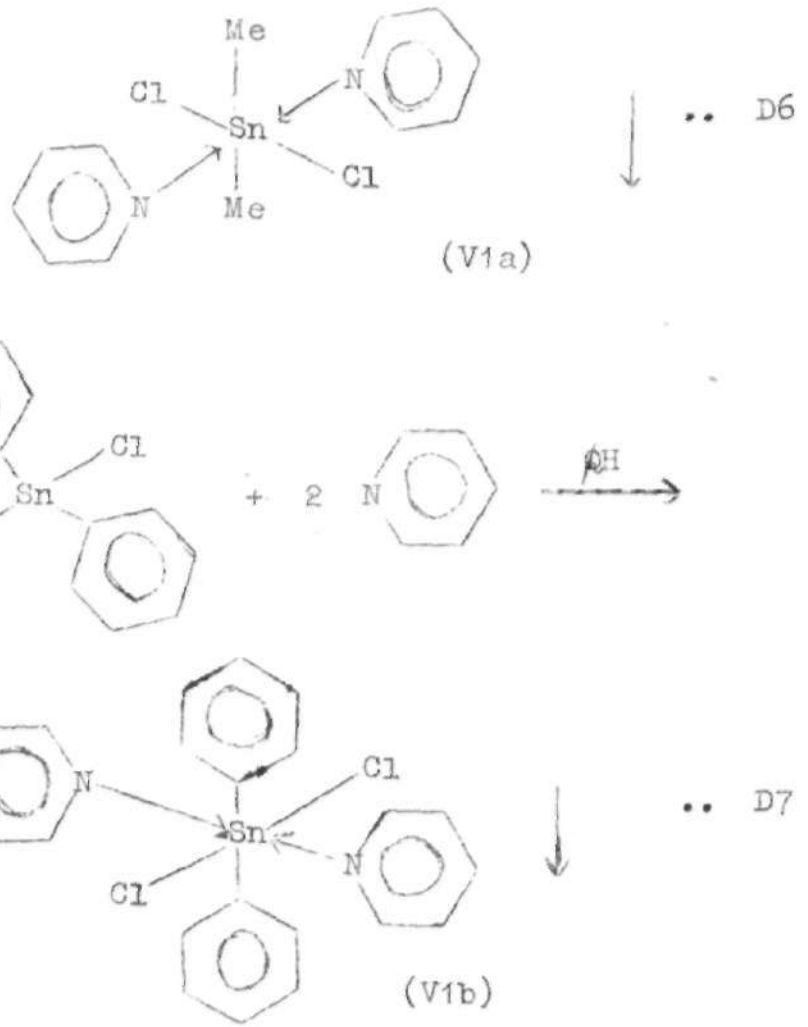
D5

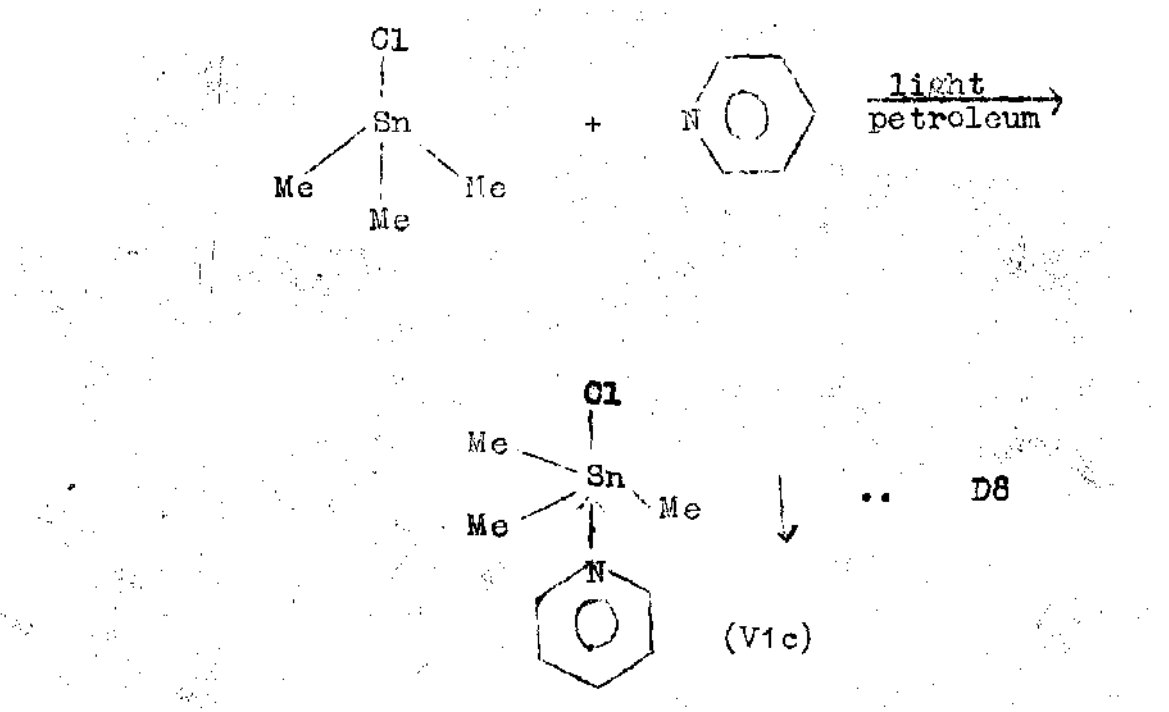
(V)

Trimethyltinchloride seemed to react with 3-acetylpyridine, but all efforts to isolate the product failed as it (the product) was very low melting (25°) and sublimed in the mildest vacuum. Fractional distillation was ineffective as the product decomposed on heating

Pyridine adducts of dimethyltindichloride (VIa), trimethyltin chloride (V1c), and diphenyltin dichloride (V1b) are known[44] to precipitate as soon as the reactants are mixed.







The 3- and 4-acetylpyridine adducts have been found not to precipitate. A clear solution is obtained when the reactants are mixed. The product however comes out of the solution as crystals on standing, and cooling may be required to bring about crystal formation as in the preparation of trimethyltinchloride -4-acetylpyridine. This perhaps could be due to either a slower reaction of 3- and 4-acetylpyridine (compared with pyridine) with organotin halides, or the adduct products of 3-and 4-acetyl-pyridine being more soluble in the solvents than the pyridine adducts.

The melting point of a compound could be said to be a direct function of its lattice energy. The melting points of the acetylpyridine adducts of dimethyltin dichloride, trimethyltinchloride and diphenyltin dichloride have been found to be considerably lower than those for their corresponding pyridine adducts. While dimethyltin-dichloride dipyridine melts at 163° [62], dimethyltindichloride bis-4-acetylpyridine and dimethyltindichloride bis-3-acetyl-pyridine melt at 115° and 109° respectively. This could be due perhaps to the increased steric tension in the molecule of the acetylpyridine adduct (compared with that of pyridine) due to the acetyl group.

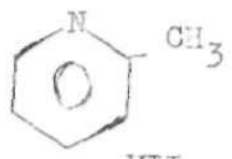
The yield of each of the adducts was high, though time was needed to allow for gradual crystallisation of the acetylpyridine adducts, unlike the corresponding pyridine adducts which precipitated in good yield as soon as the reactants were mixed. The hitherto unknown acetyl-pyridine adducts were obtained in pure form as they were easily recrystallisable from suitable solvents. Trimethyl-tinchloride-4-acetylpyridine had to be dried in a non vacuum dessicator as it sublimed, like most other trime-thyltin compounds, in vacuum.

Reaction of 2-Acetylpyridine with Dimethyltindichloride and diphenyltindichloride

Contrary to expectation, 2-acetylpyridine (VIII) reacted with dimethyltindichloride and diphenyltindichloride to give not the adducts, but products which could not be characterised.

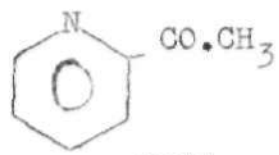
2-Acetylpyridine reacted with dimethyltindichloride in benzene to give a product whose rate of precipitation was practically independent of the concentration of the reactants. The same product was obtained when the reaction was carried out in dichloromethane, acetone, and acetonitrile Chemical analysis showed the product to contain nitrogen, but there was no aromatic signal in the nuclear magnetic resonance spectrum as would have been expected if 2-acetylpyridine were present in the product. The infrared spectrum also did not show any absorption signal due to the carbonyl group. An n.m.r. experiment done by monitoring the spectrum of a mixture of the reactants in dimethylsulphoxide (in which the product was soluble) at intervals of six hours showed a gradual decrease of the signal due to the CH_3 of the dimethyltindichloride $\delta 1.1$, and the emergence and growth of a singlet at $\delta 3.5$. Reaction of dimethyltindichloride with pyridine-2-carboxaldehyde (VIII) in benzene gave a thick oil which could not be purified.

Under similar conditions, dimethyltindichloride did not react with α-picoline (VII), though adducts of dimethyltindichloride with β- and γ-picoline are known[63]. Since dimethyltindichloride did not react with α-picoline (perhaps due to steric hinderance) but reacted with 2-acetylpyridine and pyridine-2-carboxaldehyde, the reaction of the latter might be due to their carbonyl group.



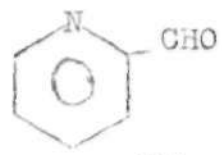
VII

α-picoline



VIII

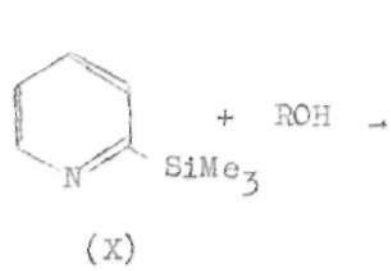
2-Acetylpyridine



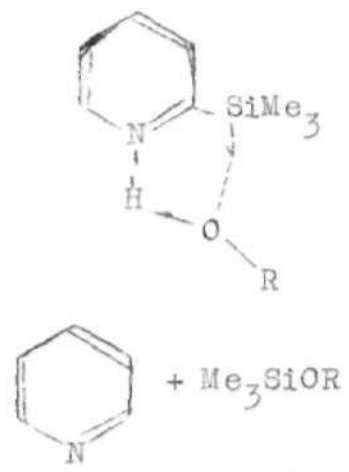
IX

pyridine-2-carboxaldel

Anderson et al[75] in explaining the solvolysis of 2-(trimethylsilyl) pyridine (X) in methanol, have suggested the following mechanism:

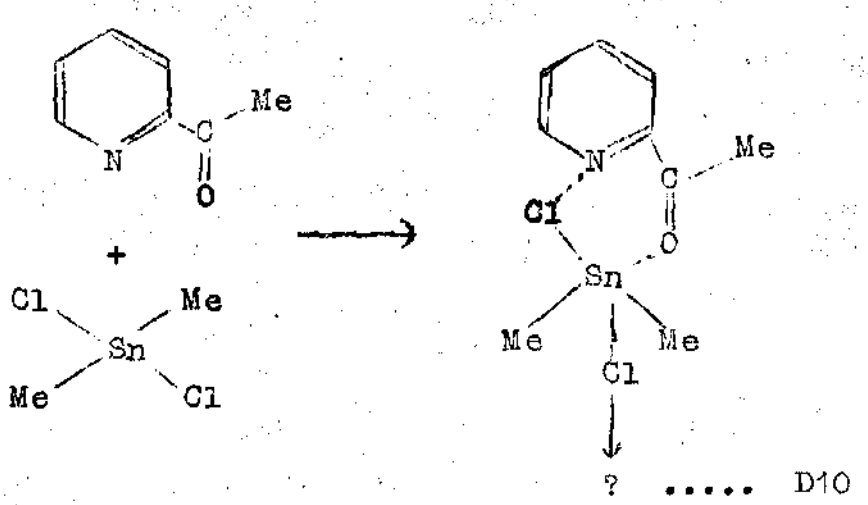


(X)



.. D9

From this analogy, it might be suggested that the carbonyl of 2-acetylpyridine attacks the tin of dimethyltindichloride, and a rearrangement follows:



The high melting point (185°) of the product from the dimethyltindichloride and 2-acetylpyridine reaction suggests that it might be a salt. Since chemical analysis showed the presence of nitrogen in the product but n.m.r. did not show any aromatic proton, it is possible that the pyridine nucleus was ruptured in the reaction.

Diphenyltindichloride reacted in a similar manner with 2-acetylpyridine to give a high melting (172°) product which could not be characterised.

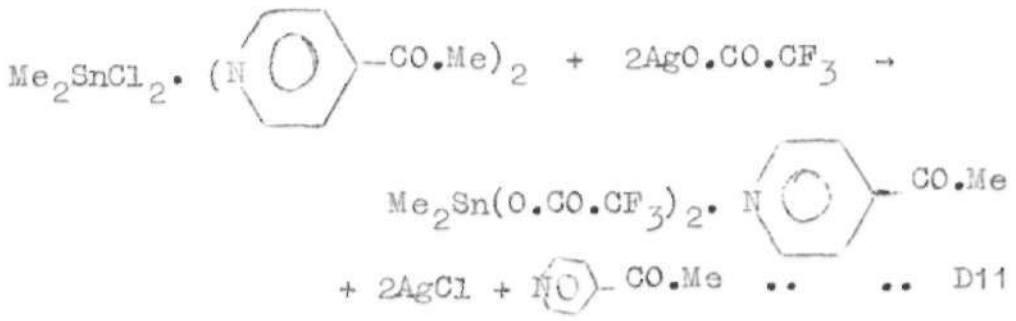
The failure of 2-acetylpyridine to react with trimethyltinchloride and triphenyltinchloride might be due to steric factors.

4-Acetylpyridine Adducts of Dimethyltin bistrifluoroacetate and trimethyltin trifluoroacetate

An indirect method has been used to prepare dimethyltinbistrifluoroacetate-4-acetylpyridine and trimethyltin trifluoroacetate, which had not been known before now.

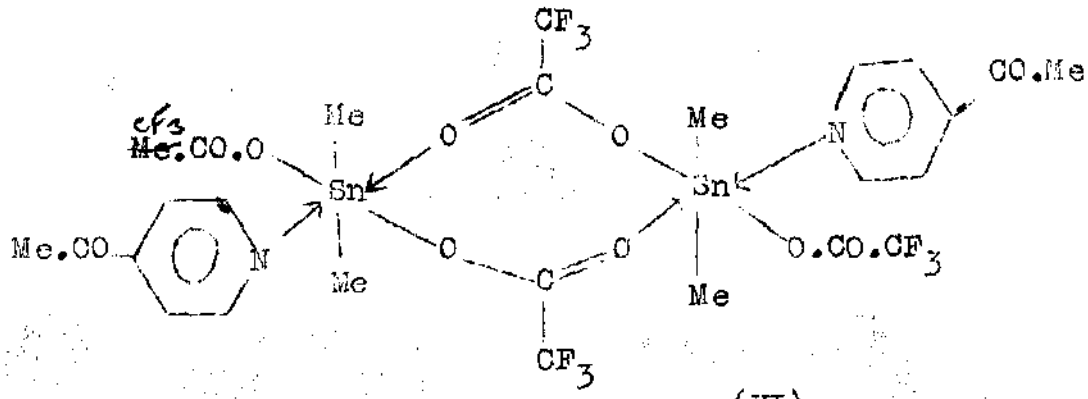
A lot has been done on reactions of organotinhalides [38, 39, 40], but not much had been published on the reactions of the adducts of organotinhalides. An organotin halide adduct, especially if hexacoordinated, would be expected to be much less reactive than the parent organotin halide. Halogen substitution reactions in such an adduct would take place most favourably through an s SNI route since the penta or hexacoordination on the tin atom would make an SN2 reaction difficult, if at all possible. Such substitution reactions would therefore most likely occur in polar solvents.

On this basis, the reaction of silver trifluoroacetate with dimethyltindichloride bis-4-acetylpyridine has been carried out in dry acetone.



After the precipitated silver chloride had been removed by filteration, the solvent was removed and the crude product crystallised in toluene. The dimethyltin bistrifluoroacetate-4-acetylpyridine (XI) came out as yellow crystalline needles, but gave round balls of dimethyltin bistrifluoroacetate (XIII) as soon as it was shaken with a nucleophilic solvent, such as CH_2Cl_2. This rather queer behaviour of the product suggests that the 4-acetylpyridine ligand is only loosely bound to the parent dimethyltinbistrifluoroacetate, and the molecules of a nucleophilic solvent on solvating the adduct would easily displace the ligand.

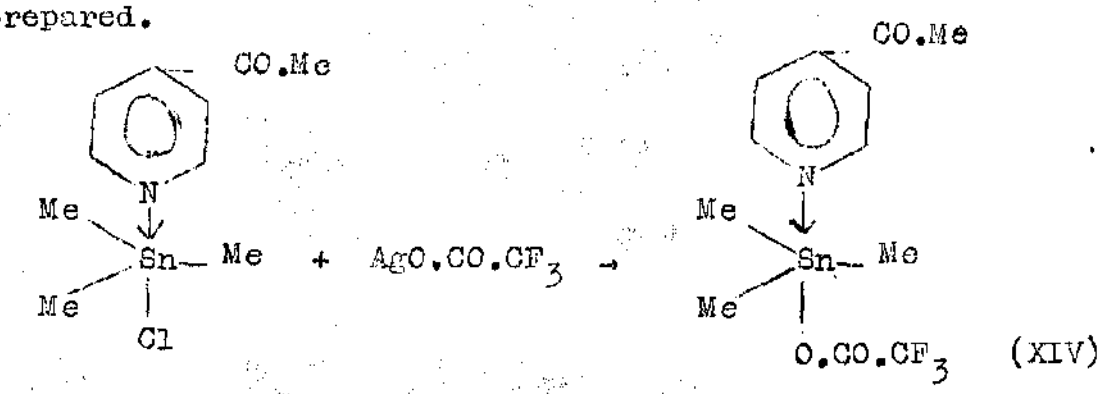
Chemical analysis has shown the product to be a 1:1 adduct; infra red and mass spectroscopy (see later) have further shown it to be a dimer in which the tin would thereby be hexacoordinated. The most probable structure would therefore be (XI)



(XI)

The adduct, the first of its kind to be reported, is hygroscopic and has queer nuclear magnetic resonance properties (see later). It could not have been prepared directly from dimethyltinbistrifluoroacetate and 4-acetylpyridine as the former is not soluble in any neutral solvent, and the adduct would not come out of nucleophilic solvent.

In a similar manner, trimethyltin trifluoroacetate-4-acetylpyridine (XIV), also a novel compound, has been prepared.



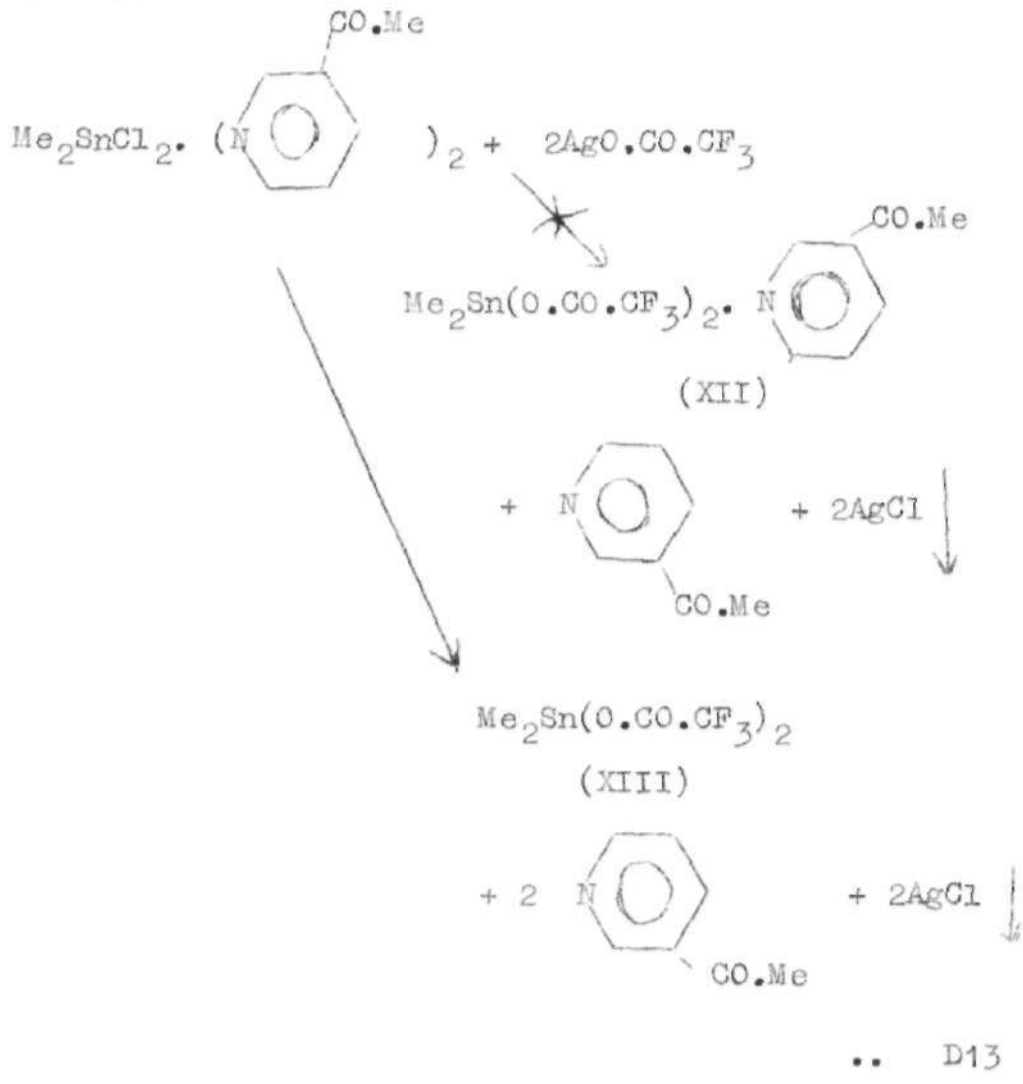
(XIV)

This adduct was better prepared in benzene as the precipitated silver chloride coagulated much more quickly than it did in acetone. Moreover, the product was soluble in benzene, unlike dimethyltinbistrifluoroacetate-4-acetylpyridine, thus reducing any product loss during filteration of the silver chloride. The adduct melted at a much higher temperature (91°) than the starting trimethyltinchloride-4-acetylpyridine (56°), unlike dimethyltinbistrifluoroacetate-4-acetylpyridine which melted at 88° while the starting dimethyltindichloride bis-4-acetylpyridine melted at 115°.

The fact that the halogen substitution reactions of some of these adducts, most likely SNI, occur even in benzene a neutral solvent seems to confirm Eaborn's[40] view that silver salts are outstandingly effective in the inter-conversion reactions of organotin halide and pseudohalides because the silver ions probably assist in breaking the tin-halide bond, thereby pushing the reaction forward.

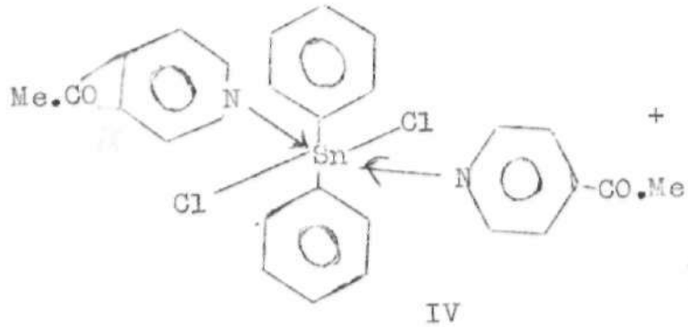
Reaction of Silver trifluoroacetate with Dimethyltindichloride bis-3-acetylpyridine

Dimethyltindichloride bis-3-acetylpyridine reacted with silver trifluoroacetate under the same condition as in the preparation of dimethyltinbistrifluoroacetate-4-acetylpyridine, to give not dimethyltinbistrifluoroacetate-3-acetylpyridine (XII) but dimethyltinbistrifluoroacetate (XIII).



Looking at the structure of dimethyltinbistrifluoroacetate-4-acetylpyridine (XI) above, it could be seen that perhaps steric factors are most likely to be responsible for the non formation of dimethyltin-bistrifluoroacetate-3-acetyl-pyridine, since the acetyl group is in the 3-position and would interfere with the other groups around the tin atom. The repulsive energy from such an interference might be sufficient to break the weak Sn ← N coordination bond to give the more stable dimethyltinbistrifluoroacetate.

Reaction of Silver Trifluoroacetate with Diphenyltin Dichloride bis-4-acetylpyridine and Diphenyltin Dichloride Bis-3-acetylpyridine



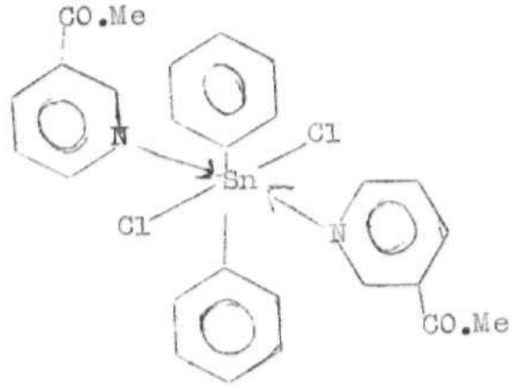
+ $2AgO.CO.CF_3$ →

Unknown .. D14

IV

Found; C, 42.69, H, 3.12; N, 6.02%

Calc. for $C_{20}H_{14}F_6N_2O_4Sn$; C, 48.60; H, 3.24; N, 3.78%



+ $2AgO.CO.CF_3$ →

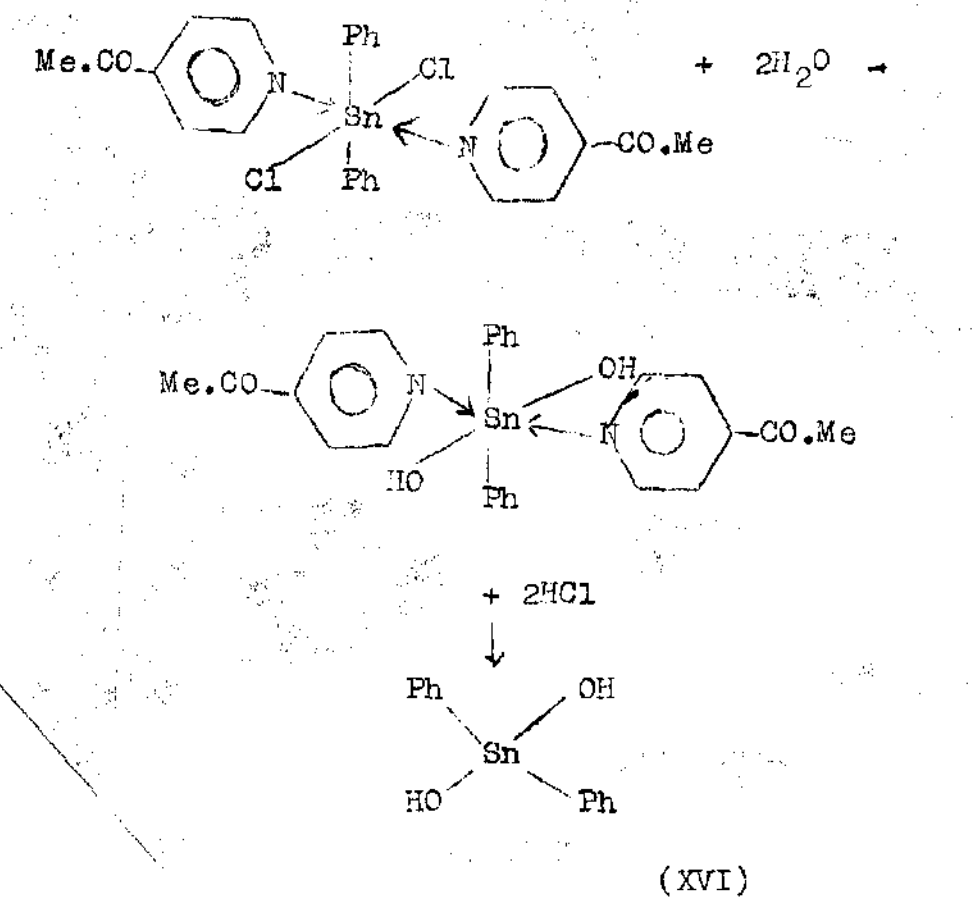
Unknown .. D15

III

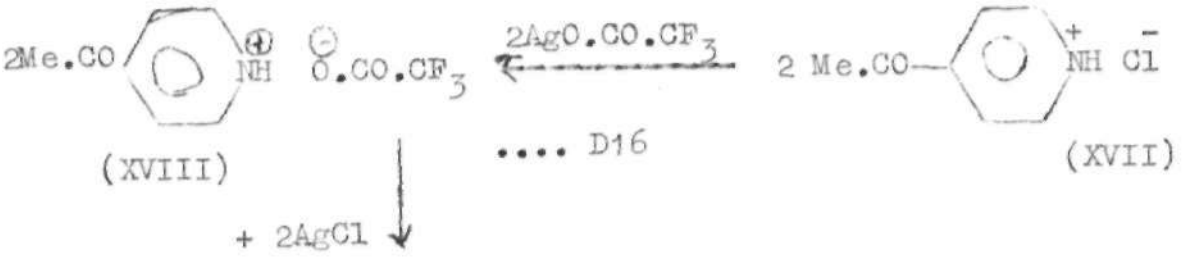
Found; C, 41.40; H, 3.07; N, 6.05%

Calc. for $C_{20}H_{14}F_6N_2O_4Sn$; C, 48.60; H, 3.24; N, 3.78%

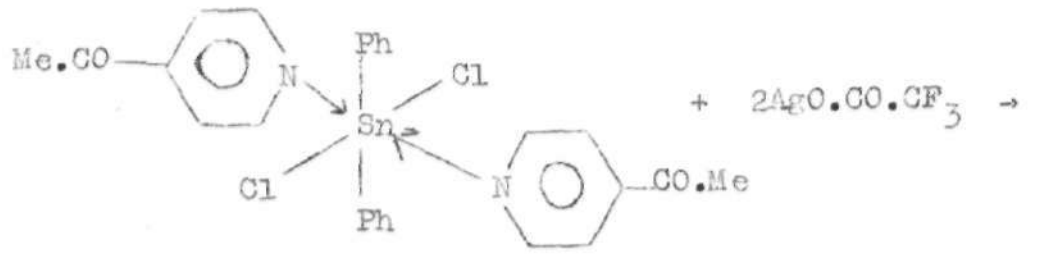
Diphenyltindichloride bis-3-acetylpyridine (III) and diphenyltindichloride bis-4-acetylpyridine (IV) both reacted with silver trifluoroacetate in dry benzene to give products whose n.m.r., i.r. and mass spectra (see later) did not show the phenyl ring. The chemical analysis results of the products were somewhat similar, but not near that for acetylpyridinium trifluoroacetate (XV) which would have been formed via hydrolysis of (III) or (IV), viz.

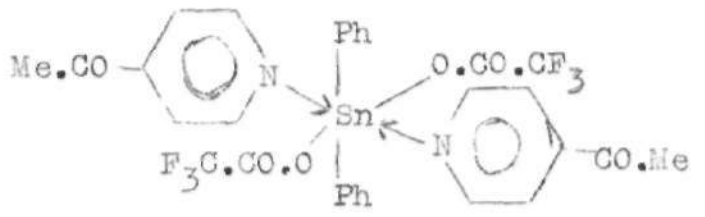


(XVI)

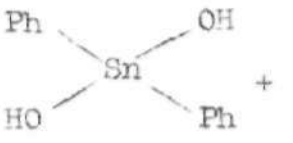


Or alternatively

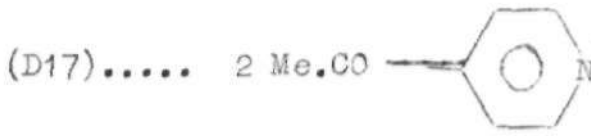




(XIX) $\xrightarrow{2H_2O}$



PTO

(D17)..... 2 Me.CO  $^{+}_{NH}$ O.CO.CF_3

If the reaction D16 or D17 occurred, then the ensuring diphenyltindihydroxide XVI would be lost with silver chloride as insoluble particles during filteration. Any trace of XVI would be removed during recrystallisation If hydrolysis was responsible for the loss of the phenyl group in some form, then the most likely route would be D17, as dry benzene was used as the solvent. If XIX was produced, it might be very hygroscopic (in analogy with dimethyltin-bistrifluoroacetate-4-acetylpyridine and would therefore pick any trace of water to give XVI and XVIII.

n.m.r., i.r., and mass spectroscopy (see later) strongly suggest the product of reaction D14 to be 4-acetylpyridinium trifluoroacetate (XVIII) and that of D15 to be 3-acetylpyridinium trifluoroacetate. Lassaigue test showed the presence of halogen in the product. The chemical analysis results for XVIII (C, 49.32; H, 3.65; N, 6.39) agreed with those for the unknown products, except for carbon. It could only be assumed, therefore, that the unknown was an impure form of acetylpyridinium trifluoroacetate, produced as a result of hydrolysis and enhanced

by steric factors due to crowding around tin atom in XIX.

Infra red Studies of the Organotin Compounds

The Sn-C Absorption Bands

The aliphatic carbon-tin stretching frequencies are the most commonly quoted infra red bands. Important structural information has been obtained by analyzing intensities and frequencies associated with the tin-carbon stretch.[42] The frequency variation occurring on going from one molecule to another or to the molecular complex depends on force constants in non-complexed molecules and reflects the ionic nature of the bonds. The Sn-C bond frequencies have been known not to be very sensitive to electronic effects in methyltin halides and depend weakly on either the number or the nature of the halogens.

Kriegsmann[65] and Cummins[66] have made a systematic study of the Sn-C absorption bands of a number of tri- and tetraorganotins. Since the Sn-C bond frequencies only weakly depend on the number of the halogens, the Kriegsmann and Cummins assignments have been used as guide lines to allocate the Sn-C frequencies of the studied methyltin chloride acetylpyridine complexes as well as the methyltin trifluoroacetates and their complexes.

Dimethyltindichloride Bispyridine

The infra red spectrum of $Me_2SnCl_2.Py_2$ has been intensively studied by Beattie et al.[44] There is only one V_{as} (Sn-C) vibration between 550 and 564 cm^{-1}. No symmetric stretch was observed, suggesting that the methyl groups are trans. This fact, when collected with some Mossbauer spectral measurements, has led to the suggestion of an octachedral structure with trans methyl groups for $Me_2SnCl_2.Py_2$.

The C-H deformation vibration of $Me_2SnCl_2.Py_2$ has shown weakly at 1185 cm^{-1}, suggesting that only very little C-H deformation has occured, due perhaps to steric factors in the octahedral structure.

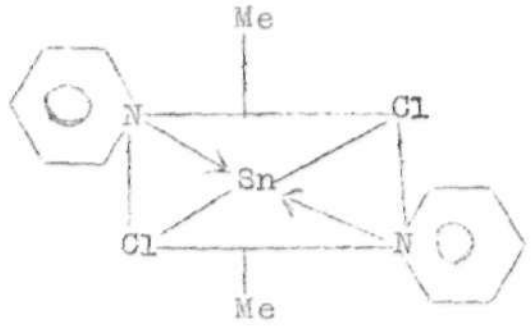


Table 1

ν_{Sn-C} Frequencies

Compound	C-H deformation Cm^{-1}	Rock Cm^{-1}	assym. stretch Cm^{-1}	Sym. Stretch Cm^{-1}
$Me_2SnCl_2.(4\text{-AcetylPy})_2$	1195 (m)	780 (s)	570 (s)	
$Me_2SnCl_2.(3\text{-AcetylPy})_2$	1195 (s)	774 (s)	565 (m)	520 (vw)
$Me_3SnCl.4\text{-AcetylPy}$	1190 (w)	786 (s)	546 (s)	
$Me_2SnCl_2.Py_2$	1185 (w)	780 (s)	566 (m)	
$Ph_2SnCl_2.(4\text{-AcetylPy})_2$	1065 (s)			
$Ph_2SnCl_2.(3\text{-AcetylPy})_2$	1070 (s)			
$Me_2Sn(O.CO.CF_3)_2.4\text{-AcetylPy}$	1200 (vs)	805 (s)	590 (m)	
$Me_2Sn(O.CO.CF_3)_2.4\text{-AcetylPy}$	1200 (s)	800 (s)	605 (s)	528 (m)
		790 (s)	590 (m)	505 (s)
$Me_3SnO.CO.CF_3$ 4-AcetylPy	1200 (s)	780 (s)	555 (s)	520 (w)

Table 2.

ν>C=O Frequencies

Compound	>C=O Stretching Frequencies (Cm^{-1})
$Me_2SnCl_2.(4\text{-AcetylPy})_2$	1690 (s)
$Me_2SnCl_2.(3\text{-AcetylPy})_2$	1685 (s)
$Me_3SnCl.4\text{-AcetylPy}$	1695 (s)
$Ph_2SnCl_2.(4\text{-AcetylPy})_2$	1700 (s)
$Ph_2SnCl_2.(3\text{-AcetylPy})_2$	1690 (s)
$Me_2Sn(O.CO.CF_3)_2.4\text{-AcetylPy}$	1705 (s), 1665 (s), 1640 (m)
$Me_2Sn(O.CO.CF_3)_2$	1655 (s)
$Me_3SnO.CO.CF_3$. 4-AcetylPy	1675 (s)

The νSn-C of the Adducts

Table I shows the Sn-C stretching frequencies as obtained from the i.r. spectra of the compounds, using Kriegsmann and Cummins' range assignments as guidelines. The spectra were run in caesium iodide medium.

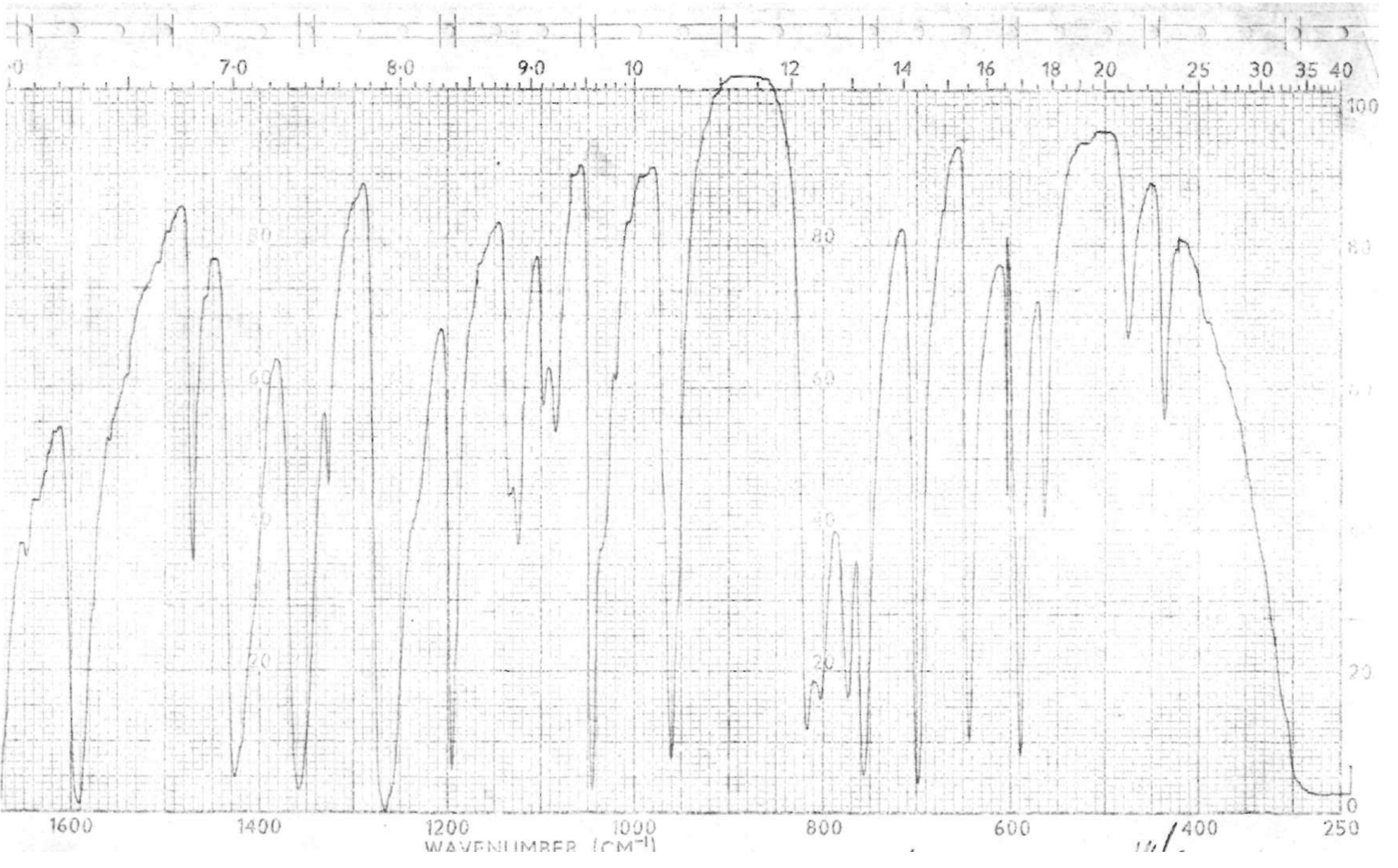
Acetylpyridine Adducts of the Methyltin Halides

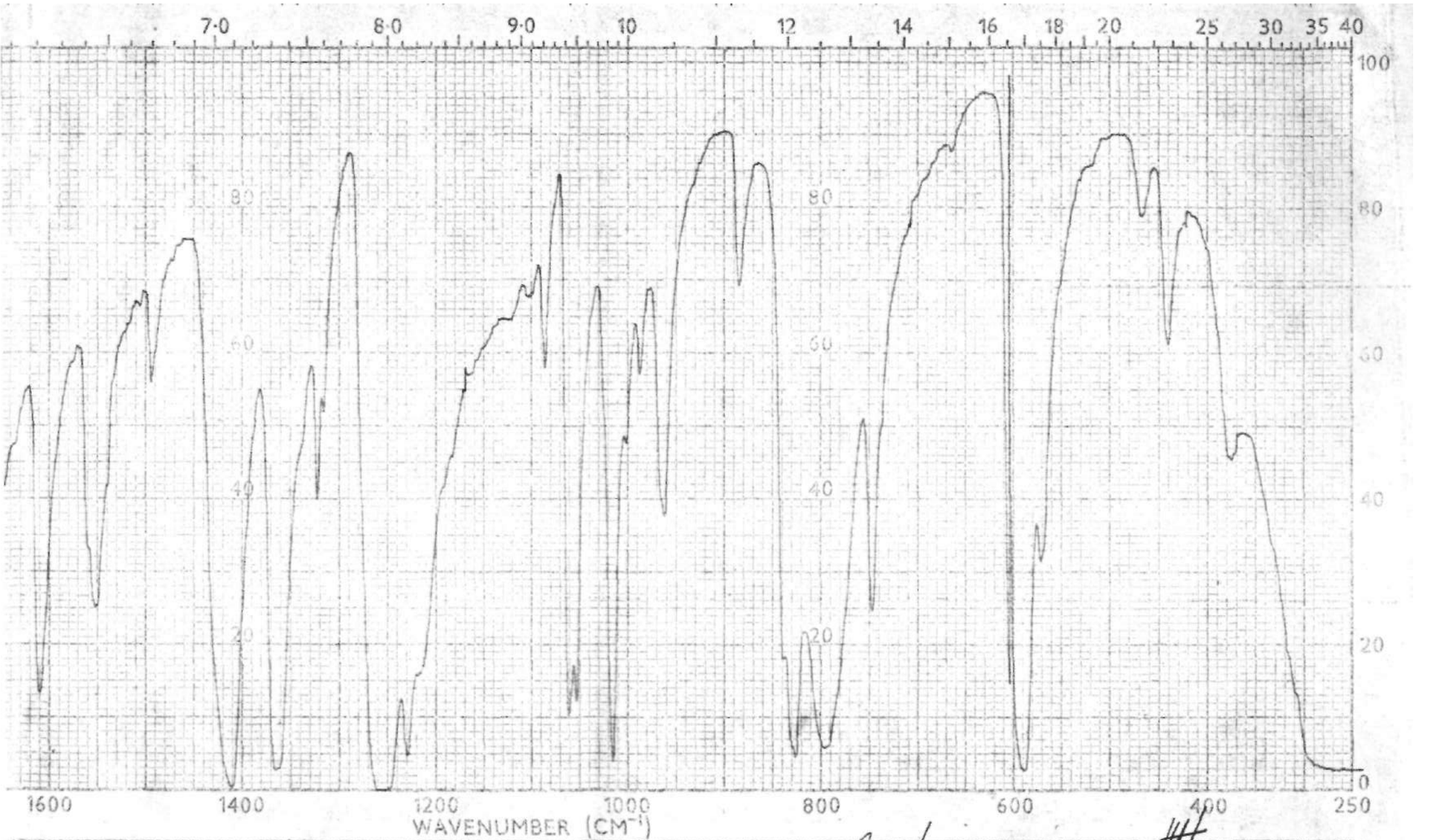
The C-H deformation frequencies of the compounds are comparable. That for $Me_2SnCl_2.Py_2$ came lowest, weakly at 1185 cm^{-1}. That for $Me_3SnCl.4$-AcetylPy came weakly at 1190 cm^{-1}, while those for $Me_2SnCl_2.(3\text{-AcetylPy})_2$ and Me_2SnCl_2-$(4\text{-AcetylPy})_2$ have came at 1195 cm^{-1}. The C-H deformation stretch gives the best information on the extent of deformation of the molecules due to steric factors, and this has been manifested in the spectra. Although not much can be inferred from the position of the bands, their intensities could give some relative extent of deformation of the molecules. While the bands for $Me_2SnCl_2Py_2$ and $Me_3SnCl.4$-AcetylPy are weak, that of $Me_2SnCl_2.(4\text{-AcetylPy})_2$ is medium while that of $Me_2SnCl_2.(3\text{-AcetylPy})_2$ is strong. The presence of acetyl group on the C4 of pyridine in $Me_2SnCl_2.(4\text{-Acetyl-Py})_2$ would produce steric tension that is more than that of $Me_2SnCl_2.Py_2$ but less than that of $Me_2SnCl_2.(3\text{-AcetylPy})_2$ which has its acetylgroup on the C3 of the pyridine.

Table 1

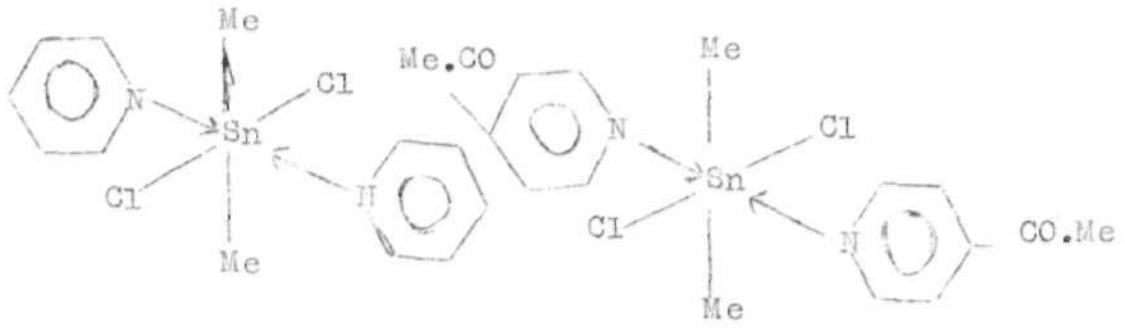
ν_{Sn-C} Frequencies

Compound	C-H deformation Cm^{-1}	Rock Cm^{-1}	assym. stretch Cm^{-1}	Sym. Stretch Cm^{-1}
$Me_2SnCl_2.(4\text{-AcetylPy})_2$	1195 (m)	780 (s)	570 (s)	
$Me_2SnCl_2.(3\text{-AcetylPy})_2$	1195 (s)	774 (s)	565 (m)	520 (vw)
$Me_3SnCl.4\text{-AcetylPy}$	1190 (w)	786 (s)	546 (s)	
$Me_2SnCl_2.Py_2$	1185 (w)	780 (s)	566 (m)	
$Ph_2SnCl_2.(4\text{-AcetylPy})_2$	1065 (s)			
$Ph_2SnCl_2.(3\text{-AcetylPy})_2$	1070 (s)			
$Me_2Sn(O.CO.CF_3)_2.4\text{-AcetylPy}$	1200 (vs)	805 (s)	590 (m)	
$Me_2Sn(O.CO.CF_3)_2.4\text{-AcetylPy}$	1200 (s)	800 (s)	605 (s)	528 (m)
		790 (s)	590 (m)	505 (s)
$Me_3SnO.CO.CF_3$ 4-AcetylPy	1200 (s)	780 (s)	555 (s)	520 (w)


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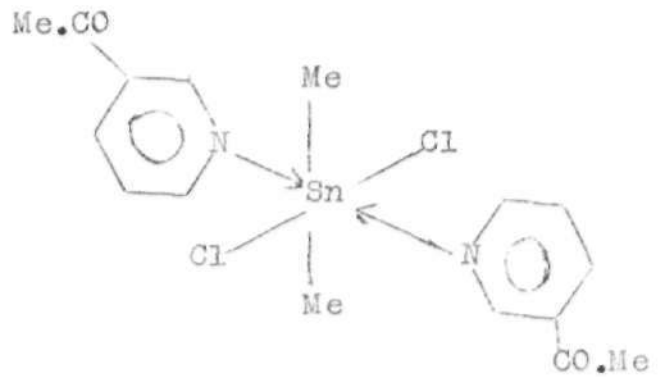


REMARKS	$Me_2SnCl_2 \cdot (4\text{-}Acetylpy)_2$	SCAN SPEED Medium SLIT Normal	OPERATOR ttt DATE 17/5/77
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Weak C-H deformation

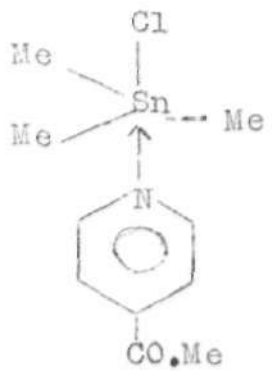
medium C-H deformation



Strong C-H deformation

The C-H deformation for $Me_3SnCl.4$-AcetylPy is weak, as the tin is only five coordinated with the Methyl groups planar.

Presence of acetylgroup on the C4 of the pyridine would not cause much steric tension.



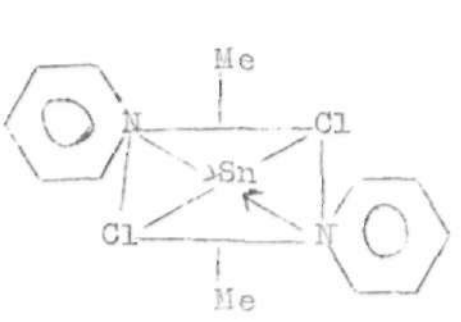
The C-H deformation modes considered are only those of the methyl groups.

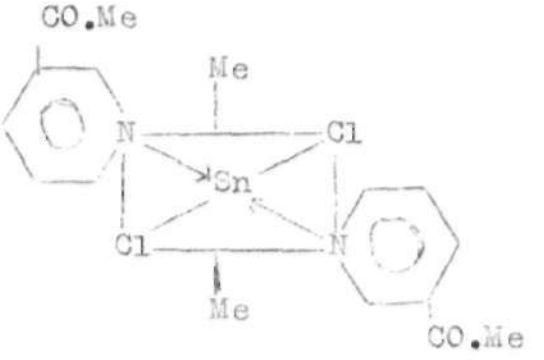
The rocking modes for all the methyl tin chloride adducts were strong. This could be due to a rather large change in the dipole moments in the tin-methyl bonds as the methyl groups rock. This would be expected because tin and carbon have unequal electronegativities, and any change in dipole moment produced by the bending due to the rocking movements would be larger than when the bond were between homonuclear atoms. The assymetric Sn-C stretch of the methyltinhalide adducts were all fairly strong. The frequencies of vibration have not come in an order good enough for any significant inference to be drawn. While νas (Me_2SnCl_2) came at 260 cm^{-1}, that of $Me_2SnCl_2.Py_2$ came at 566 cm^{-1}, $Me_2SnCl_2.(3\text{-AcetylPy})_2$ at 565 cm^{-1}, and $Me_2SnCl_2.(4\text{-AcetylPy})_2$ at 570 cm^{-1}. It would have been expected that on the basis of electron repulsion theory, the Sn-C bond should weaken when an adduct is formed since the electron density on Sn increases; νas (Sn-C) should therefore be lower than that for the parent organotin halide. One would expect therefore that the decrease in νas (Sn-C) would be a function of the electron density around Sn, which in turn would be proportional to the basicity of the donor ligand- νas (Sn-C) for the adducts would therefore be in the order

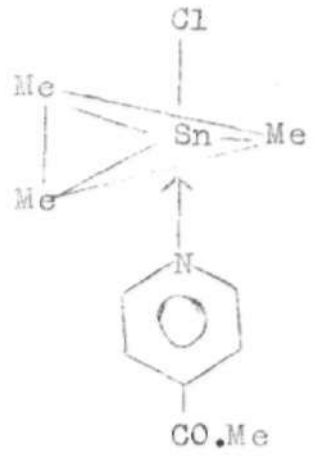
$Me_2SnCl_2 > Me_2SnCl_2(3\text{-AcetylPy})_2 > Me_2SnCl_2(4\text{-AcetylPy})_2$
$> Me_2SnCl_2.Py_2$.

But the fact that the νas (Sn-C) values for all the adducts are greater than that of the starting Me_2SnCl_2 suggests that the Sn-C bond is stronger in the adducts than in the starting organotin halide.

Only $Me_2SnCl_2.(3\text{-AcetylPy})_2$ has shown a weak νs (Sn-C). Inferring from Beattie's work on $Me_2SnCl_2.Py_2$, the absence of a νs for the adducts shows that the methyl groups are trans in the dimethyltin adducts, and planer in the trimethyltin adducts



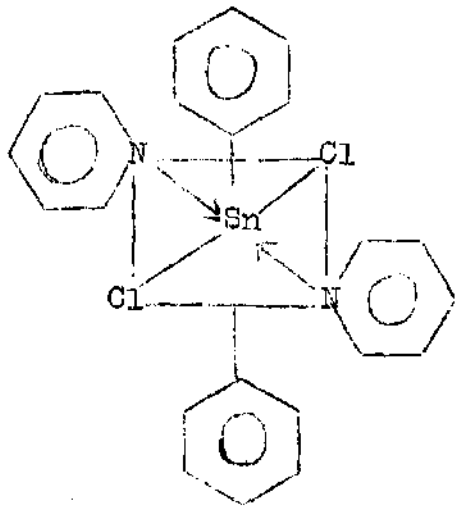


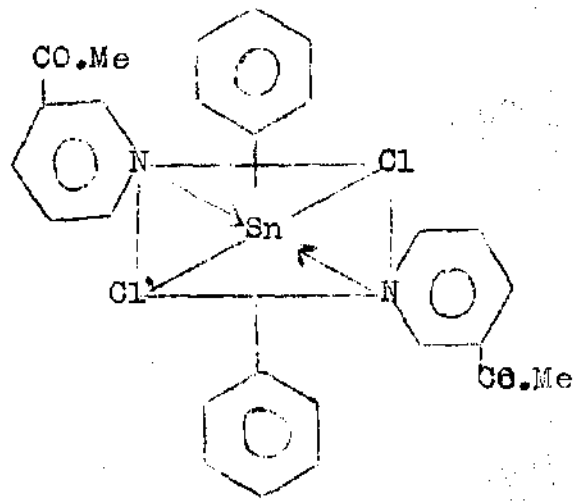


The presence of a symmetric stretch in the spectrum of $Me_2SnCl_2.(3\text{-AcetylPy})_2$ could be due to distortion of the molecule, which would be due to the steric tension produced by the acetyl group.

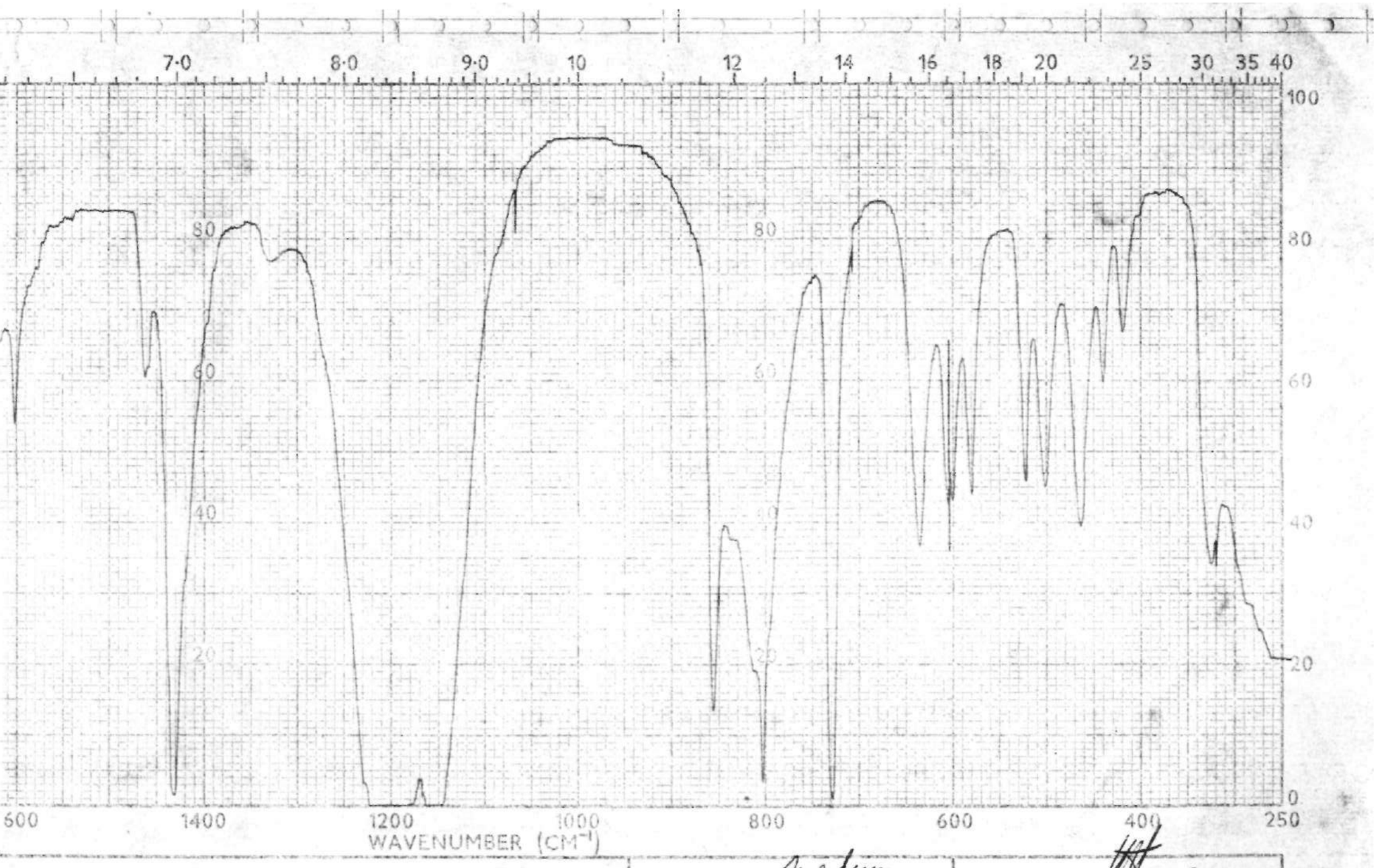
Acetylpyridine Adducts of Diphenyltin Chloride

Kriegsmann[65] and Cummins[66] have assigned the vibrations in the 1060-1075 cm^{-1} region to the C-H deformation mode in phenyltin compounds. The spectra of $Ph_2SnCl_2.(4\text{-AcetylPy})_2$ and $Ph_2SnCl_2.(3\text{-AcetylPy})_2$ showed very strong bands at 1065 and 1070 cm^{-1} respectively, showing that the C-H deformation in these compounds is strong. This is not unexpected as there would be much steric tension in the molecules, assuming that Beattie's proposed structure[44] for $Me_2SnCl_2.Py_2$ still halids for the compounds





The C-H deformation has been assigned to the phenyl protons. Looking at the above structures thus, the phenyl protons of $Ph_2SnCl_2.(3\text{-AcetylPy})_2$ would be more susceptible to deformation because of the meta-position of the acetylgroup



REMARKS

$[Me_2Sn(O{\cdot}CO{\cdot}CF_3)_2{\cdot}4\text{-Acetylpy}]_2$ ~~3 acetyl~~

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of the pyridine.

The regions assigned[65,66] to the νs (Sn-C) and νas (Sn-C) the phenyltin compounds are low (>300 cm^{-1}) The bands in this region of our spectra could not be relied upon as some of the spectra were run abroad in KBr; and KBr absorbs in the region.

The Methyltin Trifluoroacetates and their Adducts

Since the trifluoroacetate group is a much stronger electron-withdrawing group than the halogens, it would be expected that the Sn-C bond in a methyltin trifluoroacetate would be stronger than one in a methyltin in the former would be lower hence strengthening the Sn-C bond, while the tin in the latter would have a relatively higher electron density and thus a weaker Sn-C bond (electron repulsion theory). Since the Sn-C stretching frequencies are a function of the strength of the bond, the frequencies would be higher in methyltin trifluoroacetates than in methyltinhalides.

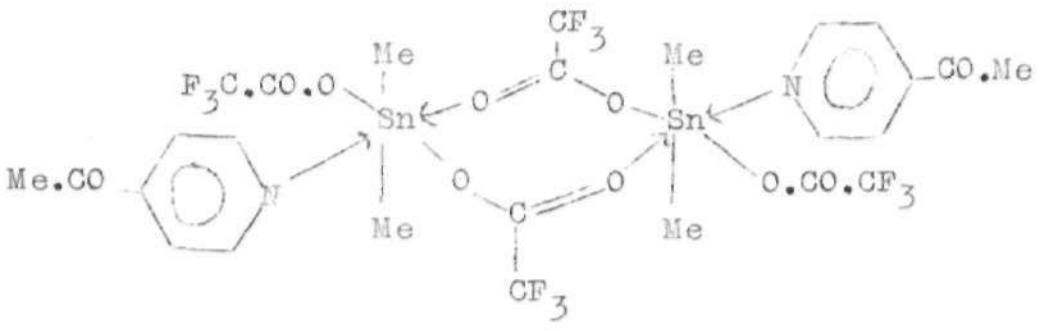
C-H deformations of Sn-Me

The C-H deformation frequencies of the trifluoroacetates, $Me_2Sn(O.CO.CF_3)_2$, $Me_2Sn(O.CO.CF_3)_2$. 4-AcetylPy, and $Me_3SnO.CO.CF_3$.4-AcetylPy, showed very strongly at 1200 cm^{-1}, suggesting strong deformation in all three

compounds.

Rocking modes of Sn-Me

As shown in table 3, the rocking modes all come strongly between 780 cm^{-1} (for $Me_3SnO.CO.CF_3$.4-AcetylPy) and 805 cm^{-1} (for $Me_2Sn(O.CO.CF_3)_2$.4-AcetylPy). The strong intensity of the bands could be due to the dipole moment that would be easily created by bending since the tin is bound to strongly electron-withdrawing trifluoroacetate group. Moreover, bending due to rocking might bring about slight interference between the methyl protons and the fluorine and oxygen of the trifluoroacetate group. This would further cause a greater electron-density change and consequently, a great dipole moment change. The resulting intense rocking modes would be most pronounced in the dimethyltin trifluoroacetates, e.g. XI



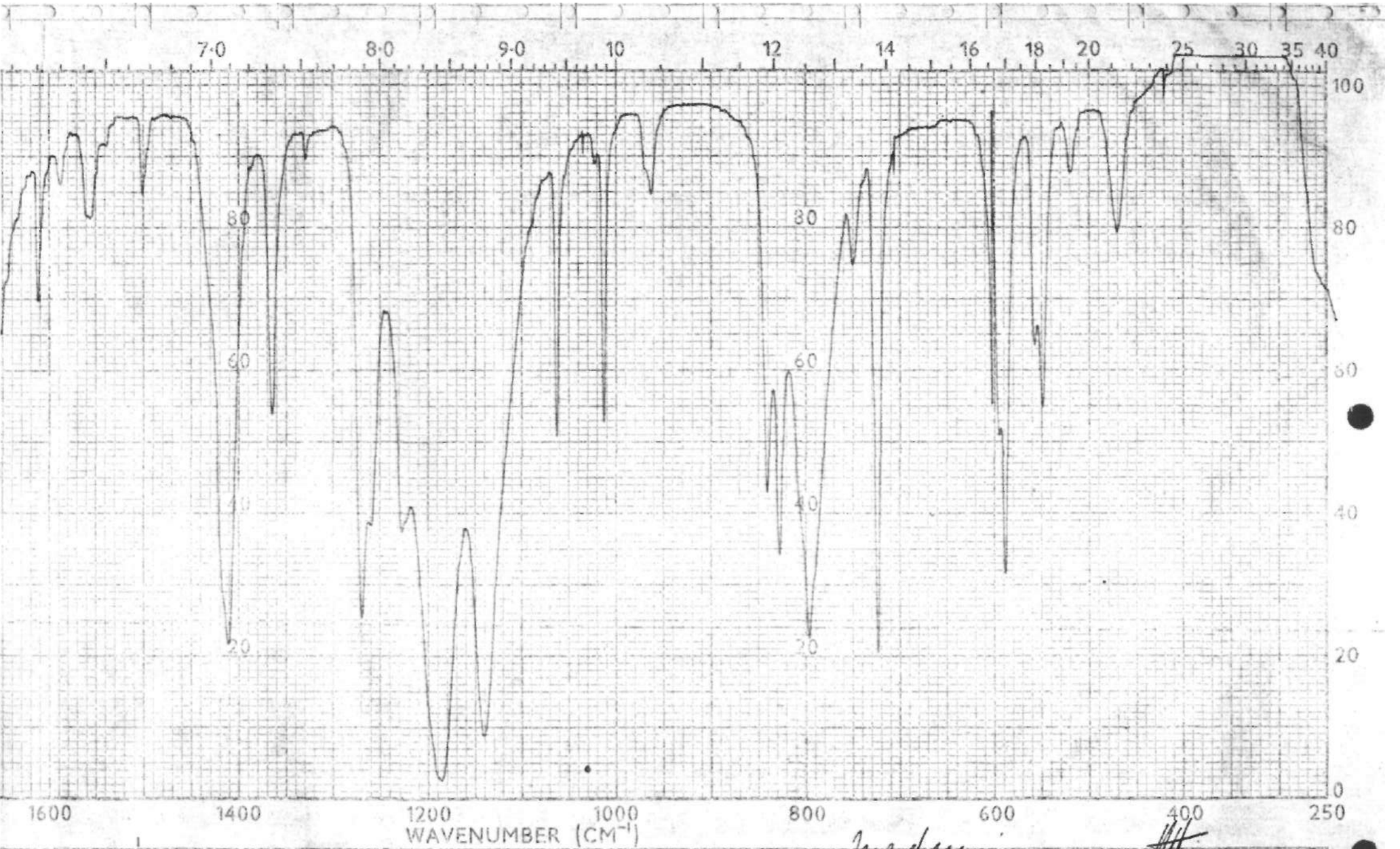
XI

Sn-C Assymetric Stretch

Although much work has been done on the methyltin halide adducts, not much has been published on the i.r. of organotin trifluoroacetates. Kriegsmann and Cummins assignments have been used in assigning the bands of the spectra of the prepared methyltin trifluoroacetates. The νas (Sn-C) for the three trifluoroacetates, as shown in table 3, come between 555 cm^{-1} (for $Me_3SnO.CO.CF_3.4$-AcetylPy) and 2 590 cm^{-1} (for the dimethyltin trifluoroacetates). Both $Me_2Sn(O.CO.CF_3)_2$ and $Me_2Sn(O.CO.CF_3)_2$.4-AcetylPy show an absorption of medium intensity at 590 cm^{-1}, while $Me_2Sn(O.CO.CF_3)_2$ shows an additional strong band at 605 cm^{-1}. As expected, all the absorptions come at frequencies higher than those for their corresponding methyltin halide adducts, most likely because of stronger Sn-C bonds.

Sn-C Symmetric Stretch

$Me_2Sn(O.CO.CF_3)_2$.4-AcetylPy does not show any symmetric stretch, showing[44] that the methyl groups are trans. The weak absorption shown by $Me_3SnO.CO.CF_3$.4-AcetylPy at 520 cm^{-1} might be due to distortion of the likely trigonalbipyramid structure probably due to coordination by the carbonyl oxygen of the trifluoroacetate group.



REMARKS

$Me_3SnO.CO.CF_3.4$-AcetylPy

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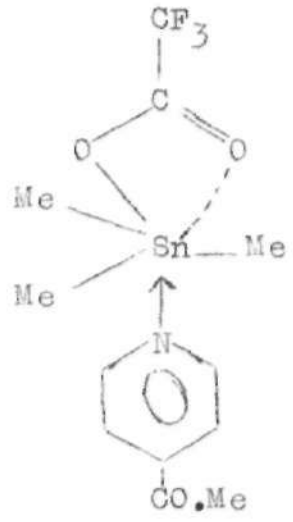
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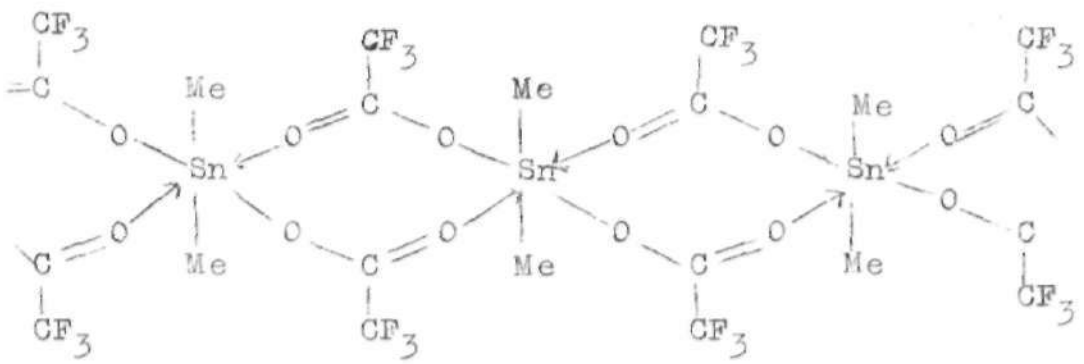
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Dimethyltin bistrifluoroacetate shows absorptions in the region allocated[65,66] for Sn-C symmetric stretch. The reason for this is not clear, but it might be due to distortion of bonds in the polymeric structure[67] since the co-ordination brought about by the trifluoroacetate oxygen would be weak.



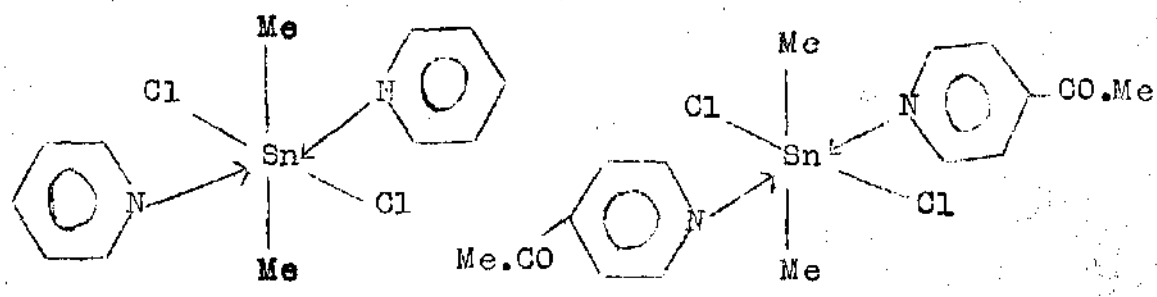
XX $\left[Me_2Sn(O.CO.CF_3)_2 \right]_n$

The Sn-N Stretch

The Sn ← N stretch of pyridine adducts, as found by Okawara et al[45], shows at 150 cm^{-1}. The stretching frequency of a bond between two atoms M_1 and M_2, is given by

$$\nu = \frac{1}{2\pi C}\sqrt{\frac{K}{M_1M_2/M_1}} + M_2$$

where C is the velocity of light and K is the force constant. Looking at the pyridine and acetylpyridine adducts of dimethyltin dichloride, the pyridine and acetylpyridine



are bound to the tin by their nitrogen. Any S - N vibration would make the whole pyridine or acetylpyridine molecule vibrate. For simplicity, one could assume that the pyridine and acetylpyridine moieties are point masses.

In the above equation, since π, C and K are constant, the magnitude of ν would be inversely proportional to the product of $M_1M_2/M_1 + M_2$, i.e.

$$\nu \propto \frac{1}{M_1M_2/M_1 + M_2}$$

and M_1M_2/M_1+M_2 is directly proportional to the value of M_1 and M_2 considering the Sn-pyridine stretch,

M_1 = 118.67 = atomic wt. of tin

M_2 = 79 = molecular wt. of pyridine

$$\therefore \quad \frac{M_1M_2}{M_1+M_2} = \frac{118.67 \times 79}{118.67 + 79} = 47.43$$

$$\nu_{Sn-Py} = \frac{1}{2\pi c}\sqrt{\frac{K}{47.43}}$$

For the tin-acetylpyridine stretch,

M_1 = 118.67

M_2 = 121

$$\therefore \quad \frac{M_1M_2}{M_1+M_2} = \frac{118.67 \times 121}{118.67 + 121} = 59.91$$

$$\therefore \quad \nu_{Sn-AcetylPy} = \frac{1}{2\pi c}\sqrt{\frac{K}{59.91}}$$

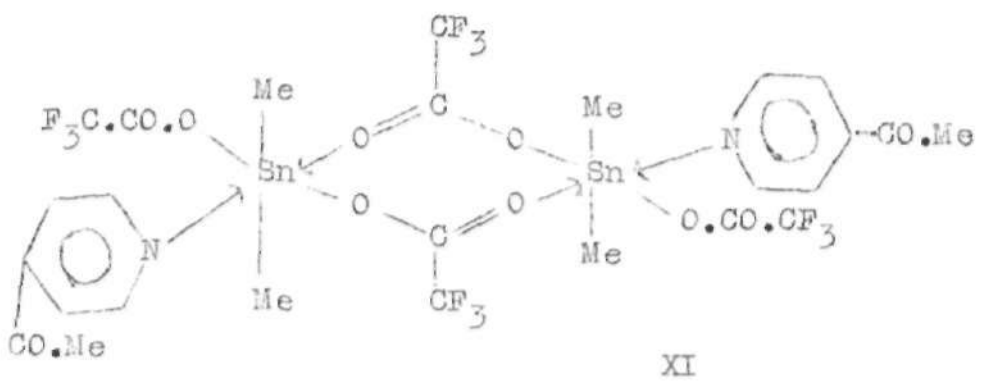
It can be seen that on the basis of molecular mass alone, the Sn-N stretching frequency in a pyridine adduct of an organotin halide would be higher than that of the acetyl-pyridine adduct of the same organotin halide.

Moreover, since the stretching frequency of a bond is directly proportional to the strength of the bond and, hence, the basicity of the pyridine or acetylpyridine in this case, ν_{Sn-N} for the pyridine adduct would be higher than that for acetylpyridine adduct, since the later's acetyl group is electron withdrawing.

Unfortunately, these expectations could not be tested as a machine that operates in the region of far i.r. was not available.

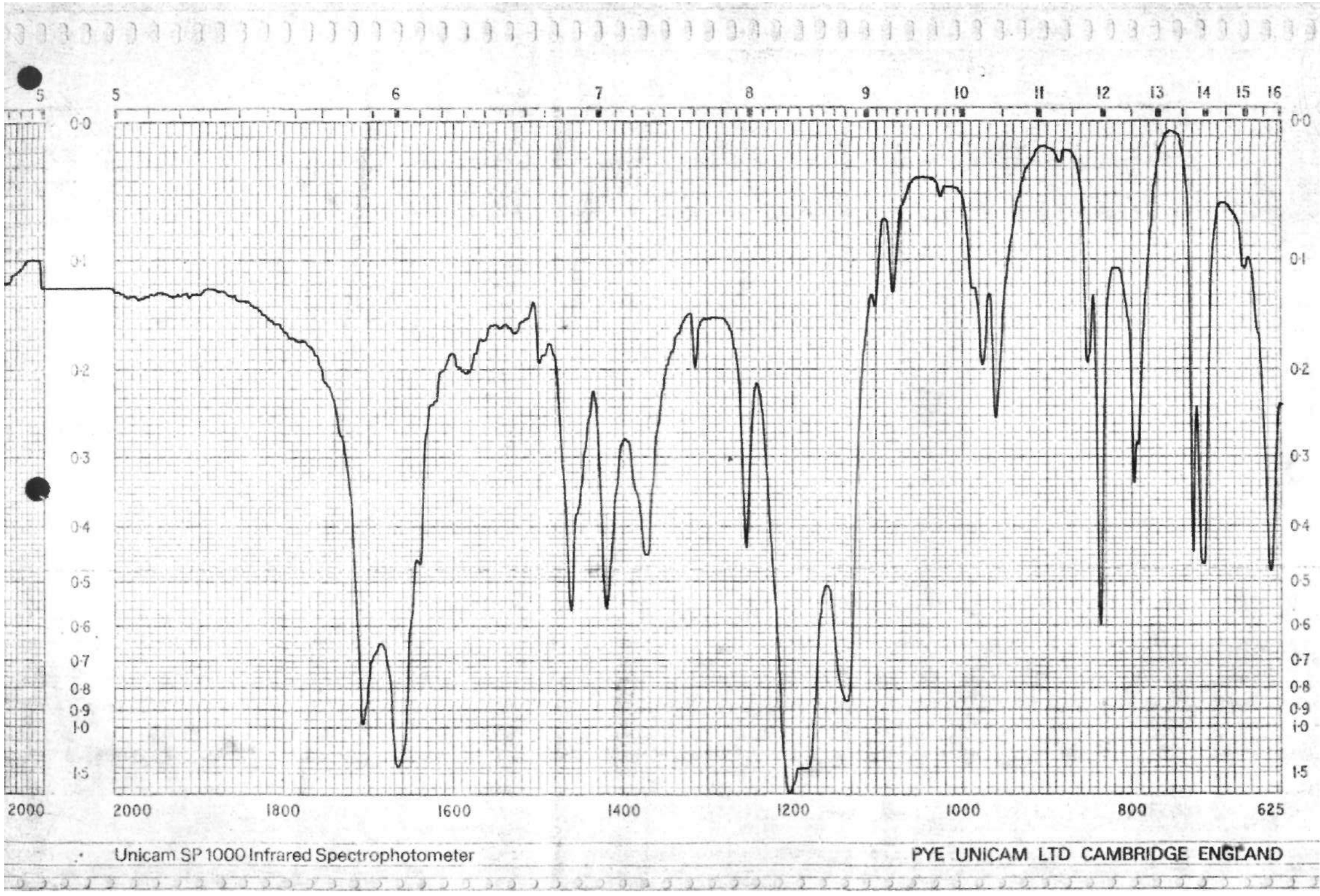
The Carbonyl Absorption of the Methyltin Trifluoroacetates

The i.r. spectrum of $Me_2Sn(O.CO.CF_3)_2.4$-AcetylPy shows a broad absorption between 1640 and 1705 cm^{-1}, with arms at 1705, 1665, and 1640 cm^{-1}. Since mass spectroscopy has shown the compound to be dimeric, the most likely structure for it would be XI.



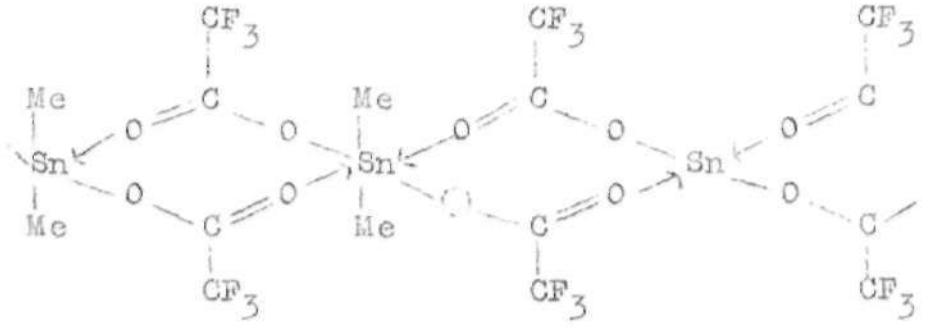
XI

If this structure is correct, there should be three types of >CO : the carbonyl of the acetylpyridine, that of


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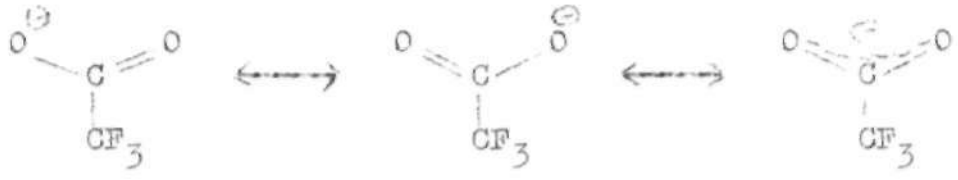
uncoordinated trifluoroacetate. These would show at different cm^{-1} in the i.r., since their carbonyl bond strengths are not equal. These are actually observed in the i.r. spectrum. Thus the structure XI is most likely to be correct for the compound.

Dimethyltin bistrifluoroacetate, from previous work on organotin carboxylates,[81] is likely to be a polymer XX.



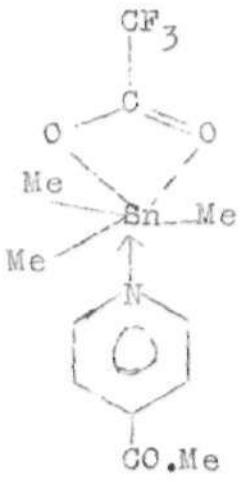
XX

In that case, the >CO absorption band would be broad since a resonance of the following type would occur in the carboxyl group



A broad band was actually observed in the i.r.

The spectrum of $Me_3SnO.CO.CF_3$.4-AcetylPy also shows a broad band. This might be due to the presence of two types of >CO in the molecule; that of the acetylpyridine and that of the trifluoroacetate group.



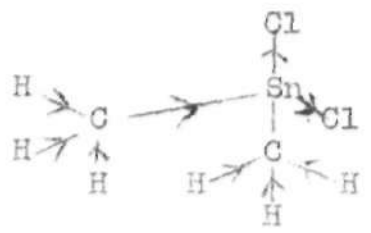
Co-ordination of the trifluoroacetate >CO on the tin is not impossible; that would make the carbonyl differ more in strength from that of the acetyl group.

NMR SPECTRA

Factors Affecting the Chemical Shifts of Organotin Compounds

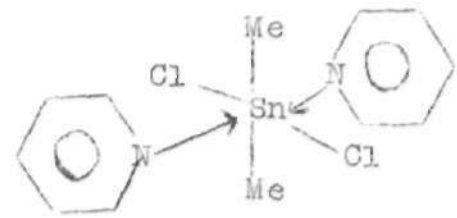
Organotin Halides and their adducts

Methyltin halides, the simplest organotin halides have been most intensively studied[48, 68]. A most important factor deciding the chemical shift for the methyl groups of a methyltin halide is the number of halogens attached to the tin atom. The halogens, being much more electronegative than tin, are electron-withdrawing. There is thus an electron drift from the methyl to tin and to the halogen, thereby deshielding the methyl protons. The more halogens there are on the tin, the more deshielded the methyl protons.

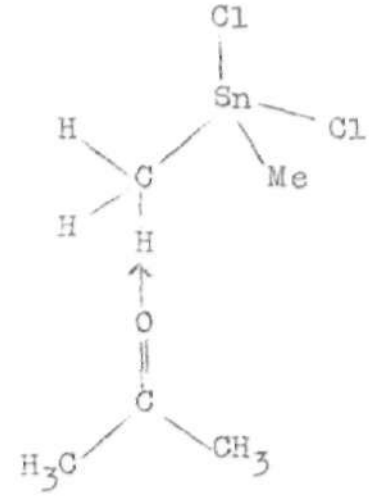


When a Lewis Base forms an adduct with an organotin halide, the electron density on the tin atom presumably increases and the net electron drift from the alkyl or

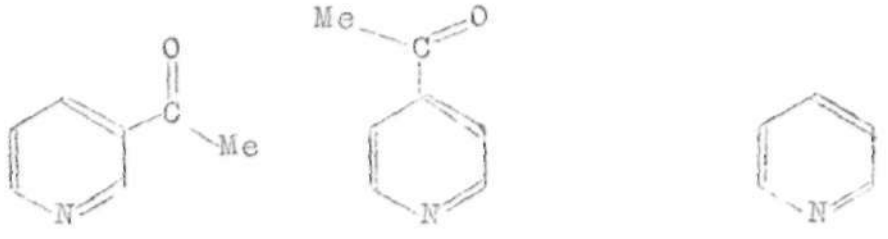
aryl protons of the organotin halide decreases. Thus a slight decrease in the chemical shift compared with the parent organotin halide occurs when it forms an adduct



A slightly less important, but not negligible, factor is the solvent in which the spectrum is run. A polar protic or aprotic solvent forms hydrogen bonds with the alkyl or aryl protons of the organotin, thereby altering the electron density of the protons. The chemical shift values for the protons may thereby be slightly altered



Basicities of 3- and 4-acetyl pyridine and their expected effects on the spectra of organotins



because of the electron-withdrawing effect of the acetyl group, 3- and 4-acetyl pyridine are expected to be less basic than pyridine. The latter should therefore form stronger adducts with organotins. On the basis of resonance, 4-acetyl pyridine should be less basic than 3-acetylpyridine since the acetyl group of the former is para-located while that of the latter is meta.



On the basis of inductive effects, however, since the carbonyl group of 3-acetylpyridine is nearer to the nitrogen of the molecule, it (3-acetylpyridine) should be less basic than 4-acetylpyridine. But since the acetyl group

of the molecule, is in the meta-position, the molecule would be more sterically hindered from getting close to the tin of an organotin to form a strong bond. On the whole therefore, it would be expected that 4-acetyl-pyridine forms stronger bonds with organotins than 3-acetyl pyridine.

Considering the factors that affect the δ values of the CH_3-Sn protons, the more basic a ligand, the more shielded are the CH_3-Sn protons when the adducts are formed, though these changes in δ-values may not be large.

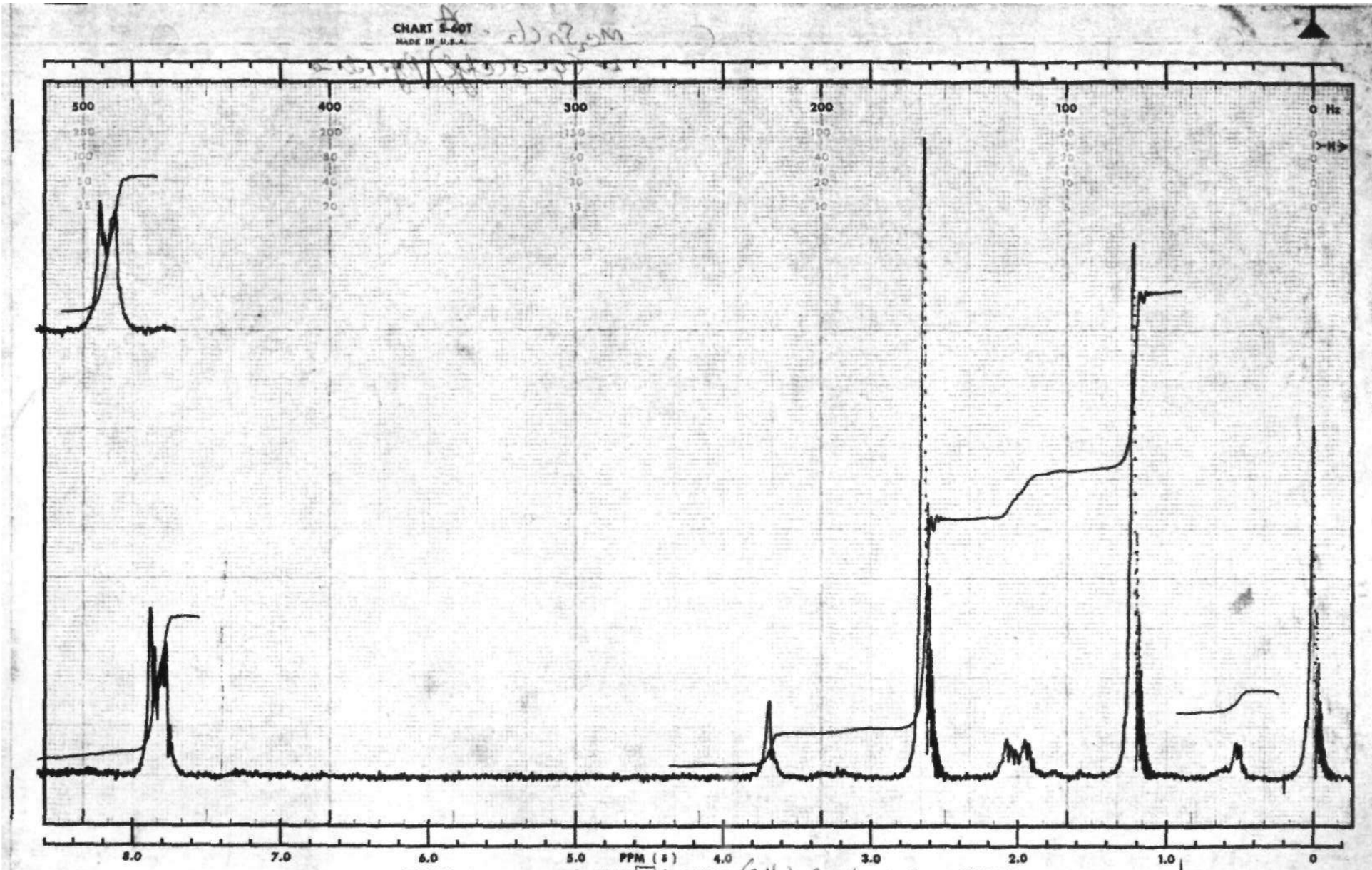
Chemical Shift Values

Pyridine and Acetylpyridine Adducts of Dimethyltindichlorid

As can be seen in Table 3, the δ values for the methyl protons of the diorganotin dihalides and their pyridine and acetylpyridine adducts have not been drastically affected by change of the co-ordination number of tin. The magnitude of $\delta(Sn\text{-}CH_3)$ for dimethyltindichloride and its adducts are however in the order.

$$(CH_3)_2SnCl_2 > (CH_3)_2SnCl_2.Py_2 > (CH_3)_2SnCl_2.(4\text{-AcetylPy})_2 > (CH_3)_2SnCl_2.(3\text{-AcetylPy})_2$$

It is fortunate that the n.m.r. spectrum of $(CH_3)_2.Cl_2.Py_2$ has been obtained perhaps for the first time. As expected, δ Sn-C.H for the pyridine adduct (91 cps)



SWEEP OFFSET (Hz): 40
SPECTRUM AMPLITUDE: 4.02
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 40

MANUAL
SWEEP TIME (SEC): 80 ~~250~~
SWEEP WIDTH (Hz): ~~25~~ 50 100 250 ~~500~~
FILTER: ~~1~~ 2 3 4 5 6 7 8
RF POWER LEVEL: 0.20

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $(CH_3)_2SnCl_2 \cdot 2$-(4-Acetylpyridine)

REMARKS:

SOLVENT: d-acetone

varian
analytical instrument division

DATE: 9-6-76

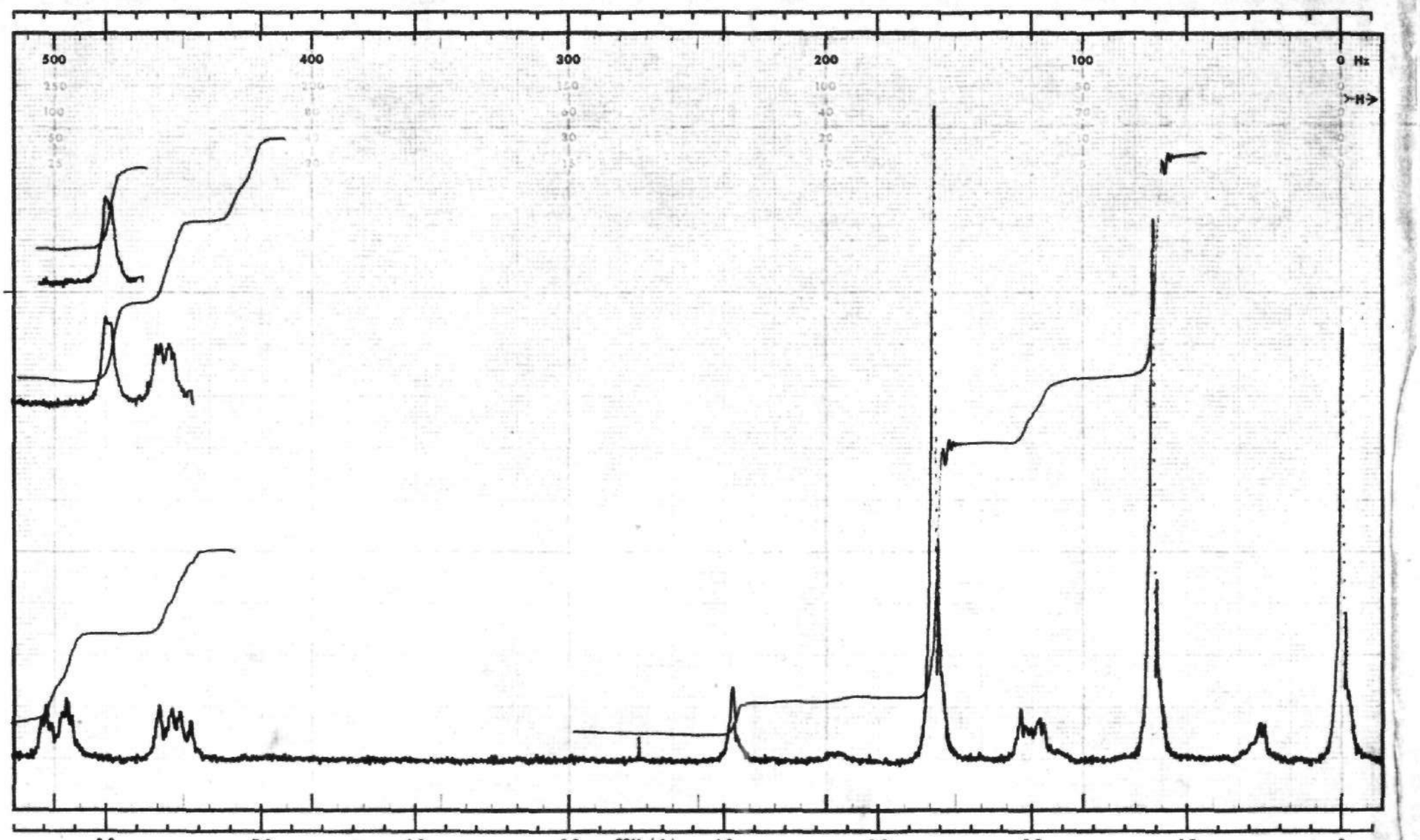
OPERATOR: [illegible]

60 MHz NMR SPECTRUM NO. 1475

is larger than that for the adduct of 4-acetylpyridine, (88 cps) which is in turn larger than that of 3-acetyl-pyridine (87 cps).

The δ ($-CO.CH_3$) values for the 3-and 4-acetylpyridine adducts (2.6ppm) did not appear to have been much influenced by the position of the acetyl group.

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



SWEEP OFFSET (Hz): -70
SPECTRUM AMPLITUDE: 4.0
INTEGRAL AMPLITUDE: 8.0
SPINNING RATE (RPS): 49

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: 0.10

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $(CH_3)_2SnCl_2 \cdot 2$ (3-Acetyl Pyridine)

REMARKS:

SOLVENT: d-Acetone

varian
analytical instrument division

DATE: 9-6-76

OPERATOR: [illegible]

60 MHz NMR
SPECTRUM NO. 1474

Table 3

Compound	Solvent	δ (Sn-CH_3) ppm Ref. TMS	δ (Sn-CH_3) Lit
$(CH_3)_2SnCl_2$	$CD_3.CO.CD_3$	1.24	1.15-1.2
$(CH_3)_2SnCl_2.Py_2$	"	1.23	-
$(CH_3)_2SnCl_2.(4\text{-AcetylPy})_2$	"	1.22	-
$(CH_3)_2SnCl_2.(3\text{-AcetylPy})_2$	"	1.21	-
$(CH_3)_2Sn(O.CO.CF_3)_2$	"	1.00	-
$(CH_3)_2Sn(O.CO.CF_3)_2$	"		
4-AcetylPy		1.05	-
$(CH_3)_3SnCl$	CCl_4	0.64	0.61-0.66
$(CH_3)_3SnCl.Py$		0.63	-
$(CH_3)_3SnCl.4\text{-AcetylPy}$	"	0.64	-
$(CH_3)_3SnO.CO.CF_3 4\text{-AcetylPy}$	"	0.7	-

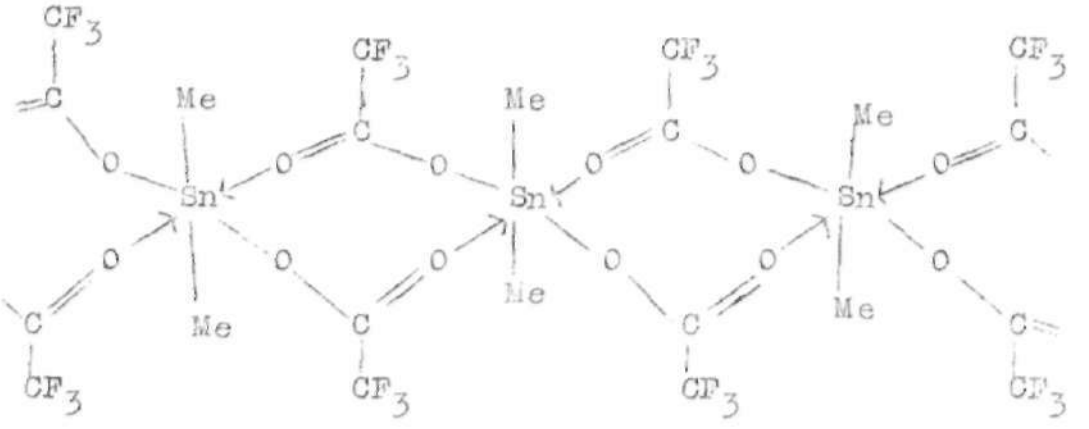
As expected, the pyridine nuclear protons, C2H and C6H, C3H and C5H, show as two AA'BB' quartets. Since the C2 and C6 are directly bonded to N, the δ value for their protons is expectedly higher than that for C3H and C5H.

The pyridine nucleus protons of the 3-acetylpyridine adducts exhibit four different signals. C5H, the least deshielded, and being coupled to C4H and C6H, shows as a quadruplet at δ = 7.5 ppm. C4H is at δ 8.3 ppm as a doublet due to coupling with C5H; each of the doublet signals appears as a triplet as a result of meta-coupling with C2H and C6H. C6H appears at δ = 8.8 ppm as a doublet as a result of ortho-coupling with C5H; the signals are weakly split as a result of meta-coupling with C4H. C5H appears as a singlet at δ = 9.2 .

The pyridine protons of dimethyltindichloride bis-pyridine appear in two groups of multiplets. The C2H and C6H, because they are nearer to the electron withdrawing tin atom, would have a slightly higher δ value than C3H, C4H, and C5H. Thus the C3H, C4H and C5H appear as a multiplet at δ = 7.5, while C2H and C6H come at 7.9 ppm.

Dimethyltinbistrifluoroacetate and Dimethyltinbistrifluoroacetate-4-acetylpyridine

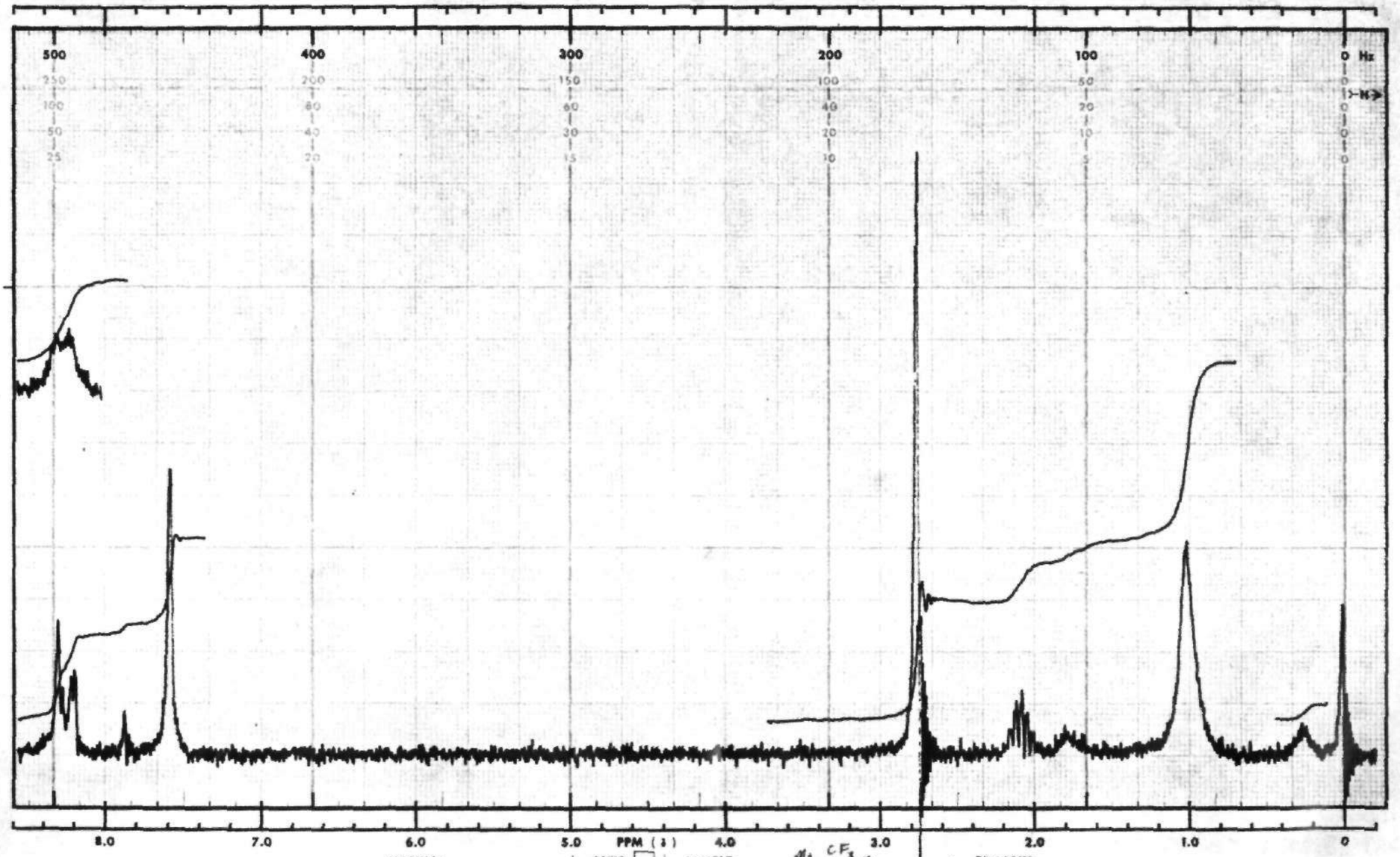
The δ ($Sn-CH_3$) for dimethyltinbistrifluoroacetate shows at 1 ppm, 0.24 ppm lower than that for dimethyltindichloride run in the same deuteroacetone solvent. One would have expected a higher δ value because of the highly electron withdrawing trifluoroacetate group, but back donation of electrons from the oxygen of the trifluoroacetate has perhaps increased the electron density on the tin atom, making the methyl protons less deshielded. From the published investigations of the structures of organotin carboxylates[67], dimethyltinbistrifluoroacetate might be a polymer of the following structure.



XX

Thus with the trifluoroacetate oxygen coordinating on it, the tin would be hexacoordinated.

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MADE IN U.S.A.

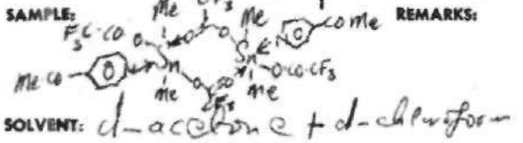


SWEEP OFFSET (Hz): 50
SPECTRUM AMPLITUDE: 1.25
INTEGRAL AMPLITUDE: 8
SPINNING RATE (RPS): 45

MANUAL | AUTO ☐

SWEEP TIME (SEC): 80 250 | (250)
SWEEP WIDTH (Hz): 25 50 100 250 500 | (500)
FILTER: 1 2 3 4 5 6 7 8 | (2)
RF POWER LEVEL: 2.10 | (.05)

SAMPLE:



REMARKS:

SOLVENT: d-acetone + d-chloroform

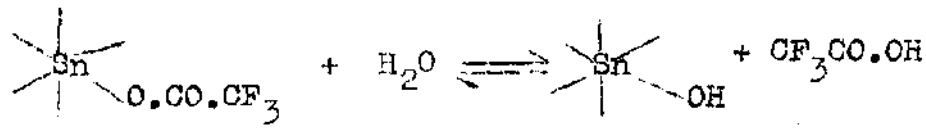
varian
analytical instrument division

DATE: 24.7.27

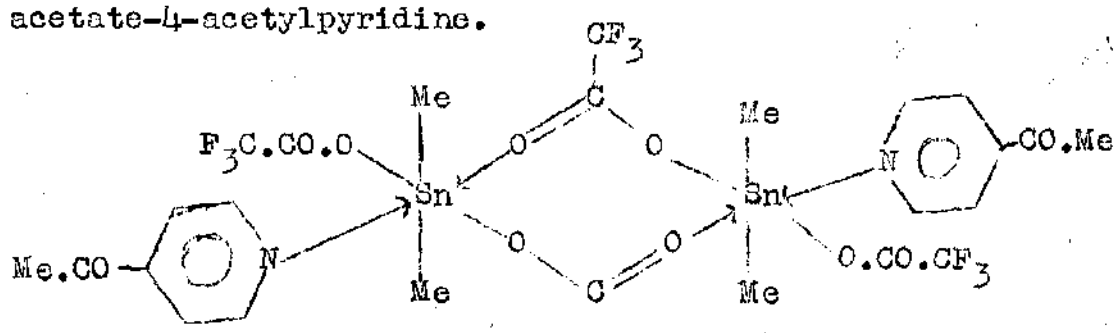
OPERATOR:

60 MHz NMR SPECTRUM NO. 1563

The Sn-Me protons of dimethyltin bistrifluoroacetate-4-acetylpyridine, perhaps the first compound of its type, give a signal at δ = 1.03 ppm, which is not significantly different from that of dimethyltin bistrifluoroacetate. The ($-CO.CH_3$) is at 2.75 ppm, the C3H and C5H are a doublet at 8.3 ppm, and C2H and C6H are a doublet at 9.1 ppm. An additional singlet appears at δ7.6, and this is thought to be due to OH, which might have been produced as a result of rapid proton exchange by the trifluoroacetate on the tin with traces of water in the solution. This is plausible as the compound is hygroscopic.

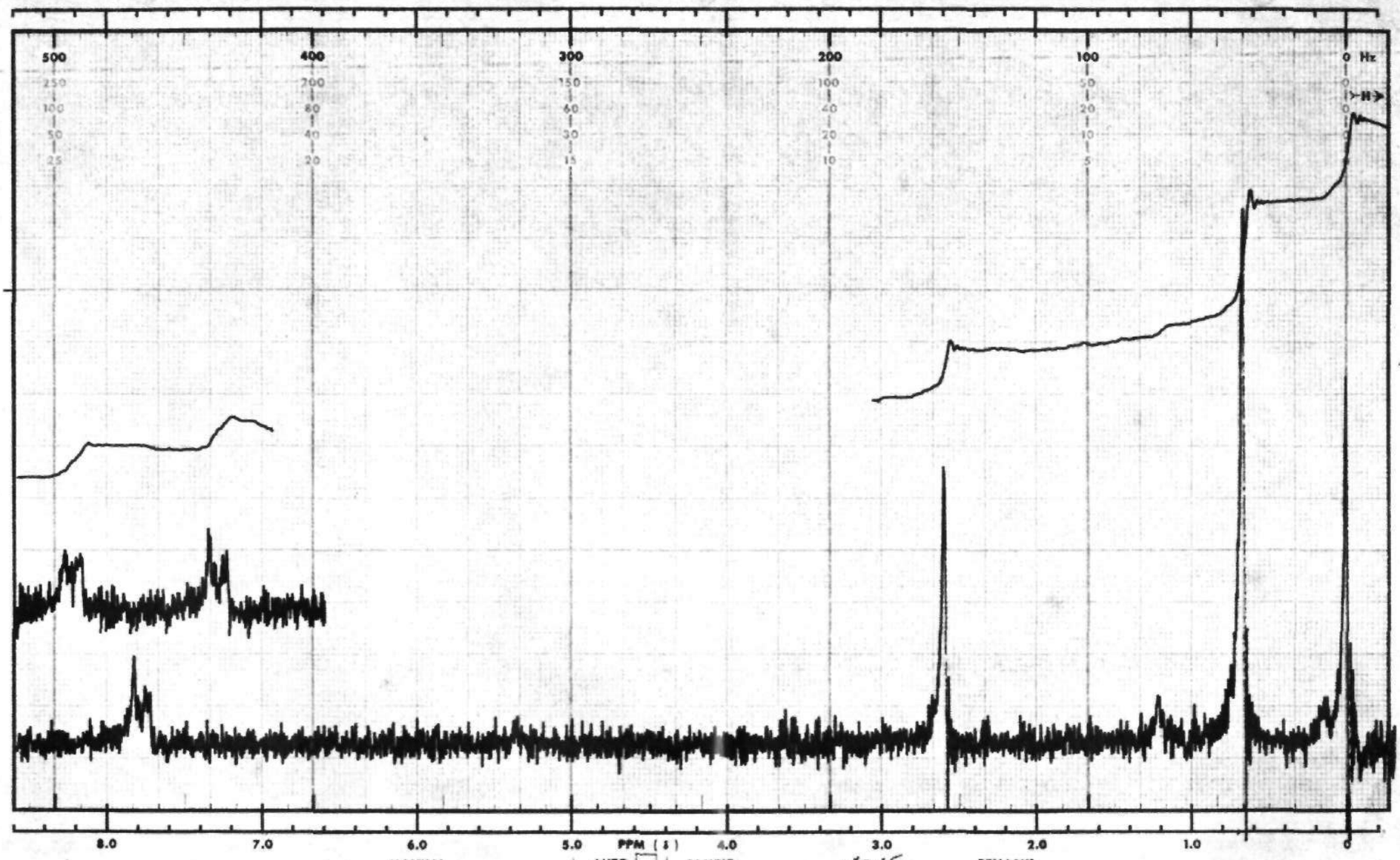


Evidence from i.r. and mass spectra (see later) as well as the structure of dimethyltin bistrifluoroacetate strongly suggests a dimeric structure for dimethyltinbistrifluoroacetate-4-acetylpyridine.



XI

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



SWEEP OFFSET (Hz): 30
SPECTRUM AMPLITUDE: 20
INTEGRAL AMPLITUDE: 7
SPINNING RATE (RPS): 40

MANUAL
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 2 3 4 5 6 7 8
RF POWER LEVEL: 0.25

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: alo·CF3
Me
Me–Sn–Me
CO Me

SOLVENT: CCl_4

REMARKS:

varian
analytical instrument division

DATE: 23/8/77

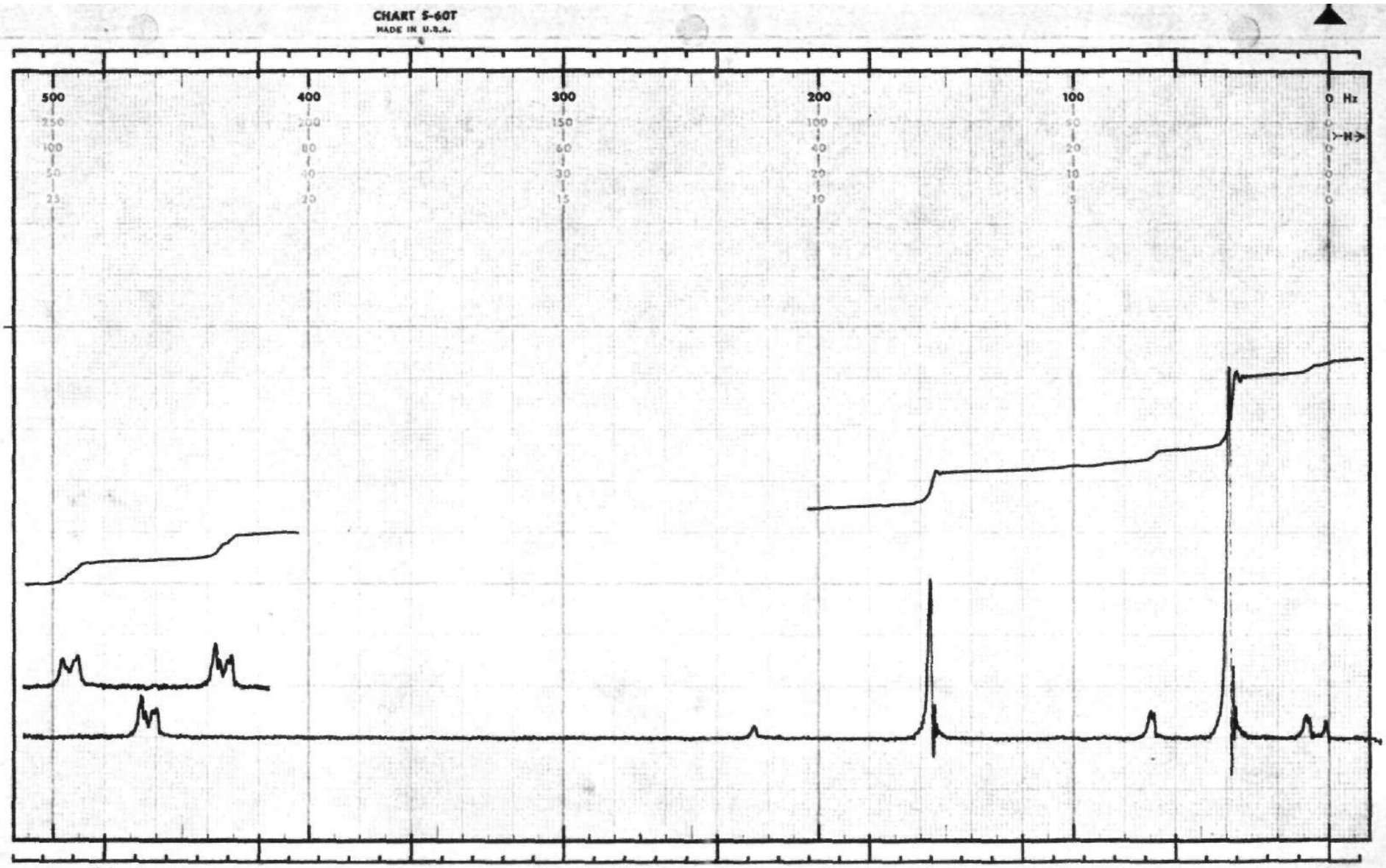
OPERATOR: Bonine

60 MHz NMR
SPECTRUM NO.

Trimethyltinchloride-4-acetylpyridine and Trimethyltin Trifluoroacetate-4-acetylpyridine

Because of the presence of three electron donating methyl groups (by inductive effect) on the tin, not much change in δ is expected in the spectrum of trimethyltin chloride and its adduct, trimethyltinchloride-4-acetylpyridine. Thus while the former has a literature δ value of 0.61 ppm, the later has also been found to be 0.64 ppm in CCl_4 solvent. $\delta(-CO.CH_3)$ is 2.55 ppm C3H and C5H of the acetylpyridine appear as a doublet at δ = 7.6 and C2H and C6H also as a doublet at 8.7 ppm.

The δ $(Sn-CH_3)$ of the trimethyltintrifluoroacetate-4-acetylpyridine has been found to be 0.7 ppm, the δ $(CO.CH_3)$ 2.6ppm, C3H and C5H a doublet at 7.8ppm and C2H and C5H also a doublet at 8.6 ppm. It is noteworthy that while the δ(C3H and C5H) of trimethyltin chloride-4-acetylpyridine is 7.6 ppm that of trimethyltin trifluoroacetate-4-acetylpyridine is 7.8 ppm. This could only mean that the protons have been more deshielded in the latter than in the former, perhaps due to the more strongly electron withdrawing trifluoroacetate group in the latter compound.



SWEEP OFFSET (Hz): 30
SPECTRUM AMPLITUDE: 2.5
INTEGRAL AMPLITUDE: 1
SPINNING RATE (RPS): 50

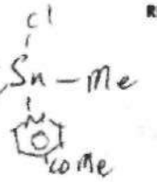
MANUAL
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: 0.05

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE:

SOLVENT: CCl_4

REMARKS:



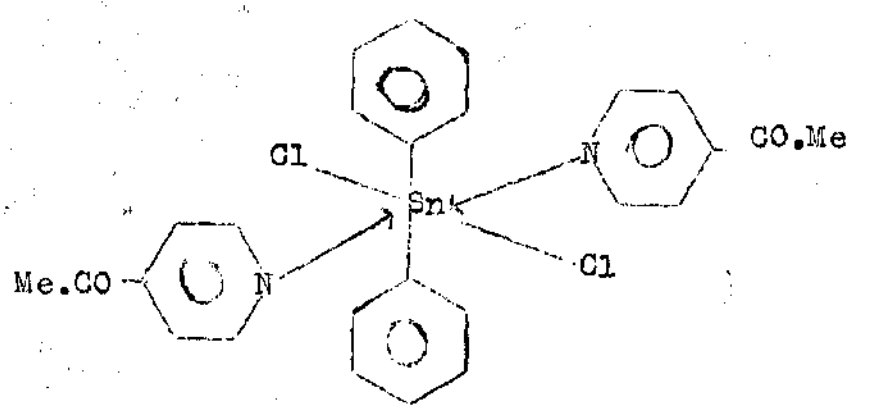
varian
graphical instrument division

DATE: 28/8/77

OPERATOR: Bonine

60 MHz NMR
SPECTRUM NO.

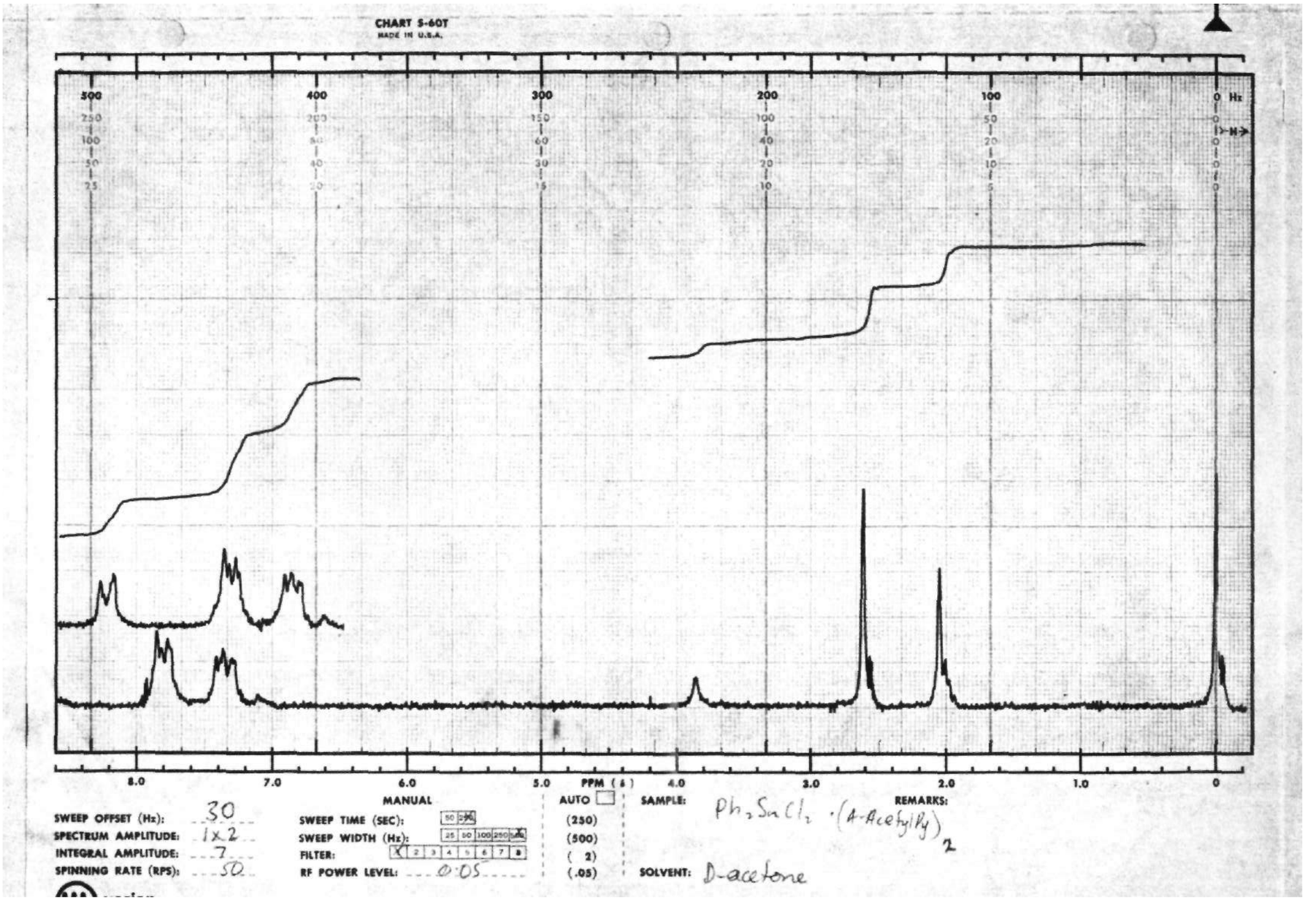
Acetylpyridine adducts of Diphenyltin dichloride



Looking at the above structure for diphenyltin dichloride bis-4-acetylpyridine, the five protons of each phenyl group would not be equivalent. The C2H and C6H of the phenyl, being nearer to the electron withdrawing tin, would be more deshielded than the C3H, C4H and C5H. The δ for C2H and C6H would therefore be higher that that for the remaining protons.

The spectrum of diphenyltindichloride bis-4-acetylPy shows a singlet at δ = 2.6 ($-CO.CH_3$), a triplet at 7.35 ppm which must be due to the C3H, C4H and C5H of the phenyl groups. A doublet of doublets appearing at δ 7.8 seems to be due to the C3H and C5H of the 4-acetylpyridine as well as the C2H and C6H of the phenyl groups. The doublet at δ8.7 is due to the C2H and C6H of the 4-acetylpyridine

Diphenyltindichloride bis-3-acetylpyridine spectrum shows its $-CO.CH_3$ at δ = 2.6 ppm the phenyl protons as a



SWEEP OFFSET (Hz): 30
SPECTRUM AMPLITUDE: 1x2
INTEGRAL AMPLITUDE: 7
SPINNING RATE (RPS): 50

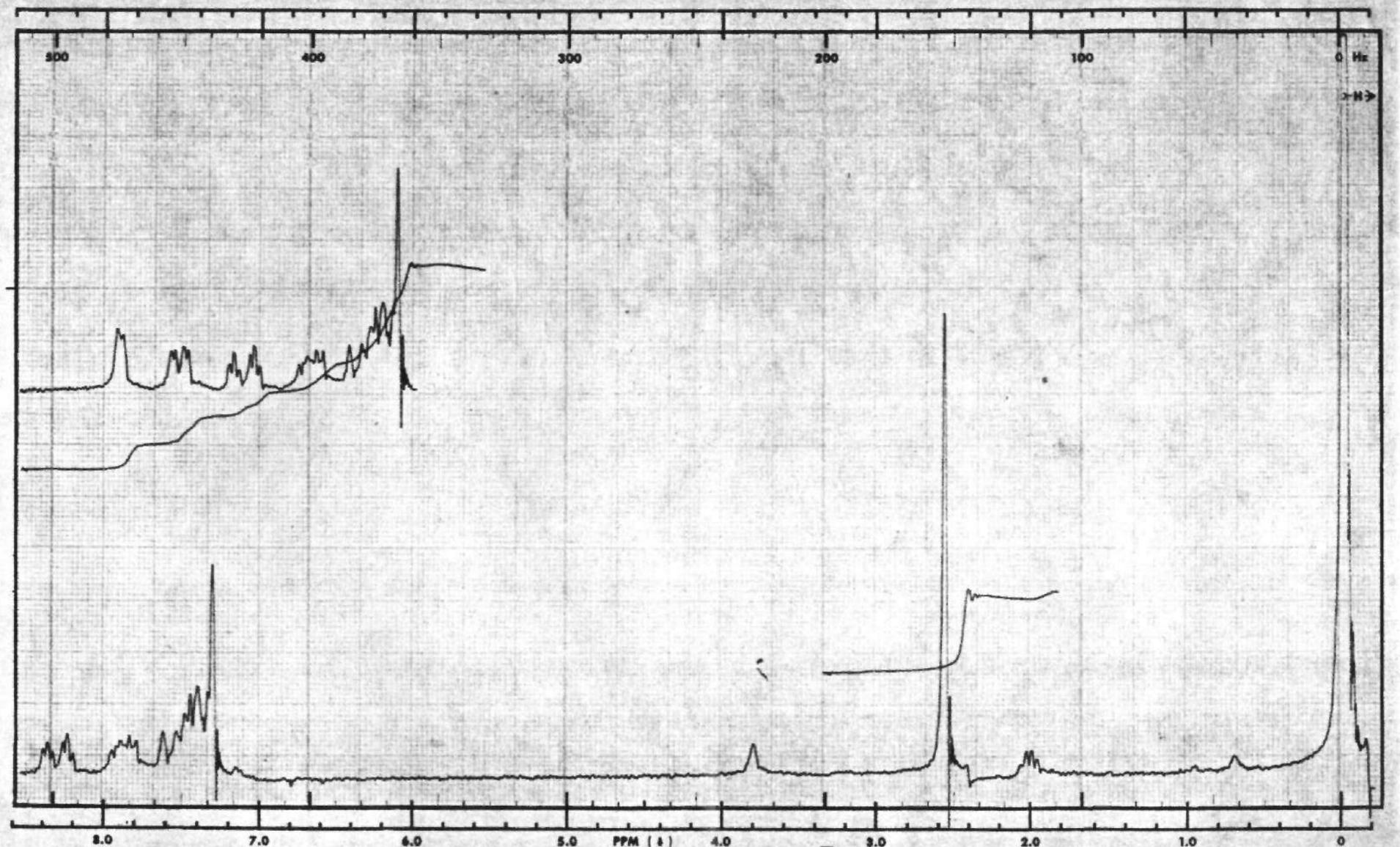
MANUAL AUTO ☐

SWEEP TIME (SEC): 50 250 (250)
SWEEP WIDTH (Hz): 25 50 100 250 500 (500)
FILTER: X 2 3 4 5 6 7 8 (2)
RF POWER LEVEL: 0.05 (.05)

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

REMARKS:

SOLVENT: D-acetone

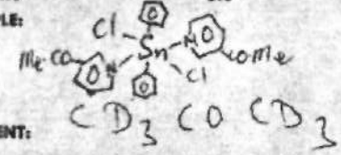


SWEEP OFFSET (Hz): 70
SPECTRUM AMPLITUDE: 10
INTEGRAL AMPLITUDE: 6
SPINNING RATE (RPS): ~~35~~ 38

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:



$CD_3CO CD_3$

REMARKS:

DATE 5/2/77 OPERATOR R. J. NINIVAGGI

60 MHz NMR
SPECTRUM NO.

multiplet at δ = 7.45 ppm, C5H of the acetylpyridine as a quadriplet at δ 7.85, C4H as a doublet of triplets at δ 8.3, C6H as a doublet of doublets at δ 8.75, and C2H as a doublet due to meta-coupling to C4H at δ9.15.

Products of Silver Trifluoroacetate with the Acetylpyridine adducts of Diphenyltindichloride

The spectrum of the product of reaction between diphenyltindichloride bis-4-acetylpyridine and silver trifluoroacetate showed signals for the 4-acetylpyridine only: δ 2.6 ($-CO.CH_3$), δ 7.85 (d, C3H and C5H) and δ8.8 ppm (d, C2H and C6H). There was no signal for the phenyl ring.

The product of diphenyltindichloride bis-3-acetylpyridine reaction with silver trifluoroacetate also showed signals for only 3-acetylpyridine in its spectrum:

δ 2.65 (s, $-CO.CH_3$), δ 7.7 (q, C5H),
δ 8.4 (d, C4H), δ 8.9 (d, C6H) and
δ 9.3 (d, (2H).

There was not even a kink to show the presence of the phenyl ring.

If follows therefore that in these reactions, the phenyl ring must have been lost in some form.

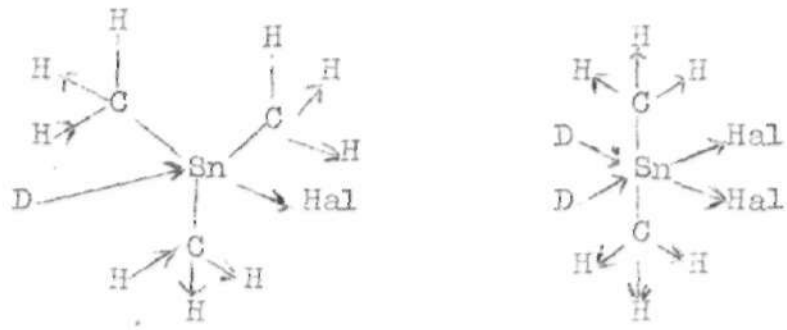
The Tin-carbon-hydrogen coupling constants of the Methyltin Compounds

Factors Affecting the Value of J Sn-C-H

There are three isotopes of tin which have unclear spin quantum number $I = \frac{1}{2}$, and only two of these, ^{117}Sn and ^{119}Sn are significantly abundant for meaningful nmr measurements. ^{117}Sn-C-H and ^{119}Sn-C-H coupling are observable in the nmr spectra of organotin compounds, and their magnitude depends on a number of factors. The methyltin compounds, being the simplest class of organotins, have been intensively studied.

It has been suggested[69] that the Sn-C-H coupling constants, J, are a measure of the percentage S-character in the tin-carbon bond. $J^{119}Sn$-C-H for Me_3SnCl, for example, in CCl_4 is 58.5 cps and 68.4 cps in water. The Me_3SnCl in CCl_4 has 25% s-character in the Sn-C bonds whereas the same compound exists in water as sp^2 hybrid Me_3Sn ions with $33\frac{1}{3}$% s-character in the Sn-C bonds. The solvent in which the spectrum of an organotin is run therefore influences the value of J(Sn-C-H). Verdonck and Van der Kelen[70] have however pointed out that a simple relationship between J and percentage S-character is not valid and that other parameters give an important contribution to the coupling.

Petrosyan et al[71] have suggested that the complexation of methyltin halides with electron-donors is mainly a p-d donor-acceptor interaction, and does not much disturb the s-electron density on the metal. The complexation is therefore followed by an increase of the relative content of s-electrons in the Sn-C-H site, owing to inductive mechanisms.



This suggestion would account for the observed increase in J(Sn-C-H) of adducts of methyl tin halides compared with those for uncomplexed methyltin halides. If there were complete rehybridisation at the tin atom as an adduct is formed, then the percentage s-character, hence J(Sn-C-H), would decrease as say an sp^3d^2 hybrid adduct is formed from an sp^3 methyltin halide.

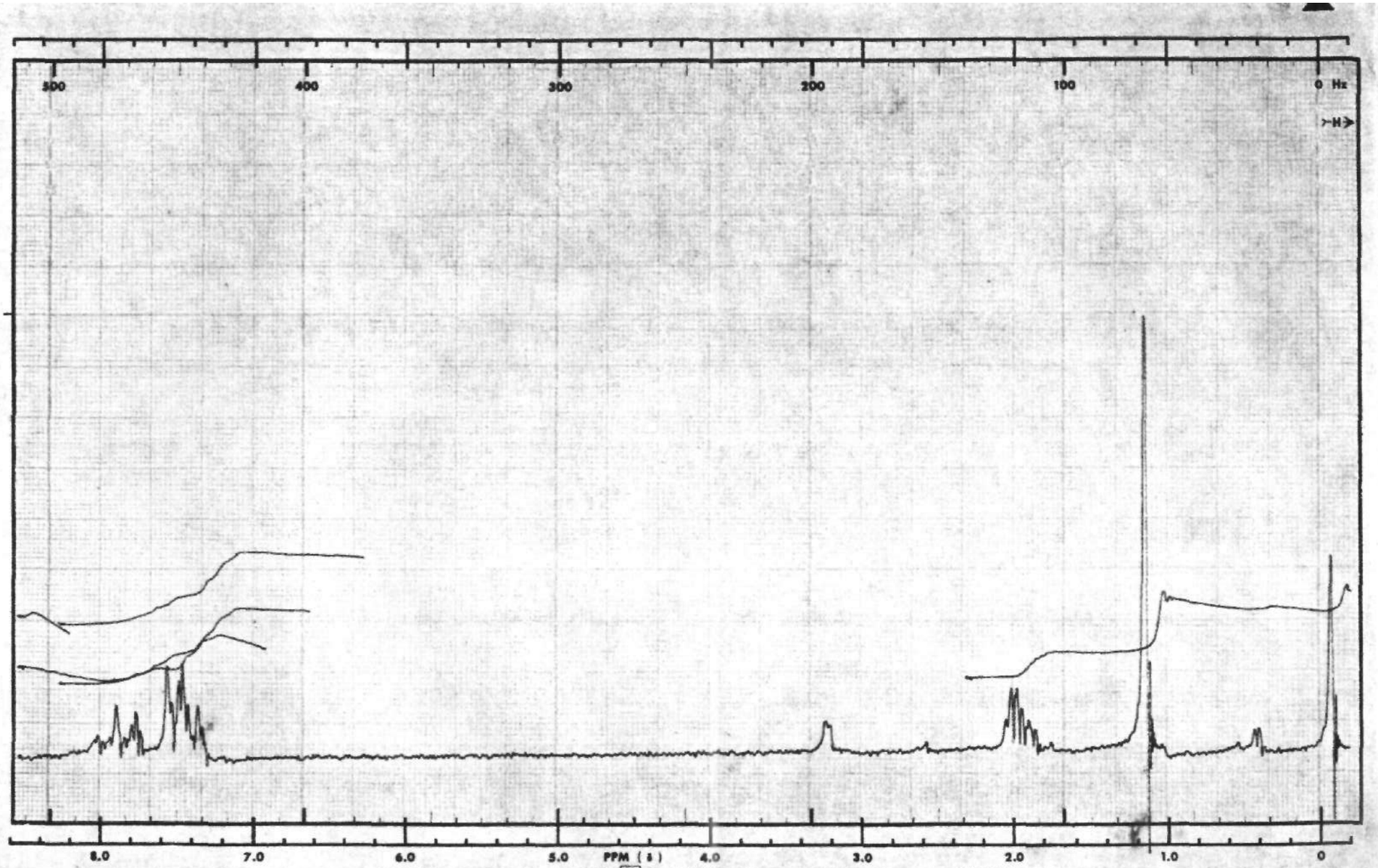
On the basis of Petrosyan's suggestion[71] therefore, the observed J(Sn-C-H) for say $Me_2SnCl_2.Py_2$ should be higher than that for $Me_2SnCl_2.(3\text{-AcetylPy})_2$, since pyridine is a stronger electron donor than 3-acetylpyridine.

Observed J(^{117}Sn-C-H) and J(^{119}Sn-C-H) for the Pyridine and Acetylpyridine adducts of Dimethyltinlichlorides and Trifluoroacetates

Table 4 shows the observed Sn-C-H coupling constants for the studied methyltin compounds. The spectra of Me_2SnCl_2, $Me_2SnCl_2.Py_2$, $Me_2SnCl_2.(4\text{-AcetylPy})_2$ and $Me_2SnCl_2.(3\text{-AcetylPy})_2$ were run in deuteroacetane to nullify any alteration in the J(Sn-C-H) value due to change in solvent. Expectedly, $Me_2SnCl_2.Py_2$ with J^{119}Sn-C-H of 90 and J^{117}Sn-C-H of 86 cps, had the highest values of coupling constants compared with the acetylpyridine adducts and Me_2SnCl_2. $Me_2SnCl_2.(4\text{-AcetylPy})_2$ had the second highest values of J^{119}Sn-C-H = 88 and J^{117}Sn-C-H = 84. $Me_2SnCl_2.(3\text{-AcetylPy})_2$ had J^{119}Sn-C-H = 87 and J^{117}Sn-C-H = 83, while Me_2SnCl_2 had J^{119}Sn-C-H = 84 and J^{117}Sn-C-H = 80 cps. The results are as expected as the electron-donor strength of pyridine and acetylpyridine are in the order

Pyridine > 4-Acetylpyridine > 3-Acetylpyridine

From these results, it can be concluded that the Sn-C-H coupling constant values could be used to predict the relative stabilities of adducts, especially of the dimethyltinhalides formed from a donor and its substituted derivatives as well as the relative basicities of the donors.



SWEEP OFFSET (Hz): ---
SPECTRUM AMPLITUDE: 12.5
INTEGRAL AMPLITUDE: 6
SPINNING RATE (RPS): 38

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: 0.05 (.05)

SAMPLE: $Me_2SnCl_2 \cdot Py_2$

SOLVENT: CD_3COCD_3

REMARKS:

5/7/77

60 MHz NMR

Acetone was chosen as the solvent because though a donor, it is not as basic as the pyridines; the adducts were recrystallised from it.

Table 4

Tin-Carbon-hydrogen Coupling Constants

Compound	Solvent	J^{117}Sn-C-H	Lit.	J^{119}Sn-C-H	Lit.
Me_2SnCl_2	$CD_3CO.CD_3$	80 (cps)		84(cps)	
Me_2SnCl_2.2Py	$CD_3CO.CD_3$	86		90	
Me_2SnCl_2. (4-AcetylPy)$_2$	$CD_3.CO.CD_3$	84		88	
Me_2SnCl_2. (3-AcetylPy)$_2$	$CD_3.CO.CD_3$	83		87	
$Me_2Sn(O.CO.CF_3)_2$	$CD_3.CO.CD_3$			88	
$Me_2Sn(O.CO.CF_3)_2$. 4-AcetylPy	$CD_3.CO.CD_3$			91	
Me_3SnCl	CCl_4	56	55.7-56	58.5	58.1 - 58.5
Me_3SnCl.Py	CCl_4	60		62	
Me_3SnCl. 3-AcetylPy	CCl_4			59	
Me_3SnCl. 4-AcetylPy	CCl_4	60		62	
$Me_3SnO.CO.CF_3$. 4-AcetylPy	CCl_4	64		66	

$J^{119}Sn-C-H$ for $Me_2Sn(O.CO.CF_3)_2$ was found to be 88 cps while that for $Me_2Sn(O.CO.CF_3)_2.4$-AcetylPy was 91 cps. Looking at the structures of $Me_2Sn(O.CO.CF_3)_2$ (XX) and $Me_2Sn(O.CO.CF_3)_2.4$-AcetylPy (XI), Sn is hexacoordinated in both compounds, but the electron density on Sn and hence on CH_3 of XI would be more than that on the Sn of XX because of the 4-acetylpyridine donor of the former, compared with the bridge bonds by the trifluoroacetate of the latter.

Observed $^{117}Sn-C-H$ and $^{119}Sn-C-H$ Coupling Constants for the Pyridine and 4-acetylpyridine adducts of Trimethyltin- and Trifluoroacetate

Although the 3-acetylpyridine adduct of trimethyltin chloride could not be isolated, an n.m.r. spectrum of the solution in CCl_4 was run. The solution was made very dilute to make it as non-polar as possible. The $J(^{119}Sn-C-H)$ has bee found to be 59 cps, 2 c.p.s. above that of the Me_3SnCl starting adduct had been formed in solution.

As seen in table 4, the $J(^{119}S-C-H)$ values for the adducts are all greater than that of Me_3SnCl providing further confirmation of Petrosyan's theory. The fact that the $Me_3SnCl.3$-AcetylPy formed in solution shows a lower $J^{119}Sn-C-H$ value than $Me_3SnCl.4$-AcetylPy and $Me_3SnCl.Py$ shows that the J_{Sn-C-H} of adducts is a function of the effective basicity of the donor ligand.

J_{Sn-C-H} for $Me_3SnCl.4$-AcetylPy has been found to equal that for $Me_3SnCl.Py$. This could be due to the fact that there are three methyl groups which furnish the tin atom with electrons by inductive mechanisms, and only one halogen atom withdrawing the electrons from the tin. An external supply of electrons to the tin from a donor ligand would increase the electron density around tin all the more. The electron-withdrawing ability of th the acetyl group would perhaps be too feeble to create any significant change in the electron density around the tin. And since J_{Sn-C-H} is a function of the electron density around the tin atom, it would not alter to any significant extent.

The J_{Sn-C-H} value for $Me_3SnO.CO.CF_3.4$-AcetylPy has been observed to be higher than the values for the trimethyltin chloride adducts.

Mass Spectra of the Studied Organotin Compounds

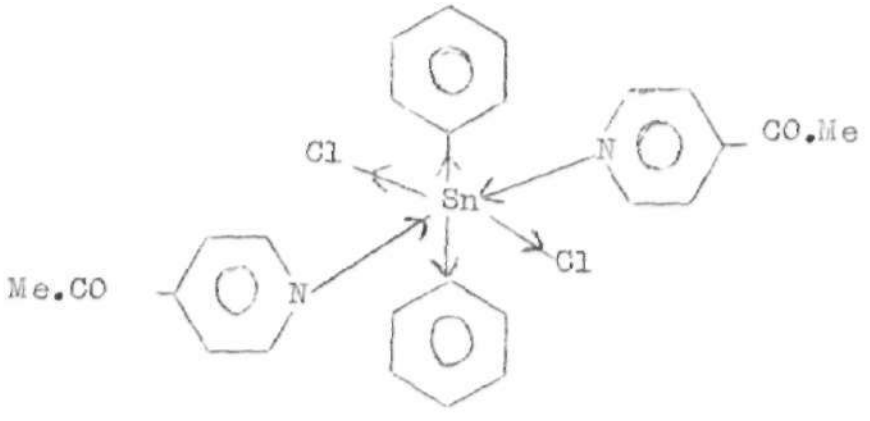
Acetylpyridine Adducts of Dimethyltindichloride

The spectra showed fragments and molecular ions of the starting materials, dimethyltindichloride and acetylpyridines as separate compounds. The adducts must have been dissociated into their respective methyltinchloride and acetylpyridine starting materials. It could be inferred therefore that the co-ordination bond formed between the ligand and the dimethyltindichloride could not have been very strong, further showing the acetylpyridines as weak donors, which are made even weaker by the electron push from the methyl groups of the organotin towards the tin by inductive means.

Acetylpyridine Adducts of Diphenyltindichloride

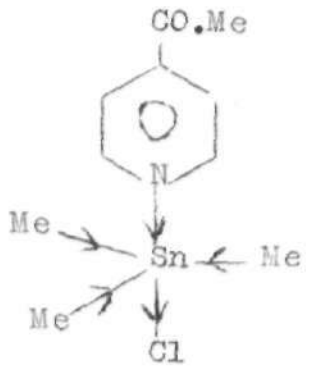
The spectra of these show the molecular ions $Ph_2\overset{+}{S}nCl_2 \cdot (4\text{-Acetylpyridine})_2$ and $Ph_2\overset{+}{S}nCl_2 \cdot (3\text{-Acetylpyridine})_2$ (587), thereby confirming the existence of the adducts. Though ions of the dissociated adducts were shown, the presence of the molecular ions suggests that the co-ordination bond formed between the ligand and diphenyltindichloride is stronger than those of ~~that~~ the acetylpyridine adducts of dimethyltindichloride. This could be due to the electron-withdrawing effect of the phenyl ring, which makes the

tin more electronegative. A fairly strong bond would therefore be formed between the tin and even a weak electron-donor.



Trimethyltinchloride-4-Acetylpyridine

The mass spectrum of this compound showed molecular ions of trimethyltinchloride and 4-acetylpyridine as independent molecules. The adducts therefore might have been dissociated into the starting materials. This might be due to weak co-ordination of the ligand on the trimethyltinchloride, due to the electron-push from the methyl groups to the tin.

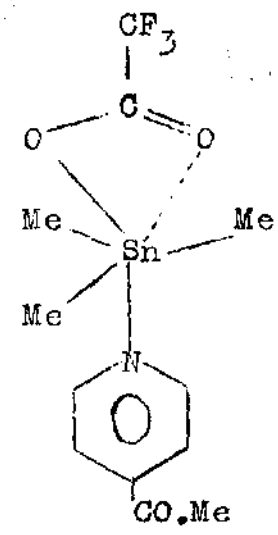


Dimethyltinbistrifluoroacetate-4-Acetylpyridine

The spectrum of this compound shows the molecular ion $Me_2Sn(O.CO.CF_3).4$-AcetylPy (497) as well as $[Me_2Sn(O.CO.CF_3)_2]_2^+.4$-acetylPy (873). Chemical analysis suggested that the compound was a 1:1 adduct, but the presence of $[Me_2Sn(O.CO.CF_3)_2]_2^+$. 4-acetylPy strongly suggest a dimeric structure for the compound. The presence of four arms in the broad i.r. absorption peak for C=O further supports the dimeric structure (XI).

Trimethyltintrifluoroacetate-4-acetylpyridine

The spectrum shows molecular ions of trimethyltin-trifluoroacetate and 4-acetylPy as separate compounds, suggesting that the co-ordination bond in the adduct could not be very strong. Though the trifluoroacetate group has a high electron withdrawing power, electron supply to the tin by the three methyl groups and possible back donation of electrons from the trifluoroacetate carbonyl would make the tin electron rich enough to be not very affinitive for the ligand.



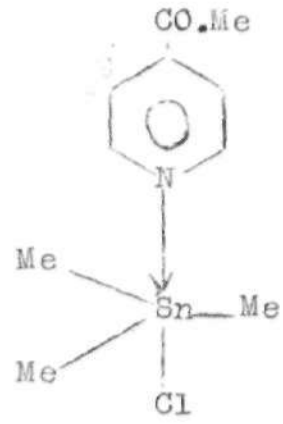
Structure of the Organotin Compounds

Although Petrosyan[71] has proposed a p → d donor acceptor for ligands and organotin halides on complexation, it would be inconceivable for rehybridisation at the tin to say sp^3d^1 or sp^3d^2 not to occur at least to a small degree if the electron donor is to get close enough to the tin atom to form a bond.

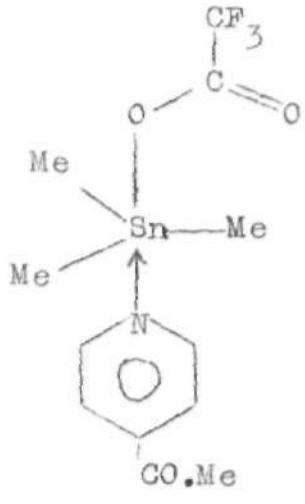
Adducts of Trimethyltin Compounds

An X-ray crystal structure determination[72] of $Me_3SnCl.Py$ revealed a regular trigonal bipyramid with equatorial methyl groups. It is conceivable therefore that the structure of trimethyltinchloride-4-acetylpyridine is also a trigonal bipyramid with equatorial methyl groups, though it would be more distorted than $Me_3SnCl.Py$ molecular structure because 4-acetylPy is a weaker electron donor compared with

pyridine. This is because the distortion of the tetrahedral Me_3SnCl molecule on complex formation with a ligand L is dependent upon the strength of the Sn-L bond[72].



Although $Me_3SnO.CO.CF_3$ has been shown to be a polymer[73] with bridging carboxyl and planar CH_3 groups, $Me_3SnO.CO.CF_4.4$-acetylPy is most likely to be a monomer, with evidence from the i.r. and mass spectrum, and as the presence of the acetylpyridine ligand would not allow the existence of bridging -CO.O groups.



Dimethyltin and Diphenyltin Compounds

Adducts of dimethyl and diphenyltin dichlorides with monodentate ligands have been assigned the octahedral structure with trans Me or Ph groups, through i.r. and Mossbauer spectroscopy.[74] The acetylpyridine adducts of dimethyltindichloride and diphenyltindichloride would therefore most likely have similar octahedral structures, though with more distortion as the ligands are weak electron donors.

Dimethyltinbistrifluoroacetate in the solid state, has been found to be a polymer (XX) with bridging CO.O. groups[75]. Dimethyltinbistrifluoroacetate-4-acetylpyridine could not be polymeric because of the acetylpyridine ligand, but i.r. and mass spectra have shown it to be a dimer (XI).

Natural and Local ways of Preserving Yams

The most serious threat to yam preservation is rot, a fungal disease. A yam tuber is naturally protected with a thick brown coat, but when this coat is broken, either by injury or slicing, to expose the yam tissue, the tuber is prone to fungal infection which starts as soon as a spore of the rot causing fungi settles on the injury. The spore grows into a mycelium, the hyphae of which penetrate the tuber, feeding on and destroying the tissue.

Personal observation, as well as interviews with farmers, have revealed that an injury on a yam tuber develops a hard coat which results after evaporation of water from the surface of the injury. A farmer knows that once this coat has developed on an injury on a tuber, the yam no longer goes bad. It is probable, therefore, that spores of the rot-causing fungi grow only on fresh injuries, and that hard coats later developed on the injury cannot be penetrated.

Farmers therefore cover an injury with earth or ash as soon as a tuber is injured. This is done in an effort to keep the injury out of reach of the spores until the protective coat is developed. But, as the farmers themselves admit, the method has not been too successful.

The earth or ash might contain the fungal spores. Moreover, earth and ash are solids and may thus not spread evenly or completely cover an injury.

The moderately warm and humid months of February through April is the critical period for yam rot, according to the farmers. And that is the period for preparing seed yams. This might imply that the spores of the rot-causing fungi are air borne; and that they grow best during this season. A possibly effective way of protecting yams and seed yams from the infection of fungi would be to wash an injury in a fungicide emulsion, which would stay long enough for the protective coat to develope on the injury.

Isolation and Identification of Yam Rot-causing Fungi

Yam rot-causing fungi were cultured on Potato-dextrose-agar (PDA) from a small piece of rotten yam. The fungi were extremely fast growing, but there was delayed sporulation. They grew equally well on yam-dextrose-agar. The white rot-causing fungi were somewhat slower growing.

Microscopic examination of the mycelia in methylene blue stain showed that there were different species of fungi that could be responsible for causing rot. A number of yam rot causing fungi preidentified by Adeniji[50,51] were confirmed. A very rapid previously growing, unidentified, fungus isolated from the brown rot was thought to

be chiefly responsible for yam brown rot, while two unidentified species of Fusarium were thought to be chiefly responsible for white rot.

A yam tuber infected with white rot goes bad very slowly compared with another infected with brown rot.

Effectiveness of the Organotin Chemicals in Inhibiting Growth of Fungi Cultured on PDA

A number of the organotin compounds tested for fungicidal activity against rot-causing fungi were found to be insoluble in water, which on economic considerations would be the ideal solvent for the compounds.

A detergent therefore had to be used as an emulsifier for the organotin compounds into at least moderately homogeneous emulsions. Tween 80 was found to be an effect emulsifier which, of itself, does not inhibit fungal growth.

Different concentrations, varying from 0.50% to 0.0025%, (w/v) of the organotin compounds were prepared by serial dilution.

Growth of the Fungi on PDA Treated with Organotin Compound

Treated sets of PDA were inoculated with fungi cultured from rotten yams-and incubated for five days at 28°C, the optimum temperature for fungal growth, The resul showed all the organotin compounds tested to be fungicidal

Cross section photographs showing depth of rot in yam slices treated with different concentrations of $Bu_3SnOSnBu_3$.



by totally inhibiting yam fungus growth at concentrations of 0.25% and above. All the trialKyl- or triaryl tin compounds totally inhibited the growth of fungi at a concentration as low as 0.05%. The dialKyl- and diaryltin compounds only partially inhibited growth of the fungi at this concentration. At 0.025%, only trimethyltinchloride 4-acetylpyridine, both new compounds were completely inhibitive to the growth of the fungi. All other chemicals partially inhibited growth. At 0.005%, only trimethyl-tinchloride-4-acetylpyridine was completely inhibitive. The dialkyl and diaryltin compounds showed only very feeble inhibitive power to fungal growth. At 0.0025%, the emulsions were too dilute to inhibit growth of the fungi.

Growth of Fungi on Slices of Yam Treated with Organotin Compounds

More concentrated emulsions of the organotin compounds (2.0% - 0.01%) were made in 5% aqueous Tween 80 detergent Fresh slices of raw yams were washed in these emulsions, inoculated with cultured yam rot-causing fungi and kept at a near constant humidity in dessicators (without dessicants) at room temperature for ten days. The slices of yam were observed for fungal growth and cut through to observe any rot. All the organotin compounds, except the 3- and 4-acetylpyridine adducts of diphenyltindichloride,

inhibited growth of the fungi and, thus, formation of rot at 2.0% concentration. At 1% concentration, all except the diphenyltin dichloride adducts and the novel dimethyltin bistrifluoroacetate-4-acetylpyridine as well as dimethyltinbistrifluoroacetate, inhibited fungal growth and rot formation. At 0.2% concentration, only the trialkyl and triaryltin compounds, except triphenyl tin oxide, totally inhibited the growth of fungi and rot formation. The dialkyl- and diaryltin compounds did not show total inhibition, but kept the growth of the fungi poor in terms of rate, density and penetration. At 0.1% concentration, only trimethyltin chloride -4-acetylpyridine and trimethyltintrifluoroacetate-4-acetylpyridine completely inhibited the fungal growth, and rot formation. Others showed partial inhibitive power. 0.02 and 0.01% concentrations of the chemicals were found to be too low to inhibit fungal growth and rot formation, though all showed some degree of inhibitive power, compound with the control experiments. The dialKyl and diaryltin compounds seemed to keep fungals growth poor, even at very low concentrations.

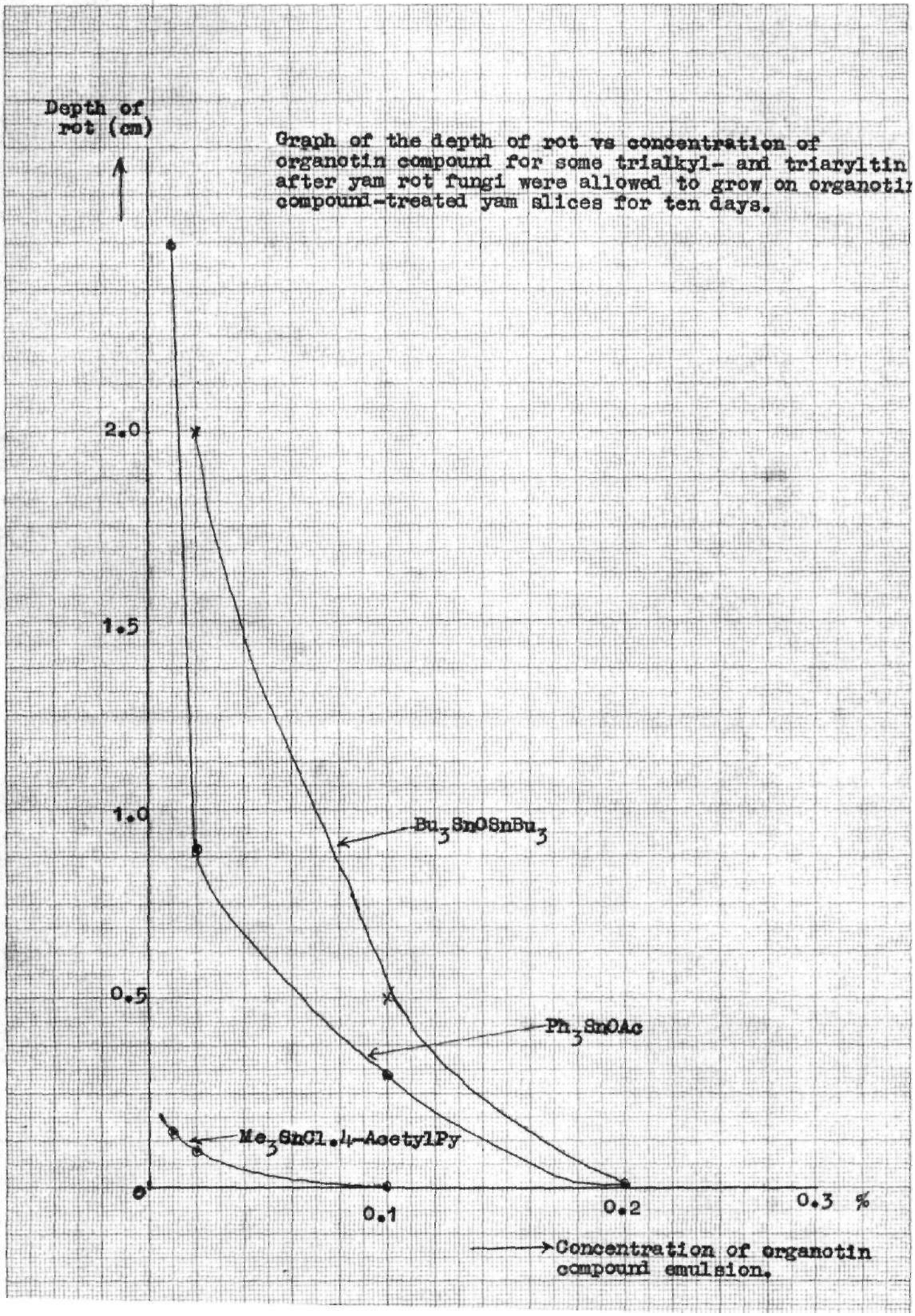
It can be seen that more concentrated organotin compound emulsions are needed to protect yams from fungus attack than are required to inhibit growth of the fungi cultured on PDA. This is expected since PDA treated with

an organotin compound has the organotin compound in it while a treated yam slice has the compound spread only on its outer surface. If a fungus hypha could penetrate the surface, the fungus would grow.

The yam slices were kept under conditions whereby the protective coat could not be formed on the sliced surface. Since the slices were in an enclosure, there would only be very little water evaporation through the sliced surface. The slices were therefore prone to fungus infection throughout the ten days of the experiment. Since the chemicals have successfully inhibited fungus growth, though at varying concentrations, one would expect even better results in the fields where an injury or slice on a yam tuber would develop the protective coat in less than two days. It is possible therefore that in the field, lower concentrations of the organotin emulsions would protect an yam injury from fungal attack until it develops the protective coat.

Comparison of the Inhibitive Ability of the Organotins Compounds

Of all the chemicals, the trimethyltin compounds have proved the strongest fungicides. As low as 0.02% emulsion of trimethyltinchloride-4-acetylpyridine was enough to stop the fungi from growing on PDA and on yams.

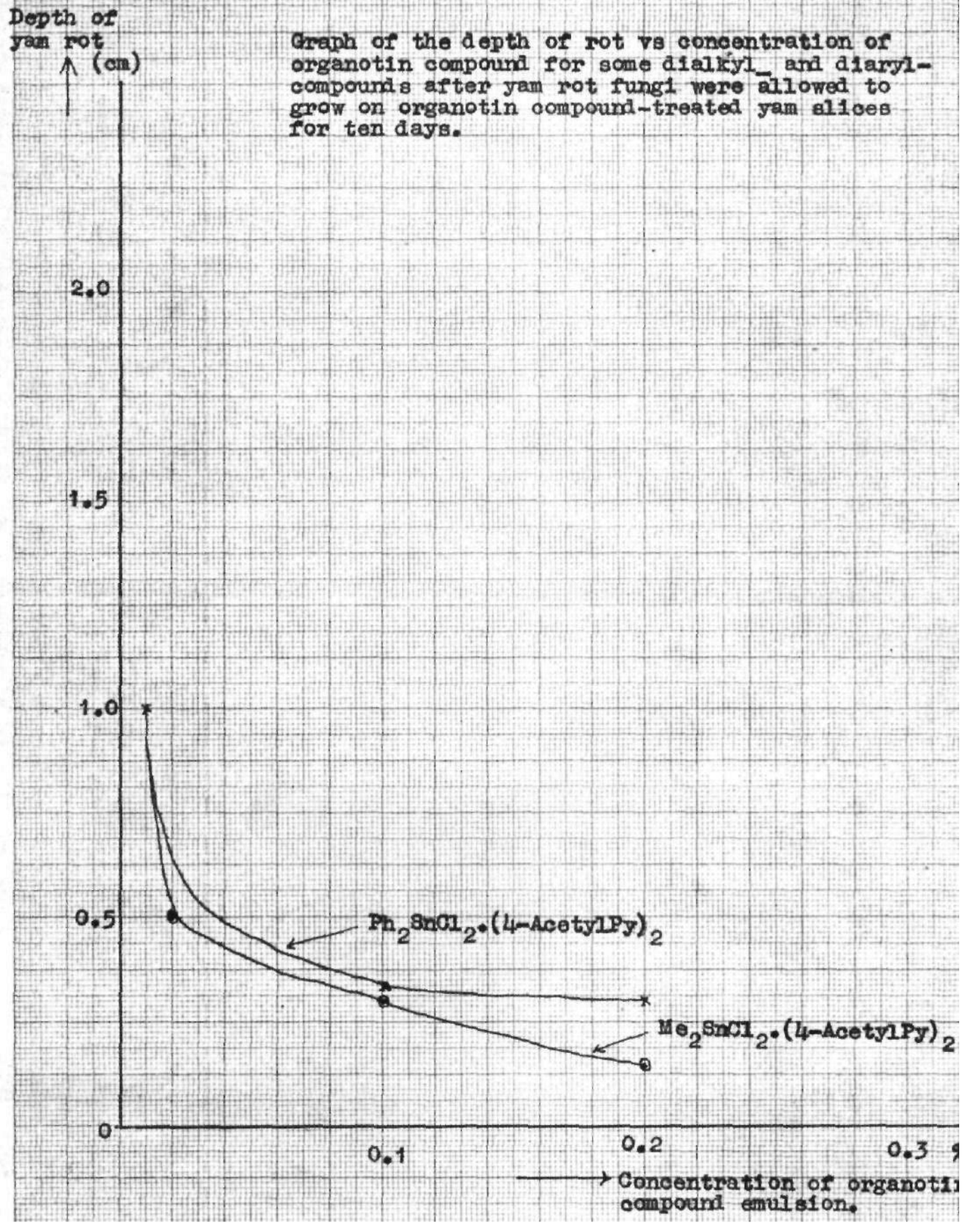

Depth of rot (cm)
Graph of the depth of rot vs concentration of organotin compound for some trialkyl- and triarylti
after yam rot fungi were allowed to grow on organoti
compound-treated yam slices for ten days.
2.0
1.5
1.0
0.5
0
$Bu_3SnOSnBu_3$
Ph_3SnOAc
$Me_3SnCl.4$-AcetylPy
0.1
0.2
0.3 %
Concentration of organotin compound emulsion.

The most likely problem in the possible use of this class of compounds in the fields as fungicides is their being very volatile. This might be reduced by mixing the compounds with some less volatile organotin compounds, especially in cases of serious fungal attack.

All the triphenyltin compounds were very active in controlling fungal growth. A 0.2% emulsion of any of the triphenyltin compounds was sufficiently strong to inhibit fungus growth on PDA and on yams. Comparatively active also was tri-n-butyltin oxide, a popular rice fungicide in the Far East[56]. The European potato fungicide[57], triphenyltin acetate, was found active in protecting yam against rot, but it was not very easy preparing the emulsion as it was light and highly insoluble in aqueous media. Tri-n-butyltin oxide and the trimethyltin compounds easily mixed with water and could thus be preferred to triphenyltin acetate, if physiological tests show them to be acceptably safe.

The dialKyl- and diaryltin compounds were not as strong as the trialKyl- and triaryltin compounds in inhibiting fungal growth, but even low concentrations of the compounds kept the growth of the fungi poor. The diphenyltin compounds have proved the least fungicidal.

Graph of the depth of rot vs concentration of organotin compound for some dialkyl_ and diaryl-compounds after yam rot fungi were allowed to grow on organotin compound-treated yam slices for ten days.



Suggested Preferential use of the Organotin Compounds in Protecting Yams Against Rot

Any fungicide to be used in protecting yam against rot has to be one that would prevent fungal growth even at low concentrations because, once the fungi begin to grow, it would be difficult to arrest their growth. A yam fungicide would prevent fungal growth, but might not arrest it. The organotin compounds that are more miscible with water would be preferred as they would be more evenly spread on the sliced surface of the yam. Tri-n-butyltin oxide and the trimethyltin compounds would be preferred in this sense. A way of preparing emulsions of these organotin compounds for use by farmers could be the initial dissolution of the compounds in aqueous alcohol, followed by mixing measured quantities of these with calculated amounts of water to give organotin compound concentrations high enough to prevent fungal growth. This method would be simple enough for the illiterate farmer.

Toxicity of the Organotin Compounds

A problem in the future use of organotin compounds as yam fungicides is their toxicity, which varies with the compounds. Triphenyltin acetate and tri-n-butyltin oxide are already being used as plant fungicides in some

countries[56,57]. All the butyltins, higher alkyltins, and phenyltins have been found to be only moderately toxic for oral ingestion warm blooded animals[76]. n-Octyl-organotins are so mildly toxic either acutely or chronically[77] that they are incorporated even in food wrappers and containers (plastic foil and bottles).[78] Trimethyltin compounds have been found to be the most poisonous class of organotins, though no organotin compound is regarded as highly toxic[79].

For use on yams therefore, one might suggest the use of the higher alkyltin compounds for the preservation of yams to be consumed later. A Mixtures of the higher alkyltin compounds and triaryl compounds e.g. trioctyl-tins and triphenyltin acetate, would be ideal. For the preservation of seed yams, the more poisonous organotins like trimethyltin compounds might be used since a lot of the organotin would weather away with time. All classes of the organotins should be suitable for preservation of seed yams. All these suggestions could however be implemented only after satisfactory physiological tests.

Weathering and Degeneration of Organotin Compounds

It has been found[59] that organotin fungicides are degraded on weathering to give inorganic tin, which is non-poisonous. This is fortunate as a coat of an organotin

compound on a preserved tuber of yam deteriorates with time, giving inorganic tin and compounds which would easily be washed away, leaving a negligible amount of the organotin, which could be further reduced when the coat of the tuber is peeled before cooking.

For seed yams, the organotin protective would need to stay only long enough for the protective coat to be formed. A seed yam to be preserved could be airdried after washing in the fungicide. The organotin fungicide would weather with time in the soil so that presumably, the new yam tuber produced would contain only negligible amounts of any absorbed organotin.

Suggestions on Methods of Manufacture

Nigeria is fortunate to have tin and petroleum as mineral resources. Present in petroleum are a number of compounds that could be used for preparing organotin compounds. For example, benzene, and other hydrocarbons could serve as good starting materials for the preparation of phenyl halide (usually bromide) and alkyl halides which are the chief starting materials for the preparation of tetraorganotins, from which various organotin compounds could be prepared.

~~Alcohol, which could be used in solibilizing the fungicides, is produced from molasses, residue in the~~

Alcohol, which could be used in solubilizing the fungicides, is produced from molasses, residue in the manufacture of sugar which is a major Nigerian product.

E X P E R I M E N T A L

N.m.r. spectra were run with a varian T-60 spectrometer using tetramethylsilane as internal standard and deuteroacetone or carbon tetrachloride as solvent, except where otherwise stated. I.r. spectra were run in either potassium bromide or caesium iodide discs.

All melting points uncorrected were taken with the Kofler hot stage microscope.

Elemental microanalyses were carried out by Scandinavian Microanalytical Laboratories.

Tin Tetramethyl

(Edgell and Ward Method.[80])

Fifty grams (2.06g. atoms) of magnesium turnings and 600ml. of sodium wire-dried di-n-butyl ether were placed in a 1-litre three-neck round-bottomed flask fitted with a stirrer of the Hershberg type, and an Allihn reflux condenser with a dropping funnel. A solution of 225g (1.59 moles) of freshly distilled methyl iodide in an equal volume of di-n-butyl ether was placed in the dropping funnel and then, after then addition of a few crystals of iodine to the magnesium suspension, a 4ml. portion of this methyl iodide solution was added with stirring to the reaction flask. After gentle heating, the formation of the Grignard reagent, methyl magnesium iodide, started. The remaining methyl iodide solution was added dropwise over a period of three hours at a rate just sufficient to cause gentle refluxing. After the addition the reaction mixture was allowed to cool to room temperature, 75g (0.29 moles) of anhydrous stannic chloride was added dropwise for two hours under gentle reflux. The reaction mixture was heated under steady

reflux (85 - 95°) for one hour and then allowed to stand for eight hours. After replacing the Allihn condenser with a claisen head and West condenser, the crude product was distilled from the reaction mixture. A mixture of tin tetramethyl and n-butyl ether, distilling at 85 - 95°, was obtained. The tin tetramethyl was isolated by fractional distillation using a Dufton column. The main fraction of tin tetramethyl (39.50g, 76.83%) distilled at 76° (Lit.[80] 76.6°) nmr (sample & TMS & $CDCl_3$) δ0.085ppm (singlet) (Lit.[81] 0.08ppm, 12H, S, 4 x CH_3).

Dimethyltindichloride

(Comproportionation Method.[83])

Tetramethyltin (9.0g, 0.05M) was added dropwise to stannic chloride (13.1g, 0.05M) in a 50Ml. round bottomed flask, with ice cooling. The mixture was heated under gentle reflux on a heating mantle for four hours, and them left to cool. The yellowish, viscous mixture solidified on cooling giving a dirty white mass of crystals. This was removed and dried in vacuo. (19.5g). The product was recrystallised four times in benzene/hexane mixture (50/50). m.p. 106 - 107° (Litt.[61] 107 - 108°); n.m.r. (CD_3COCD_3+TMS) δ1.24 (6H, S, 2 x CH_3), J^{117}Sn-C-H 80 cps, J^{119}Sn-C-H 84cps; n.m.r. ($CDCl_3$ + TMS)δ1.22 (6H, S, 2 x CH_3), J^{117}SN-C-H 66cps, J^{119}Sn-C-H 70cps (Litt.[81]: (CCl_4 + TMS)

δ1.15 - 1.24, J^{117}Sn-C-H 66 - 67cps, J^{119}Sn-C-H 69 - 70cps).

i.r. (CSI) ν(Sn-C) $560_{(s)}$, $520_{(m)}$ [Lit.[83] (CS_2) ν(Sn-C) $560_{(s)}$ $540_{(m)}$]

Trimethyltinchloride

(Comproportionation Method.)[80]

Stannic chloride (5.24g, 0.02M) was added dropwise to tetramethyltin (10.8g, 0.06M) with ice cooling. The mixture was heated under reflux on a steam bath for two hours and left to cool. A mass of white needles of crystals appeared. This was removed and dried in a dessicator. (14g, 87.28%). The product was recrystallised three times from pentane. m.p. 36 - 37° (Litt.[84] 37 - 38°); n.m.r. (CCl_4 + TMS)δ0.62ppm, J^{119}Sn-C-H 58.5cps, J^{117}Sn-C-H 56cps [Litt.[81]. (CCl_4 + TMS)δ0.61 - 0.66ppm, J^{119}Sn-C-H 58.1 - 58.5, J^{117}Sn-C-H 55.7 - 56]

i.r. (CSI) νmax 650cm^{-1} (S) [Litt.[81] i.r. (cyclohexane) νmax 542cm^{-1} (S), 513(w)]

Dimethyltindichloride bis-4-acetylpyridine

Dimethyltindichloride (2.21g, 0.01M) in sodium wire-dried benzene (50ml.) and 4-acetylpyridine (2.42g, 0.02M) also in dried benzene (25ml.) were mixed and left to stand

overnight at room temperature. Yellow granular crystals separated out. These were filtered off, washed with dried benzene (50 ml.) and dried <u>in vacuo</u> (3.70g, 79.90%). The product was recrystallised three times from dry acetone. m.p. 114 - 115°. Elemental analysis: Calc. for $C_{16}H_{20}Cl_2N_2O_2Sn$ C, 41.60%; H, 4.36%; N, 6.07%. Found C, 41.84%; H, 4.45%; N, 5.76%. nmr ($CD_3.CO.CD_3$ + TMS): δ1.2 (6H, S, 2 x CH_3), δ2.63 (6H, S, 2 x - $CO.CH_3$), δ7.8 (4H, d, 4 x C3H), δ9.26 (4H, d, 4 x C2H). J^{117}Sn-C-H 84cps, l.r J^{119}Sn-C-H 88cps; Sn-C 1195(m), 780(s), 570(s)

>C=O 1690(s)

<u>Mass Spec</u>

78 ($C_5H_4N^+$); 106 ($C_6^+H_4NO$); 121 (C_7H_7NO)
120 (Sn); 135 ($MeSn^+$); 155 ($SnCl^+$);
170 ($MeSn^+Cl$) 185 ($Me_2S\overset{+}{n}Cl$); 191 ($S\overset{+}{n}Cl_2$);?
206 ($MeS\overset{+}{n}Cl_2$); 221 (Me_2SnCl_2)

<u>Dimethyltindichloride bis-3-acetylpyridine</u>

Dimethyltindichloride (2.21g, 0.01M) in dried benzene (50Ml) and 3-acetylpyridine (2.42g, 0.02M) in dried benzene (25ml) were mixed and left to stand overnight at room temperature. Yellow granular crystals slowly separated out. These were filtered off, washed with dried benzene (50ml) and dried <u>in vacuo</u>. The product was recrystallised three times in dry acetone. (3.5g, 75.59%) m.p. 109 - 110°.

Elemental analysis: Calc. C, 41.60%; H, 4.36%; N, 6.07%
(for $C_{16}H_{20}Cl_2N_2O_2Sn$)
Found C, 41.90%; H, 4.41%; N, 5.95%

nmr: δ($CD_3.CO.CD_3$+TMS) δ2.6 (6H,S, 2xCH_3.CO-),
δ7.5(2H,q,2xC5H), δ8.3 (2H,d, 2xC1H)
δ8.8(2H,d,2xC6H), δ9.2 (2H,s, 2xC1H)
J^{113}Sn-C-H 83, J^{119}Sn-C-H 87

i.r.: Sn-C, 1195(s), 774(s), 565(m), 520(w)
c=O, 1685(s)

Mass Spec.

120 (Sn^+); 121 (C_7H_7NO); 135 ($MeSn^+$); 155 ($SnCl^+$);
170 ($MeSn^+Cl$); 185 (Me_2Sn^+Cl); 206 ($MeSnCl_2^+$);
221 ($Me_2SnCl_2^+$)

Trimethyltinchloride-4-acetylpyridine

Trimethyltin chloride (2.0g, 0.01M) in carbon tetrachloride (10ml.) and 4-acetylpyridine (2.42g, 0.02M) in carbon tetrachloride (5ml.) were mixed. The resulting clear yellow solution was cooled overnight light brownish crystals were formed. These were removed by filteration, 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: Calc. C, 37.48%; H, 4.99; N, 4.37% (for $C_{10}H_{16}ClNOSn$)

Found C, 37.69%; H, 5.00%; N, 4.43%

nmr: (CCl_4 + TMS): δ0.61C9H, S, 3 x CH_3),

δ2.55 (3H, S, CH_3.CO-), δ7.6(2H, d, C3H and C5H), δ8.7 (2H, d, C2H and C5H)

J^{117}_{Sn-C-H} 54; J^{119}_{Sn-C-H} 58

i.r.: Sn-C, 1190(w), 786(s), 546(s)

c=O, 1695(s)

Mass Spec.

120 (Sn^+); 121 ($C_7H_7NO^+$); 135 ($SnMe^+$); 150 ($SnMe_2^+$); 155 ($SnCl^+$); 165 ($SnMe_3^+$); 185 ($SnMe_2Cl^+$); 200 ($SnMe_3Cl^+$)

Diphenyltindichloride bis-4-acetylpyridine

Diphenyltindichloride (1.725g, 0.005M) in carbon tetrachloride (50ml.) and 4-acetylpyridine (2.42g, 0.02M) also in carbon tetrachloride (25ml.) were mixed. A dirty white precipitate was formed. This was filtered off, washed with carbon tetrachloride (100ml.), and dried *in vacuo*. The product was recrystallised three times in carbon tetrachloride/benzene (50/50) mixture (2.55g, 87%). m.p. 94 - 96°.

Elemental analysis: Calc. C, 53.27%; H, 4.10%; N, 4.78 (for $C_{16}H_{16}Cl_2N_2O_2Sn$)

Found C, 52.69%; H, 4.05; N, 4.68

nmr: (CD_3COCD_3 + TMS): δ2.6(6H, S, 2 x CH_3.CO-)
δ7.35 (6H, t, part of Ph_2Sn), δ7.8 (8H, t,
2 x C3H, 2 x C5H, and part of Ph_2Sn), δ8.7(4H, d,
2 x (2H and 2 x C6H)

l.r. Sn-C, 1065(s)
C=O, 1700(s)

Mass Spec.

120 ($S\dot{n}$); 121 (C_7H_7NO); 155 ($S\dot{n}Cl$); 191 ($S\dot{n}Cl_2$);
197 ($S\dot{n}Ph$); 232 ($S\dot{n}ClPh$) 268 ($S\dot{n}Cl_2Ph$); 274 ($S\dot{n}Ph_2$);
309 ($S\dot{n}Ph_2Cl$) 345 ($Cl_2S\dot{n}Ph_2$); 389 (Ph $SnCl_2$.4-AcetylPyl_2)

Diphenyltindichloride bis-3-acetylpyridine

Diphenyltindichloride (1.725g, 0.005M) in 25ml. of benzene/CCl_4 mixture (50/50) and 3-acetylpyridine (2.42g, 0.02M) in a 25ml. portion of the benzene/CCl_4 mixture, were mixed and warmed. The resulting clear solution was left to stand for 12 hours. Light yellowish crystals were formed. The mass of crystals was filtered off, washed with carbon tetrachloride (20ml.) and dried in vacuo The product was recrystallised three times from benzene/CCl_4 mixture (50/50) (2.35g, 77%). m.p. 62 - 64°.

Elemental analysis: Calc. C, 53.27%; H, 4.10; N, 4.78 (for $C_{26}H_{24}Cl_2N_2O_2Sn$)
Found C, 52.78%; H, 4.14; N, 4.70

nmr: (CD_3.CO.CD_3 + TMS): δ2.6 (6H, s, 2 x CH_3.CO-),

δ7.45 (10H, m, Ph_2Sn-), δ7.85 (2H, q, 2 x C5H)
δ8.3 (2H, d, 2 x C4H), δ8.75 (2H, d, 2 x C6H),
δ9.15 (2H, d, 2 x C2H)
I.r.:, Sn-C, 1070(s)
>C=O, 1690(s)

Mass Spec.

120 (Sn^+); 121 (C_7H_7NO); 155 ($S\overset{+}{n}Cl$); 191 ($S\overset{+}{n}Cl_2$);
197 ($S\overset{+}{n}Ph$); 232 ($S\overset{+}{n}ClPh$); 268 ($S\overset{+}{n}Cl_2Ph$); 274 ($S\overset{+}{n}Ph_2$);
309 ($Cl_2S\overset{+}{n}Ph_2$); 345 ($Cl_2S\overset{+}{n}Ph$); 389 ($PhS\overset{+}{n}Cl_2$.4-AcetylPy)
430 ($Ph_2S\overset{+}{n}Cl$.4-AcetylPy); 587 ($Ph_2S\overset{+}{n}Cl_2$(4-AcetylPyl$_2$)

Dimethyltindichloride Dipyridine

Dimethyltindichloride (2.21g, 0.01M) in dry benzene (25ml.) and pyridine (1.582g; 0.02M) in dry benzene (25ml.) were mixed. A white precipitate was formed. The precipitate was filtered off, washed with dry benzene (50ml.) and dried *in vacuo*. The product was recrystallised three times in dry acetone (3.00g, 79.11%). m.p. 162 - 163° (Lit.[62] 163°).

Elemental analysis: Calc. C, 38.13%; H, 4.24; N, 7.41 ($C_{12}H_{16}Cl_2N_2Sn$)
Found C, 38.12%; H, 4.28; N, 7.39

nmr: (CD_3COCD_3 + TMS): δ1.24 (6H, s, 2 x CH_3), δ7.5 [.6H, m, 2(C3H, C4H, C5H)], δ7.9 [4H, m, 2(C2H,C5H)]

J^{117}_{Sn-C-H} 86cps, J^{119}_{Sn-C-H} 90cps

i.r. Sn-C, 1185 (w), 780 (s), 566 (m)

Lit[73] 563 (m)

Dimethyltinbistrifluoroacetate-4-acetylpyridine

Dimethyltindichloride bis-4-acetylpyridine (2.315g., 0.005M) in hot, dry acetone (50ml.) and silver trifluoroacetate (2.21g; 0.01M) also in hot, dry acetone (50ml.) were mixed. A white precipitate was formed. The mixture was boiled on a water bath for ten minutes in the dark to minimize photolysis of the silver chloride. The mixture was filtered hot, and the solvent removed from the filterate by distillation, leaving a brown, viscous oil. This was dissolved in dry toluene (50ml.) and cooled overnight. Yellow flakes of crystals were formed. These were filtered off, washed with a little toluene, and dried in vacuo (2.05g). The product was recrystallised three times in dry toluene. m.p. 88 - 89°

Elemental analysis:

Calc. C, 31.47%; H, 2.62; N, 2.82 (for $C_{13}H_{13}F_6NO_5Sn$)

Found C, 31.50%; H, 2.81; N, 2.73

nmr. ($CD_3.CO.CD_3$ + TMS): δ1.03 (12H, s, 4 x CH_3)

δ2.75 C6H, s, 2 x CH_3.CO-), δ7.6 (s, OH);

δ8.3 (4H, δ, 2 x C3H and C5H of 4-acetylpyridine);

δ9.1 (4H, d, 2 x C2H and C6H of 4-acetylpyridine).

$J^{119}Sn-C-H$ 91cps

i.r. Sn-C, 1200 (vs), 805 (s), 590 (m)

C=O, 1690 (vs)

Mass Spec.

120 (Sn^+); 121 $(C_7H_7NO)^+$; 135 $(SnMe)^+$; 139 $(SnF)^+$, 361 $(MeSn(O.CO.CF_3)_2)^+$; $(Me_2Sn(O.CO.CF_3)_2.L)^+$; 873 $(Me_2SnO.CO.CF_3)_2\ _2.L^+$

Trimethyltintrifluoroacetate-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 mixture was filtered hot and the filterate, still containing dispersed silver chloride, was kept in the dark for fourty eight hours. The filterate was refiltered and the now clear filterate was evaporated until a brown viscous oil was left. This was cooled overnight. A mass of yellow crystals formed this was removed and dried in a dessicator. The product was recrystallised five times from carbon tetrachloride. (1.80g, 90%). m.p. 91 - 92°.

Elemental analysis:

Calc. C, 36.21%; H, 4.02; N, 3.52 (for $C_{12}H_{16}F_3NO_3Sn$)

Found, C, 35.85%; H, 3.92; N, 3.49

nmr: (CCl_4 + TMS): δ0.7 (9H, s, 3 x CH_3), δ2.6 (3H, s, CH_3.CO-), δ7.8 (2H, d, C3H and C5H), δ8.6 (2H, d, C2H and C5H)

J(^{117}Sn-C-H) 64, J^{119}Sn-C-H 66

i.r. Sn-C, 1200 (s), 780 (s), 555 (s), 520 (w)

C=O, 1675 (s)

Mass Spec.

120 (Sn^+); 121 $(C_7H_7NO)^+$; 150 (Me_2Sn^+); 154 $(MeSnF)^+$ 165 (Me_3Sn^+); 169 (Me_2SnF^+); 184 $(Me_3SnF)^+$; 263 ($Me_2SnO_2C.CF_3$); 278 ($Me_3SnO_2C.CF_3$)

Reaction Between Dimethyltindichloride bis-3-acetylpyridine and Silver Trifluoroacetate

Dimethyltindichloride bis-3-acetylpyridine (2.315g, 0.005M) in hot, dry acetone (50ml.) and silver trifluoroacetate (2.21g, 0.01M) also in hot, dry acetone on a water bath for ten minutes. A white precipitate of silver chloride separated out. The mixture was filtered hot, and the filterate evaporated until a brown, viscous oil was left. This was mixed with hot toluene and cooled overnight. Small fibres of crystals separated out.

These were filtered off, washed with a little toluene, and dried <u>in vacuo</u> (1.40g.). The product was recrystallised twice in toluene. Chemical analysis, melting point, and n.m.r. showed the product to be dimethyltinbistrifluoroacetate m.p. 243-246° (Lit[85] 243 - 246°).

Calc. for $Me_2SnCO.CO.CF_3)_2$, C, 19.22; H, 1.60.

Found: C, 19.15; H, 1.53.

nmr. ($CD_3.CO.CD_3$ + TMS) δ1.00 (6H, S, 2 x CH_3)

$J^{119}Sn-C-H$, 88cps.

i.r., Sn-C, 1200 (s), 800 (s) 790 (s), 605 (s)
290 (m) 528 (m), 505 (s)

C=O 1655s

<u>Dimethyltinbistrifluoroacetate</u>

Dimethyltindichloride (2.21g, 0.01M) in dry acetone (50ml.) and silver trifluoroacetate (4.42g, 0.02M) also in dry acetone (30ml.) were mixed. A white precipitate of silver chloride was formed. The mixture was boiled under reflux for ten minutes on a water bath and filtered hot. The filterate was left to stand in the dark for twenty four hours to ensure complete precipitation of the silver chloride. The filterate was refiltered, and the resulting clear solution evaporated to dryness. A white powder was left. This was removed and dried <u>in vacuo</u>. The product was recrystallised twice from dry acetone. (2.69, 71.80%) m.p. 243 - 246 (Lit[85] 243 - 246

nmr ($CD_3.CO.CD_3$+TMS): δ1.06 (6H, s, 2 x CH_3)

J^{119}_{Sn-C-H}, 88cps.

i.r., Sn-C, 1200 (s), 790 (s), 600 (s), 590 (m),
525 (m), 505 (s)

C=O, 1650 (s)

Reaction of Dimethyltindichloride with 2-Acetylpyridine

Dimethyltindichloride (2.21g, 0.01M) in dry benzene (30ml.) and 2-acetylpyridine (2.42g, 0.02M) were mixed and left to stand overnight. Brown crystals separated out. These were filtered off, washed with some dry benzene, and dried *in vacuo* (2.56g.) The filterate was evaporated to dryness, and the resulting red powder dried *in vacuo* (0.894g.) Both products were recrystallised twice from acetonitrile to give a white mass of crystals m.p. 185°.

Elemental analysis:

Calculated for $Me_2SnCl_2.(2\text{-AcetylPy})_2$

C, 41.60%; H, 4.36; N, 6.07

Found: C, 27.33%, H, 3.48; N, 3.17

nmr (DMSO + TMS): δ1.05 (6H, s, 2 x CH_3)

δ3.5 (S, unknown)

i.r. Sn-C 790 (s), 570 (vw)

Attempted Reaction of Trimethyltinchloride with 3-Acetyl-Pyridine

Trimethyltinchloride (2.00g, 0.01M) in carbon tetrachloride (15ml.) and 3-Acetylpyridine (1.21g, 0.01M) also in carbon tetrachloride (10ml.) were mixed. The mixture was left to stand for a few hours and then cooled overnight. Light yellowish crystals were formed, but all efforts to isolate the crystals failed as the product melted at about 5°. Distillation was ineffective, distillation under reduced pressure sucked away the trimethyltinchloride.

Reaction of Silver Trifluoroacetate with Diphenyltindi-chloride bis-4-acetylpyridine

Diphenyltindichloride bis-4-acetylpyridine (5.86g, 0.01M) in dry benzene (40ml.) and silver trifluoroacetate (4.42g, 0.02M) in dry benzene (40Ml) were mixed in a 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 filterate was evaporated to give a brown viscous oil. The oil was mixed with dry toluene and cooled overnight. Brownish crystals were formed. The The product was filtered off, washed with a little f toluene, and dried in vacuo (2.56g.) The product was recrystallised thrice from toluene m.p. 118 - 120°.

Elemental analysis:

Calculated for $Ph_2Sn(O.CO.CF_3)_2.(4\text{-AcetylPy})_2$:

C, 48.60%; H, 3.24; N, 3.78

Found: C, 42.69%; H, 3.12; N, 6.02

nmr. ($CD_3.CO.CD_3$ + TMS): δ2.6 (s, - $CO.CH_3$),

δ7.85 (d, C3H and C5H of 4-acetylPy)

δ8.80 (d, C2H and C6H of 4-acetylPy)

Reaction of Silver Trifluoroacetate with Diphenyltindichloride bis-3-acetylpyridine

Diphenyltindichloride bis-3-acetylpyridine (5.86g. 0.01M) in dry benzene (40ml.) and silver trifluoroacetate (4.42g., 0.02M) in dry benzene (40 ml.) were mixed in a round bottomed flask. A white precipitate was formed. The mixture was boiled under reflux on a water bath for twenty minutes in the dark. The silver chloride precipitate was filtered off and the filterate evaporated until a brown viscous oil was left. The oil was mixed with dry toluene and cooled overnight. The product was filtered off, washed with a little toluene, and dried in vacuo (3.20g). The product was recrystallised thrice from toluene. m.p. 93 - 95°.

Calculated for $Ph_2Sn(OCO.CF_3)_2.(3\text{-acetylPy})_2$:

C, 48.60%; H, 3.24; N, 3.78.

Found: C, 41.40%; H, 3.07; N, 6.05.

Nmr ($CD_3.CO.CD_3$ + TMS); δ2.65 (s, $-CO.CH_3$)

δ7.7 (q, C5H of 3-acetylPy)

δ8.4 (d, C4H of 3-acetylPy)

δ8.9 (d, C6H of 3-acetylPy)

δ9.3 (d, C2H of 3-acetylPy)

Reaction of Diphenyltindichloride and 2-AcetylPyridine

Diphenyltindichloride (1.725g., 0.005M) in 20ml. of benzene/CCl_4 mixture (50/50) and 2-acetylpyridine (1.21g, 0.01M) also in the benzene/CCl_4 mixture (10ml.) were mixed in a 50ml. round bottomed flasked which was stoppered and left to stand for 48hrs. at room temperature. A thick, dark-red oil separated out. The solvent was removed by distillation and the oil cooled overnight. No solid was formed even after prolonged cooling. The oil was triturated with petroleum spirit (60.80) and it solidified giving a dirty white paste. This was filtered off, washed with more petroleum spirit, and dried in vacuo (3.66g., m.p. 172°). All efforts to purify the crude product failed.

nmr ($CD_3.CO.CD_3$ + TMS): δ2.6 (s, $-COCH_3$) δ

δ7.3 (m, phenyl).

Attempted reaction Between Dimethyltin dichloride bis-4-acetylpyridine and silver thiocyanate

Dimethyltindichloride bis-4-acetylpyridine (2.31g, 0.005M) in hot, dry benzene (150ml.) and silver thiocyanate (4.42g, 0.03M) suspended in hot, dry benzene (150ml.) were

mixed in a round bottomed flask. The mixture was refluxed in the dark for 48hours, at the end of which it was filtered hot. The filterate was evaporated to dryness, yielding a yellowish powder. (2.04g). The powder was recrystallised thrice from dry di-isopropyl ether, chemical analysis, melting point and spectroscopy showed it to be the starting material, dimethyltindichloride bis-4-acetylpyridine.

Identification of Yam rot-causing fungi

Smears of rotten yam (both white and brown) were made on potatodextrose agar (PDA) and yam dextrose agar (YDA) in petridishes. The cultures were subjected to an incubation temperature of 28°. The fungi grew well after two days but did not sporulate. However, the white-rot-causing fungi sporulated after two weeks.

Fresh smears were made on slices of autoclaved yam in petridishes and subjected to the incubation temperature (28°) for a week. A number of fungi grew and sporulated. Smears of the hyphae of the fungi were made on microscope slides, stained with methylene blue, and studied under the microscope. Some of the fungi were identified thus:

White rot-causing fungi - Fusarium (2 species, one yellow, one pink)

brown rot-causing fungi - Aspergillus niger
- Aspergillus flavus
- Penicillium spp.
- Black fungus with septation.

The black fungus was found to be extremely infectious and fast growing, but did not sporulate even on yam culture.

Effect of Some Organotin Compounds on the Growth of Yam rot Causing Fungi on Potato Dextrose Agar (PDA)

Two grams of the organotin compound (see below) was dispersed in a 5gm/litre aqueous solution of Tween 80 emulsifier (100ml.) This was labelled mixture 'a'. 50ml. of mixture 'a' was diluted to 100ml. with the Tween 80 solution, to make mixture 'b'. 20ml. of mixture 'b' was diluted to 100ml. with the Tween 80 solution, to make 'c'. 50ml. of 'c' was similarly diluted to 100ml. making 'd' 20ml. of 'd' was diluted in like manner to 100ml, making 'e'. 50ml. of 'e' was similarly diluted to make 'f'. 5ml. of each mixture was mixed with 20ml. of molten PDA in petridishes. The petridishes of PDA were left under u.v. light for 24hrs. to allow the water to evaporate and the PDA to set. Six petri dishes were thus obtained with six different concentrations of each organotin compound, viz

(a) 0.50%

(b) 0.25%

(c) 0.05%

(d) 0.025%

(e) 0.005%

(f) 0.0025%

The organotin compound PDA in the petridishes were innoculated with hyphae of yam rot-causing fungi cultured from rotten yams on PDA and incubated for five days at 28°.

The experiment was repeated using a number of organotin compounds (below). Control experiments were carried out using 5ml. of distilled water in place of 5ml. of organotin suspension.

The PDA cultures were observed for fungal growth at the end of 5 days.

Abbreviations:

NG = No mycelia growth

VSG = Very scanty mycelia growth

SG = Scanty mycelia growth

PG = Profuse mycelia growth

Results:

Concentration of Organotin Compd. in PDA / Organotin Compound	0.50%	0.25%	0.05%	0.025%	0.005%	0.0025%
Ph_3SnOAc	NG	NG	NG	SG	SG	PG
Ph_3SnOH	NG	NG	NG	VSG	SG	PG
Ph_3SnCl	NG	NG	NG	SG	SG	PG
$Bu_3SnOSnBu_3$	NG	NG	NG	VSG	SG	PG
Me_3SnCl.4-Acetyl-Pyridine	NG	NG	NG	NG	NG	SG
Me_2SnCl_2 $(4\text{-AcetylPy})_2$	NG	NG	SG	SG	PG	PG
Me_2SnCl_2 $(3\text{-AcetylPy})_2$	NG	NG	SG	SG	PG	PG
Ph_2SnCl_2 $(4\text{-AcetylPy})_2$	NG	NG	VSG	SG	PG	PG
Ph_2SnCl_2 $(3\text{-AcetylPy})_2$	NG	NG	VSG	SG	PG	PG
$Me_3SnO.CO.CF_3$· 4-AcetylPy	NG	NG	NG	NG	SG	SG
$Me_2Sn(O.CO.CF_3)_2$ 4-AcetylPy	NG	NG	VSG	SG	PG	PG

Activity of Some Organotin Compounds in Protecting Yam Against Rot

2 gm. of Organotin Compound (below) was suspended in a 0.50% (w/v.) aqueous solution of Tween 80 (100ml.) using an emulsifier. From this stock were prepared 100ml. each of 1%, 0.2%, 0.1%, 0.02% and 0.01% by serial dilution using the 0.5% Tween 80 as dilutant. Small slices of yam were cut and washed in the prepared mixtures, a slice per emulsion. After a few minutes, the yam slices were smeared with hyphae of rotten yam fungi cultured on PDA Each of the smeared slices was kept in a separate dessicator (without a dessicant) to maintain constant humidity, and left to stand at room temperature for ten days. The slices were then observed for fungal growth. Sections through areas of innoculation were cut and the depth of rot, if any measured.

The experiment was repeated using a number of organotin compounds (below). Control experiments were also set up using blanks of 0.5% solutions of Tween 80 in distilled water.

Results:

Control Experiments

Chemical	Surface observation of yam slice	Depth of rot
0.5% aqueous Tween 80 solution	Profuse mycelia growth	Across the 3-cm thick slice
Distilled water	Profuse mycelia growth	2.5cm

Abbreviations

NG = No mycelia growth

VSG = Very sparse mycelia growth

SG = Sparse mycelia growth

PG = Profuse mycelia growth

SO = Surface observation of yam slice

XS = Depth of rot in yam slice in centimetres

Concentration of emulsion / Organotin Compound		2.0%	1.0%	0.2%	0.1%	0.02%	0.01%
$Bu_3SnOSnBu_3$	SO	NG	NG	NG	SG	PG	PG
	XS	0.00	0.00	0.00	0.50	2.00	2.00
Ph_3SnOAC	SO	NG	NG	NG	VSG	PG	PG
	XS	0.00	0.00	0.00	0.30	0.90	2.50
Ph_3SnCl	SO	NG	NG	NG	SG	PG	PG
	XS	0.00	0.00	0.00	0.30	0.50	1.5
Ph_3SnOH	SO	NG	NG	SG	SG	PG	PG
	XS	0.00	0.00	0.50	0.90	1.50	1.60
Me_2SnCl_2 $(4\text{-AcetylPy})_2$	SO	NG	NG	SG	SG	SG	SG
	XS	0.00	0.00	0.15	0.3	0.5	0.5
Me_2SnCl_2 $(3\text{-AcetylPy})_2$	SO	NG	NG	SG	SG	SG	PG
	XS	0.00	0.00	0.16	0.30	0.50	0.60
$Me_3SnCl.$ 4-AcetylPy	SO	NG	NG	NG	NG	NG	SG
	XS	0.00	0.00	0.00	0.00	0.10	0.10
Ph_2SnCl_2 $(4\text{-AcetylPy})_2$	SO	SG	SG	SG	SG	SG	PG
	XS	0.15	0.25	0.30	0.30	0.50	1.00
Ph_2SnCl_2 $(3\text{-AcetylPy})_2$	SO	SG	SG	SG	SG	SG	PG
	XS	0.10	0.20	0.30	0.55	0.50	1.10
$Me_2Sn(O.CO.CF_3)_2$ 4-AcetylPy	SO	NG	SG	SG	SG	SG	SG
	XS	0.00	0.20	0.30	0.30	0.40	0.40
$Me_2Sn(O.CO.CF_3)_2$	SO	NG	SG	SG	SG	SG	PG
	XS	0.00	0.15	0.30	0.30	0.50	0.60
$Me_3SnO.CO.CF_3$ 4-AcetylPy	SO	NG	NG	NG	NG	SG	SG
	XS	0.00	0.00	0.00	0.00	0.10	0.15

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