CHAPTER 4

CHAPTER 4

SYNTHESES OF ALKENYLTIN (IV) COMPOUNDS.

§ 4.1 INTRODUCTION :

The preparation and characterisation of σ-bonded α-unsaturated organic derivatives of tin are reported in this chapter. A list of the new alkenyls of tin, are given in table 1.

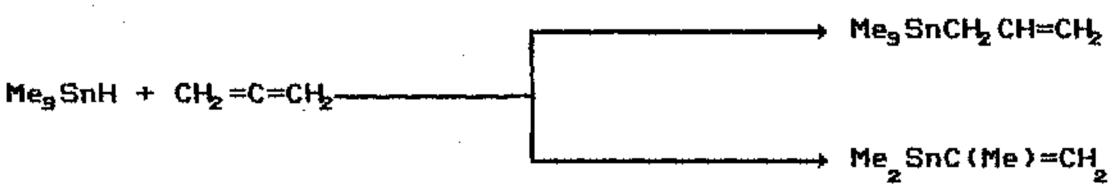
TABLE 1

LIST OF NEWLY SYNTHESISED HOMOLEPTIC ALKENYLS OF TIN.	
1) $[Ph_2C=C(Ph)]_2SnCl_2$ m.p.259°C, λ_{max}= 235nm	2) $[Me_2C=CH]_3SnCl$ b.p.50°C, 0.5 torr λ_{max}=215nm
3) $[Me_2C=CH]_4Sn$ m.p.115°C, λ_{max}=215nm	4) $[Me_2C=(Ph)]_3SnCl$ m.p.>270°C, λ_{max}=214nm
5) $[Me_2C=CH]SnMe_2Cl$ m.p.>275°C, λ_{max}=212nm	6) $[Me_2C=CH]Sn(Ph)_3$ m.p.>270°C, λ_{max}=220nm
7) $[Me_2C=CH]Sn(\nabla C_6H_{11})_3$ m.p.56°C, λ_{max}=218nm	8) $[Ph_2C=C(Ph)]_2Sn(Me)_2$ m.p.>280°C, λ_{max}=212nm

Interest in these derivatives lie in their structural and bonding studies and chemical reactivities.[1] The syntheses of these compounds are significant in several ways, specially from the point of view of novel structural features.

Although a general description of the organotin chemistry is reviewed briefly in CH 1 , it would not be inappropriate to recall here some of the relevant literatures on the syntheses of alkenyltin compounds:

Hydrostannation of olefin[1a] is used for the preparation of compounds of the general type $>Sn-H + A=B \longrightarrow >Sn-A-B-H$, e.g. $R_3SnH + CH_2=CHR' \longrightarrow R_3SnCH_2CH_2R'$. These reactions may also be used for attaching organic radicals containing functional groups to tin metal. Hydrostannation of allene results into the formation of two alkenyls, e.g.

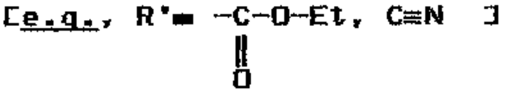


However, with unsymmetrically substituted allenes the number of products increases and from the corresponding reaction with $MeCH=C=CH_2$ five products have been isolated and characterised[2].

Organotin hydrides have been found to add more readily to acetylenes than olefins and Van der Kerk and Noltes[3] reported a number of addition reactions of the following type leading to the formation of tin alkenyls:

$$R_3SnH + R'C\equiv CH \longrightarrow R_3SnCH=CHR'$$

The same reaction if carried out with two molar proportions of triphenyltin hydride and one molar proportion of acetylene leads to the symmetrical distannyl ethane[4]. Detailed studies of the structures and stereochemistry of the products of hydrostannation of acetylenes, initiated by Futton[5] reveals that if R' in $HC\equiv CR'$ be a strongly electron withdrawing part,



[*e.g.*, $R' = -\underset{\underset{O}{\|}}{C}-O-Et$, $C\equiv N$]

then relatively large amount of the α-adducts are formed[6].

Dialkenyl tin halide may also be prepared from a different route using tin(II) halides by reaction with a suitable organometallic reagent of the type R_2PbX_2[7] or R_2TlX[12] where R is an alkenyl part and X is halogen *e.g.*,

$$(ClCH=CH)_2PbCl_2 + SnCl_2 \longrightarrow (ClCH=CH)_2SnCl_2 + PbCl_2$$

$$(MeCH=CH)_2TlBr + SnBr_2 \longrightarrow (MeCH=CH)_2SnBr_2 + TlBr$$

For the sake of convenience in understanding, a schematic representation of the reaction sequences for the preparation of different alkenyltin chlorides consistent with reaction stoichiometry, is presented below:

$$R{-}Br + 2Li \longrightarrow R{-}Li + LiBr\downarrow$$

$$3\ R{-}Li + SnCl_4 \longrightarrow R_3SnCl + 3\ LiCl\downarrow$$

[where R≡ alkenyl groups]

or,

$$R{-}Br + Mg \longrightarrow RMgBr$$

$$3RMgBr + SnCl_4 \longrightarrow R_3SnCl + 3MgBrCl\downarrow$$

Organomagnesium compounds (Grignard reaction), are used as the most convenient method for the preparation of tetraorganotin compounds in the laboratory, by reacting with tin(IV) halides, and has the industrial importance also in the manufacture of tetrabutyl, tetraphenyltin compounds. In most of the cases the yields are also high though large excess of Grignard reagent may be employed to achieve complete alkylation of tin, the excess may be reduced by raising the reaction temperature over the boiling point of commonly used solvent ether, which is done by distilling off ether after all of the reactants had been added followed by the addition of the higher boiling solvent like benzene or toluene, or by carrying out the reaction in higher boiling ether such as tetrahydrofuran.

§ 4.2 SCOPE AND OBJECTIVES :

The inclusion of tetraalkenyltins and mixed alkenyltins in this study is primarily to synthesise the alkenyltin halocompounds. The tin-carbon bonds of the tetraorganotins may then be cleaved by haloacid/halogen where required, to synthesise the organotinhalo compounds. These organotinhalo compounds e.g. R_3SnCl may be utilised to synthesise biologically important derivatives such as dithio/thio carboxylates. With this aim in view, a number of tetraorgano alkenyls or mixed alkenyls tins have been synthesised. Studies are on going to develope a suitable route to convert these compounds to the corresponding halotin derivatives.

§ 4.3. EXPERIMENTAL AND CHARACTERISATION

Tin was estimated gravimetrically by conversion of the compound to tin(IV) oxide and finally to volatile stannic iodide, essentially by the method of Van der Kerk and Luijten[10].

Elemental analysis for carbon, hydrogen, nitrogen and sulfur were carried out in RSIC-NEHU, NCL-PUNE and CDRI-LUCKNOW, India.

UV spectral data were taken in Shimadzu UV-160 spectrophotometer. "Uvasol"(Merck) solvents viz., methanol was used as solvent.

The IR spectra were recorded in the range between 4000-300 cm^{-1} for most of the compounds using Pye-Unicam-SP-300S infrared spectrophotometer and using CsI optics and Nujol as mulling agent.

The following abbreviations have been used to express the intensity of the different IR absorption bands: v.s.= very strong, s= strong, m= medium, w= weak, b= broad, sh= shoulder.

^{1}H NMR spectra have been recorded in VA-EM-390; 90 MHz NMR spetrophotometer at RSIC, NEHU, Shillong, using $CDCl_3$ as solvent. In all these cases tetramethyl silane was used as the internal standard.

The ligand aromatic protons and tin aromatic protons appeared as a complex multiplate as expected. Attempts were not made to assign the individual signals in this region.

§ 4.3.1. PREPARATION OF STARTING MATERIALS :

All the manipulations involving benzene were carried out in closed condition with utmost precaution and care. All the solvents namely benzene, petroleum ether (boiling range 60°-80°C and 100°-120°C), chloroform, diethyl ether, methanol etc., used in the experiments were purified and dried by literature methods[11]. The different organotin(IV) chlorides namely, triphenyltin chloride, diphenyltin dichloride, tricyclohexyltin chloride, tributyltin chloride, butyltin trichloride, dimethyltin dichloride, dibutyltin dibromide were used as procured from Aldrich/Fluka or after purification using soxhlet followed by recrystalisation or by simple crystalisation from suitable solvents.

All the melting points of these compounds reported here were uncorrected .

The alkenyl bromides used here as starting material for newly synthesised organotin(IV) alkenyl chlorides involve three major steps which are discussed in detail in the following parts.

§ 4.3.1.1 PREPARATION OF TRIBENZYLTIN CHLORIDE :

Tribenzyltin chloride was prepared by the method of Sisido et.al.[12]. 17.8gm (150mmol) of tin powder was suspended in 150ml boiling water on oil bath at 100°C with efficient continuous stirring. 57gm (450mmol) of benzyl chloride was added in during 2 minutes and refluxing was continued for $1\frac{1}{2}$ hour. The solid mass obtained, contained unreacted tin powder and the product. This was extracted with acetone using soxhlet for four hours. The acetone was evaporated under diminished pressure leaving pale yellow solid. This on crystalisation from ethylacetate gave 20.2gm of white crystals of silky appearence(m.p.142°-144°C)[12]

%	carbon	hydrogen
Found(cal)	58.50(58.96)	4.88(4.91)

§ 4.3.1.2.PREPARATION OF ANHYDROUS STANNIC CHLORIDE :

Anhydrous stannic chloride was prepared in the laboratory using the literature method[19]. 51gm (428.9 mmol) of metallic tin was converted into anhydrous stannic chloride by the passage of gaseous chlorine, generated by the reaction of concentrated hydrochloric acid and solid potassium permanganate. The generated chlorine was passed through two traps containing water to make it free from any HCl vapour, followed by another trap containing concentrated sulfuric acid to make it dry, before it was allowed to react with metallic tin. The vigorousity of the reaction was controlled by keeping the system cooled externally by water. The excess of chlorine, was destroyed by the addition of slight excess of metallic tin foil. The stannic chloride produced was distilled out under nitrogen atmosphere (b.p.114°C, d=2.226), when a colourless liquid was collected and was preserved in a wel-stoppered bottle in N_2 atmoshphere. (yield 111.3 gm, 98%)

§ 4.3.1.3. PREPARATION OF $Ph_2C{=}C(Ph)Br$

A) PREPARATION OF CARBINOL, $Ph_2C(OH)CH_2Ph$:

3gms (125 mmol) of dry magnesium turnings were taken in a one litre three necked round bottomed flask, fitted with a pressure equalising dropping funnel, magnetic stirring index and a double surface reflux condenser. A solution of 15gm (14.36ml, 118.5 mmol) of dry benzyl chloride in 100ml of sodium dried ether was taken in pressure equalising funnel. The reaction was carried out under the inert condition of nitrogen atmosphere. A small amount of crystals of iodine were added as catalyst for initiation of the reaction. The vigorousity of the reaction was kept under control by adjusting the rate of addition of benzyl chloride fitted with the arrangements for external cooling on requirement. The addition of benzyl chloride was maintained at such a rate that continuous refluxation occured during the addition. After the addition was over, the refluxing condition was maintained for further one hour by gentle external heating. Stirring was continued till the reaction mixture came to room temperature. The completion of the reaction was also indicated by the dissolution of all magnesium.

To the resulting Grignard reagent, a solution of 23gm (126.3 mmol) of benzophenone in 150ml dry ether was added dropwise at room temperature condition along with constant stirring at such a rate that the mixture starts refluxing. The refluxation was continued till the addition was complete and then for further one hour more during which the reaction mixture turned from greenish-black to grey. After the reaction was over the reaction mixture was cooled in a freezing mixture of ice-salt. The cooled reaction mixture was poured into a mixture of 750 gms of crushed ice and the required amount of sulfuric acid. The stirring was continued for the complete dissolution of the solid, 25 gms of solid ammonium chloride was added to facilitate the hydrolysis, more ether was needed (approx. 200ml) to dissolve all the products. The etheral layer was separated by using a separating funnel. The ether layer was then washed with sufficient amount of water, sodium bicarbonate solution, followed by sufficient amount water till the washings were neutral to litmus. The etheral solution was then concentrated when a light yellowish-green oily semi-solid material was formed. The volatiles were removed by steam distillation from the semi-solids. The solid residue thus obtained was collected and dried in vaccuum and recrystalised from 95% alcohol. Recrystalisation could be done from carbon tetrachloride also. The melting point of the recrystalised product (31gm) was 88°C with 90% yield[27].

Elemental analysis: Found (Calcd.)

C	H
87.58	6.50
(87.59)	(6.56)

B) DEHYDRATION OF THE CARBINOL $Ph_2C(OH)CH_2Ph$:

Dehydration was effected by 200ml of a mixture of glacial acetic acid and sulfuric acid in the ratio of 3:1 by volume, in which the carbinol was dissolved. The reaction mixture turned brown, and it was warmed on a water-bath for about two hours and then stirred overnight at room temperature. The dehydrated product was extracted with ether, repeatedly. The different portions of the ether washings were collected and this combined etheral extract was further washed repeatedly for about 10 times with portions of 50ml water, bicarbonate solution, followed by water again. The ether was then removed by distillation to obtain the solid dehydrated product. The same step of dehydration was also carried out by using dry HCl[11] where a gaseous stream of dry HCl produced by the reaction of concentrated sulfuric acid with sodium chloride was passed through hot solution of 10gm (36mmol) of carbinol in 100ml of toluene for six hours, with constant stirring. The reaction mixture was kept saturated with HCl vapour overnight. After the reaction was over the solvent layer was separated out which was washed intensively with water, dilute solution of sodium bicarbonate followed by water again till the washings were neutral to litmus. The solvent was separated and then dried over anhydrous sodium sulfate. The dry solution was filtered out and concentrated when rectangular shaped colourless crystals came out.(m.p.68°C).[11]

Elemental analysis: Found (Calculated)

C	H
93.45	6.25
(93.70)	(6.30)

c) SIMULTANEOUS BROMINATION AND DEHYDROBROMINATION OF $Ph_2C{=}CHPh$

This step involves bromination and dehydrobromination _in situ._. 50 gm (195.3 mmol) of $Ph_2C{=}CHPh$ was taken in a round bottomed flask and was dissolved in minimum amount of carbon tetrachloride under ice cold condition. Required amount (31.25 gm, 195.31 mmol) of bromine, from a pressure equalising funnel, was added slowly along with constant stirring for two hours. Initially the colour of bromine was found to disappear as soon as it was added. After the addition was over, the reaction mixture was stirred overnight. The product soluble in CCl_4 medium was separated by using separating funnel and washed repeatedly with water, till aqueous layer was feebly acidic. Then the extract was washed repeatedly with $NaHCO_3$ solution followed by water till the aqueous part became neutral. The CCl_4 part was concentrated under vaccum. This concentrated part gave the product. The yield of the crude product was 70% which was recrystalised from 95% alcohol when the pure product separated out as yellowish needle shaped crystals (m.p. 115°C)[28].

Elemental analysis: Found (Calcd.)

C	H
71.33	4.40
(71.60)	(4.47)

The same product may also be obtained by a different route.[28] 50 gm (195.3 mmol.) of the alkene $Ph_2C{=}CHPh$ was dissolved in minimum volume of warm glacial acetic acid. (31.25gm, 195.31 mmol) of bromine was added to the acetic acid solution with constant stirring. After the addition was over, the reaction mixture was warmed on water bath with occasional shaking. After 30 minutes precipitation started, which was collected, washed repeatedly with water, bicarbonate solution followed by water till the washings were neutral to litmus. Recrystalisation was done using ethanol as solvent. The yield was 58% (115°C)[28]. The recrystalised product was used in the subsequent operations when required.

§ 4.3.14. PREPARATION OF $Me_2C{=}C(Ph)Br$:

A) PREPARATION OF $Me_2C(OH)CH_2Ph$:

20gms (833.3 mmol) of dry magnessium turnings and 250ml dry ether were taken in a one litre three necked round bottomed flask, fitted with a pressure equalising dropping funnel, magneting stirring index and a double surface reflux condenser. 105.4 gm (95ml, 833.3 mmol) of dry benzyl chloride was taken in pressure equalising funnel. The reaction was carried out under nitrogen atmosphere. A small amount of crystals of iodine was added as catalyst for initiation of the reaction. In this case the initiation took place within five minutes. The vigorosity of the reaction was adjusted by the controlled rate of addition of benzyl chloride besides occasional cooling of the system externally, to maintain continuous refluxation throughout the time of addition. After the addition was over, the refluxing condition was maintained for further one hour by external heating with hot water after which only stirring was continued till the reaction mixture came to room temperature. The completion of the reaction was indicated by the dissolution of all magnesium metal.

To the resulting Grignard reagent, 48.4 gm (61ml, 833.3 mmol) of acetone was added dropwise at room temperature along with constant stirring at such a rate that the reaction mixture started refluxing and this was continued till the addition was complete. After the addition was over the refluxation was continued gently for further one hour, when the reaction mixture turned from greenish-black to grey. After the reaction was over, the reaction mixture was cooled in a freezing mixture of ice-salt. Then the cold reaction mixture was poured into a mixture of 750gm of crushed ice and the required amount of sulfuric acid. The stirring was continued till complete dissolution of the solid was complete. To facilitate the hydrolysis, 25 gm of solid ammonium chloride was added. 200ml ether was needed more to dissolve all the products. The etheral layer was separated by using the separating funnel. The ether layer was then washed with sufficient amount of water, sodium bicarbonate solution, followed by sufficient amount of water again till the washings were neutral to litmus. The etheral solution was then concentrated when light yellowish-green oily semi-solid material came out. The volatiles and unreacted benzyl chloride were removed by steam distillation. The liquid residue was extracted with ether, ether fractions were collected and the combined ether extract was dried over magnesium sulphate and ether was removed by distillation at atmospheric pressure.The liquid obtained was directly used for the next step of dehydration.

B) DEHYDRATION OF THE CARBINOL $Me_2C(OH)CH_2Ph$:

Dehydration was effected by a warm solution of a 36.64 ml conc. sulfuric acid and 146.4 ml glacial acetic acid by volume, in which the carbinol was dissolved. The reaction mixture turned reddish brown in colour, and it was warmed on a water-bath for about four hours and then stirred overnight at room temperature. The dehydrated product was extracted with ether, repeatedly. The different portions of the ether washings were collected and this combined etheral extract was further washed repeatedly for about

10 times with portions of 50ml water, followed by bicarbonate washing, followed by water again. The ether was then removed by distillation to obtain the liquid dehydrated product. The same dehydration step was also carried out[11] by using dry HCl where a gaseous stream of dry HCl produced by the reaction of concentrated sulfuric acid with sodium chloride was passed through hot solution of 10gm (75.8 mmol) of carbinol in 100ml of toluene for six hours, with constant stirring. The reaction mixture was kept saturated with HCl vapour overnight. After the reaction was over the solvent layer was separated out which was washed intensively with water, dilute solution of sodium bicarbonate, followed by water again, till the washings were neutral to litmus. The solvent was separated and then dried over anhydrous sodium sulfate. The ether was then removed by distilation, the liquid thus obtained was further distilled at 16 torr with 67% yield of $Me_2C=CH(Ph)$ (b.p. 77°C at 16 Torr).

Elemental analysis: Found (Calcd.)

C	H
90.0	9.58
(90.2)	(9.70)

c) BROMINATION OF $Me_2C=C(Ph)H$:

Bromination was carried out by the slow dropwise addition of bromine(80 gm, 500 mmol) dissolved in 100ml of carbon tetrachloride under ice cold condition, to the solution of the alkene $Me_2C=C(Ph)H$ in minimum amount (25ml) of carbon tetrachloride from a pressure equalising dropping funnel, along with constant overnight stirring. The colour of bromine was found to disappear almost completely within 24 hours. The reaction mixture was then washed with sodium meta-bisulphite solution, sodium chloride solution (10% by w/v), sodium bicarbonate solution (10% by w/v) and finally by three portions of 50ml water. The resulting liquid was then dried over anhydrous sodium sulphate. The solvent was then removed by distillation to get 85% of the product $(CH_3)_2CBr-CHBr(Ph)$ b.p. 105°C at 0.35 Torr, yield 108gm, 85% .

IR(thin film) : 725(s), 765(s), 1120(s), 1216(m), 1392(m), 1400(m), 1475(s).

^{1}H NMR ($CDCl_3$): δCH_3 1.8 (s,3H); δCH_3 1.9 (s,3H); $\delta \, {>}C{=}C{<}_{H}$ 5.2 (s,1H); δPh 7.3(m,5H).

Elemental analysis: Found (Calcd.)

C	H
41.00	4.01
(41.09)	(4.10)

D) DEHYDROBROMINATION OF $Me_2CBr-CHBrPh$:

108gm (369.8 mmol) of 1,2-dibromo-2-methyl-1-phenyl propene, $Me_2CBr-CHBrPh$ was added dropwise onto a thorough mixture of dried sand and 41gm (370 mmol) potassium tertiary butoxide cooled in ice bath. The mixture was stirred overnight. Distillation afforded 57.2gm (73% yield) olefin $Me_2C=CPhBr$ (b.p. 87°C at 6 Torr).

Elemental analysis: Found (Calcd.)

C	H
56.52	5.13
(56.87)	(5.21)

IR(thin film) : 650(s), 700(s), 759(vs), 853(vs) 880(vs) 920(w) 1032(m), 1070(s), 1210(w), 1240(m), 1370(m), 1382(m), 1445(s), 1490(m), 1600(w), 1652(w,br).

^{1}H NMR ($CDCl_3$): δCH_3 1.7 (s,3H); δCH_3 2.0 (s,3H); δPh 7.3(m,5H)

§ 4.3.15. PREPARATION OF $Me_2C{=}CHBr$:

214.8gm (176.8 mmol,d =3.00) of bromine was added dropwise into 99.99gm (172.4 mmol, d =0.78) tertiary butyl alcohol under refluxing condition over steambath . After an induction period of few minutes, the bromine colour started to disappear rapidly and the rate of addition of bromine was adjusted to keep the exothermic reaction under control. As the reaction proceeded, two distinct layers separated in the reaction vessel. After cooling, the top layer consisting mostly unreacted alcohol and water, was separated and discarded. The lower layer was collected and washed repeatedly with water and then dried over fused $CaCl_2$. Distillation through the 8" Dufton col umn, gave 1,2 dibromo isobutane (~ 200 gm) b.p. 38–42°C at 10 torr, which was sufficiently pure for the next phase of reaction.

The dibromide formed (~200gm) was added dropwise to a wel-stirred mixture of KOH (66 gm) in ethylene glycol (180ml), taken in a 3-necked copper flask, immersed in an oil bath at 125–130°C. Isobutenyl bromide (~65 gm) based on tertiary butyl alcohol was collected, and then washed with 20ml 5% KOH solution and then with 3 × 75ml water. The reaction mixture was dried over fused $CaCl_2$, fractionated from small piece of sodium on 8" Dufton coloum (b.p. 92°C at 760 torr). [7,14,15]

Elemental analysis: Found (calcd)

C	H
35.1	4.99
35.5	5.18

IR (cm^{-1}) : 530(m), 580(s), 800(m), 1600(m)

^{1}H nmr (CDCl$_3$): $\delta \, {>}C{=}C{<}_{H}$ 5.85(s, 3H), δCH_3 1.7(s, 3H), δCH_3 1.9(s, 1H)

§ 4.3.2. SYNTHESES OF NEW TIN ALKENYLS:

A number of new tin alkenyls have been synthesised and their composition established. The detailed description follows. All the manipulations involving air sensative materials such as stannic chloride were carried out under the inert atmosphere of pure and dry nitrogen with rigorous exclusion of air and moisture, unless otherwise stated. Solvents were distilled from appropiate drying agents and stored under the inert atmosphere of nitrogen. ^1H NMR spectra were recorded at the VA-EM-390 NMR spectrophotometer operating at 90 MHz, using tetramethyl silane as internal standard. IR spectra were recorded using the Perkin-Elmer 1720X FT-IR spectrophotometer, Beckman IR-20 and Pye-Unicam SP-300s spectrophotometers.

§ 4.3.2.1. SYNTHESIS OF $[Ph_2C=C(Ph)]_2SnCl_2$:

0.5 gm(20.83 mmol) of wel-dried magnesium was taken in a 250ml three necked 500 ml round bottomed flask, fitted with an efficient double surface refluxing condenser, attached to a nitrogen gas inlet and a pressure equalising dropping funnel. First the system was evacuated and then the system was filled with dry nitrogen gas and cooled. 150ml sodium dried ether was taken into a round bottomed flask to which a few crystals of resublimed iodine was added as a catalyst which imparted a yellow colour to the solution.

7.5 gm (22.38 mmol) of the triphenyl ethelene bromide, prepared earlier, was dissolved into minimum amoumt of dry ether and was slowly added in drops to magnesiumin from a pressure equalising dropping funnel. The initiation occured within few minutes indicated by the decolourisation of the iodine colour of the reaction mixture. The refluxing condition was maintained by the occasional warming of the reaction vessel externally by the use of hot water and also by the controlled rate of the addition of the bromide. The refluxing condition was maintained even after the addition of the bromide was over till all magnesium was converted into the Grignard reagent.

Then 1.9 gm (7.28 mmol, d= 2.26) of freshly distilled stannic chloride was pippeted out and disolved in 30ml of sodium dried benzene and the corresponding solution was taken into the pressure equalising dropping funnel under high flow of nitrogen. As stannic chloride solution in benzene was added at room temperature, to the Grignard reagent, a visible change in colour took place. The dropwise addition was complete within half an hour. On increasing the rate of addition to the high level, the solution became yellow coloured and therefore the rate was maintained at optimum level. After the addition was over, gradually the reaction vessel was found to collect white precipitates at the bottom of it. Still the refluxing condition was continued for more than 18 hours. Then the volatiles were removed at low pressure and the pasty mass obtained was extracted with benzene repeatedly. The benzene extract on concentrating gave colourless crystals (yield 70 %, m.p.259°C) which was established to be $[Ph_2C{=}C(Ph)]_2SnCl_2$ by elemental analysis and other spectral data.

Elemental analysis:Found(calcd.):

C	H	Cl	Sn
69.09 (68.58)	4.50 (4.28)	10.32 (10.14)	16.85 (16.98)

Relevant Spectral data:

IR:(nujol) 465(w), 585(w), 700(s), 740(m), 770(m), 800(m), 900(w)
1026(w), 1070(w), 1560(m), 1586(w)
1735(w)

^{1}HNMR ($CDCl_3$): δ 7.0-8.5 (m)
(*vide* table 3)

§ 4.3.2.2. SYNTHESIS OF $[Me_2C{=}C(H)]_3SnCl$:

2 gm (289.8 mmol) of lithium were cut into thin pieces and taken into a three necked flask containing 100ml of sodium dried ether. The flask was also fitted with pressure equalising dropping funnel and a double surface reflux condenser. 19.28gm (142.8 mmol, d =1.318) of isobutenyl bromide were taken in the pressure equalising dropping funnel. The reaction was carried out in nitrogen atmosphere. Initially $\frac{1}{6}$th of the total amount was added to the lithium at a time. The initiation was done by external heating using hot water The refluxing condition was maintained throughout the reaction by the controlled rate of addition of bromide. The reaction mixture gradually changed from ash colour to greyish-yellow along with the appearence of turbidity. After the addition was over, the refluxation was continued till the lithiation was complete.

Then 8.85 gm (35.6 mmol, d =2.26) of $SnCl_4$ solution in 30ml of dry benzene was added dropwise at room temperature under nitrogen atmosphere along with constant stirring .After the completion of the addition the refluxation was continued for 16 hours. Then the volatiles were removed first and thereafter the sticky reaction product mixture was extracted first with petroleum ether to wash out the yellow sticky part, when a colourless compound as precipitate was collected. As this colourless solid was also soluble in petroleum ether and the solubility was much less than the yellow sticky part, the solid dissolved in petroleum ether fraction during washing was recollected by allowing this to crystalise at −18°C, when colourless needle shaped crystals were obtained. The process was continued till the crystalisation was complete and no more crystals came out from petroleum part. The identity of this solid is discussed in the section 4.3.2.3. Then the petroleum ether was distilled out to get a yellow liquid which was identified to be $[Me_2C{=}C(H)]_3SnCl$ by elemental and spectral data, yield 3gm, b.p.50°C at 0.5 Torr.

Elemental analysis:Found(calcd.):

C	H	Cl	Sn
44.99 (45.08)	6.38 (6.57)	10.93 (11.11)	36.90 (37.23)

Relevant Spectral data:

IR:(nujol) : 530(m), 580(s), 800(m), 1600(m)

^{1}HNMR : δ 5.85 (s,3H), δ 2.1 (s,9H), δ 1.6(s,9H).
(<u>vide</u> table 3)

§ 4.3.2.3. SYNTHESIS OF $[Me_2C=C(H)]_4Sn$

The solid crystaline product was obtained as a biproduct of the earlier reaction (<u>vide</u> 4.3.2.2) which was recrystalised from petroleum ether as a colourless needle shaped crystals(yeild gm, m.p. 115°C)

Elemental analysis:Found(calcd.):

C	H	Sn
56.48 (56.65)	8.00 (8.26)	34.92 (35.08)

Relevant Spectral data:

IR(nujol) : 580(s), 530(m), 800(m), 1600(m)

^{1}HNMR ($CDCl_3$): δ 5.4(s,4H), δ 1.9(s,12H), δ 1.6(s,12H).

§ 4.3.2.4. SYNTHESIS OF $[Me_2C=C(Ph)]_3Sn\ Cl$

0.663gm (96.08mmol) of metallic lithium was cut into thin pieces and taken into a three necked flask containing 100ml of sodium dried ether. The reaction must be carried out in ether, not in THF, as in the THF, lithium reagent rearranges to an allyl derivative. The flask was also fitted with pressure equalising droping funnel and a double surface reflux condenser. 10gm (47.4mmol, d =1.318) of the bromide $Me_2C=C(Ph)Br$ were taken in the pressure equalising dropping funnel.The reaction was carried out in nitrogen atmosphere. Initially $\frac{1}{6}$ th of the total amount of the bromide was added to the lithium at a time. The initiation took place on external heating using hot water which occured within few minutes after which no external heating was required further. This refluxing condition was maintained throughout the reaction by the controlled rate of addition of the bromide. The reaction mixture gradually changed colour from ash colour to greyish-yellow along with the formation of turbidity. After the addition was over, the refluxation was continued til the lithiation was complete.

Then 2.03gm (7.8mmol) of $SnCl_4$ solution in 20ml of dry benzene was added dropwise from pressure equalising funnel under refluxing condition in an inert atmosphere of nitrogen alongwith constant stirring. The colour of the reaction mixture changed from dark yellow to light yellowish white, along with the formation of white precipitate at the bottom wall of the reaction vessel. After about two hours, colour changed to flesh colour and then deepened gradually to chocolate colour. The refluxation was continued for 16 hours along with constant stirring. The volatiles were removed first to get a pasty mass which was repeatedly extracted with benzene, using 20ml of it at a time. All the benzene washings were collected and this was then concentrated to get the yellow coloured product (yield 60% m.p. >270°C) which was established to be the desired one.

Elemental analysis:Found(calcd.):

C	H	Cl	Sn
65.66 (65.76)	5.89 (6.03)	6.33 (6.49)	21.45 (21.72)

Relevant Spectral data:

IR:(nujol) 465(w), 585(m), 620(s), 650(s), 665(s), 690(vs) 710(vs)
780(s), 800(m), 830(s), 870(s), 900(m) 980(s), 1010(m),
1030(m), 1065(m), 1115(w), 1155(vs), 1250(m),
1255(m), 1270(w), 1330(m), 1600(s).

^{1}HNMR: δ 6.4–7.6(m,15H,), δ 1.9(3H), δ 1.4(3H).
(<u>vide</u> Table 3)

§ 4.3.2.5. PREPARATION OF $[Me_2C{=}C(H)]Sn(Cl)Me_2$

2 gm (289.8 mmol) of lithium were cut into thin pieces and taken into a three necked flask containing 100ml of sodium dried ether. The flask is also fitted with pressure equalishing funnel and a double surface reflux condenser. 14.63 ml (142.8 mmol) of isobutenyl bromide $Me_2C{=}C(H)Br$ were taken in the pressure equalising dropping funnel. The reaction was carried out in nitrogen atmosphere. Initially $\frac{1}{6}$ th of the total amount of bromide was added to the lithium at a time. The initiation was effected by external heating using hot water which occured within few minutes, when no more external heating was required. This refluxing condition was maintained throughout the reaction by the controlled rate of addition of bromide. The reaction mixture gradually changed colour from ash colour to greyish-yellow and turbidity formed. After the addition was over, the refluxation was continued til the lithiation was complete.

Then 15.7 gm (71.39 mmol) of Me_2SnCl_2 solution in minimum volume of sodium dried benzene was dropwise added at room temperature under nitrogen atmoshphere alongwith constant stirring. The precipitate started to appear as soon as the addition of dimethyl tin dichloride solution was started. The reaction mixture was refluxed for more than one hour even after the completion of the addition of Me_2SnCl_2 solution. The volatiles were removed then and the dry reaction product mixture was extracted repeatedly first with petroleum ether to wash out any unreacted Me_2SnCl_2 and then with benzene. The benzene fractions were collected and concentrated to get the product (yield 96% m.p.>275°C) found to be established as

$[Me_2C{=}C(H)]Sn(Cl)Me_2$ by elemental and different spectral analytical data.

Elemental analysis:Found(calcd.):

C	H	Cl	Sn
29.86 (30.07)	5.34 (5.43)	14.26 (14.82)	49.53 (49.66)

Relevant Spectral data:

IR:(nujol) 560(s),600(s),790(vs) 1195(m),1205(m), 1375(m), 1390(w), 1455(m), 1620(vw), 2568(s), 2580(vs).

^{1}NMR $CDCl_3$: δ 6.9–8.1(m,5H), δ 1.9(s,3H), δ 1.6(s,3H), 0.06(s,6H) (<u>vide</u> Table 3)

§ 4.3.2.6. SYNTHESIS OF $[Me_2C{=}C(H)]SnPh_3$:

0.5gm (72.47 mmol) of lithium were cut into thin pieces and taken into a 500ml three necked flask containing 100ml of sodium dried ether. The flask was also fitted with pressure equalising funnel and a double surface reflux condenser. 3.71ml (36.22 mmol, d =1.318) of isobutenyl bromide $Me_2C{=}C(H)Br$ was taken in the pressure equalising dropping funnel. The reaction was carried out in nitrogen atmosphere. Initially $\frac{1}{6}$th of the total amount of the bromide was added to the lithium at a time. The reaction initiated on warming with hot water, within few minutes, when no external heating was required more. This refluxing condition was maintained throughout the reaction by the controlled rate of addition of bromide. The reaction mixture gradually changed colour from ash colour to greyish-yellow along with the formation of turbidity. After the addition was over, the refluxation was continued til the lithiation was complete.

Then 13.9 gm (36.07 mmol) of Ph_3SnCl solution in sodium dried benzene was dropwisely added at room temperature under nitrogen atmoshphere alongwith overnight constant stirring. The precipitate started to form as soon as the Ph_3SnCl was added. The reaction mixture was refluxed for four hours even after the completion of the addition of Ph_3SnCl.

The volatiles were removed and then the reaction product mixture was extracted first with petroleum ether to wash out any unreacted Ph_3SnCl and then with benzene. The benzene extract was then concentrated to get the desired product (yield 95% m.p.>270°C)

Elemental analysis:Found(calcd.):

C	H	Sn
64.95 (65.20)	5.39 (5.43)	29.30 (29.36)

Relevant Spectral data:

IR(nujol): 640(m), 650(s), 665(w), 690(vs) 720(vs) 780(s) 990(m), 1020(m), 1070(s), 1120(w), 1250(vw), 1290(vw), 1580(s), 1600(m).

^{1}HNMR: δ 6.9-8.4 (m,15H,),δ 5.8 (s,1H), δ 1.9 (s,3H), δ 1.7 (s,3H).

(*vide* Table 3)

§ 4.3.2.7. SYNTHESIS OF $[Me_2C{=}C(H)]SnCy_3$:

0.5gm (72.47 mmol) of lithium were cut into thin pieces and taken into a 500ml three necked flask containing 100ml of sodium dried ether. The flask is also fitted with pressure equalishing funnel and a double surface reflux condenser. 3.71ml (36.22 mmol, d =1.318) of isobutenyl bromide $Me_2C{=}C(H)Br$ were taken in the pressure equalising dropping funnel. The reaction was carried out in nitrogen atmosphere. Initially $\frac{1}{6}$th of the total amount of bromide was added to the lithium at a time. The reaction was initiated by external heating using hot water which occured within few minutes when no external heating was required further. This refluxing condition was maintained throughout the reaction by the controlled rate of addition of bromide. The reaction mixture gradually changed colour from ash colour to greyish-yellow along with the formation of turbidity. After the addition was over, the refluxation was continued til the lithiation was complete.

Then 14.61gm (36.21mmol) of Cy_3SnCl solution in dry benzene was added dropwise at room temperature under nitrogen atmoshphere alongwith overnight constant stirring .The precipitate formed as soon as the Cy_3SnCl was added. The reaction mixture was refluxed for four hours even after the completion of the addition of Cy_3SnCl.

The volatiles were removed and then the reaction product mixture was extracted first with petroleum ether to wash out any unreacted Cy_3SnCl and then with benzene. The benzene extract was then concentrated to get the desired product(yield 70%, m.p. 56°C)

Elemental analysis:Found(calcd.):

C	H	Sn
62.30 (62.42)	9.25 (9.46)	28.31 (28.41)

Relevant Spectral data:

IR:(nujol) 320(w), 345(w), 450(w), 510(w), 550(w), 565(w), 600(w), 620(w), 650(w), 660(w),

790(s), 810(w), 840(m), 870(m), 900(w) 990(vs), 1010(w), 1040(m), 1065(w), 1080(w), 1130(w), 1170(s), 1255(w), 1270(w), 1290(w), 1320(w), 1340(w), 1370(m), 1600(m), 1440(s), 1600(m), 2564(s), 2575(vs).

^{1}HNMR: δ0.6–1.4 (33H,m) δ1.5 (3H,s), δ1.7(3H,s), δ5.2(1H,s) (*vide* Table 3)

§ 4.3.2.8. SYNTHESIS OF $[Ph_2C{=}C(Ph)]_2Sn\ Me_2$:

0.5gm (20.83mmol) of wel-dried magnesium was taken in a 500ml three necked round bottomed flask, fitted with an efficient refluxing condenser, attached to a nitrogen gas inlet and a pressure equalising funnel. First the system was evacuated using pump and then it was filled with nitrogen gas and cooled. 250 ml sodium dried ether was taken into a round bottomed flask to which a few crystals of resublimed iodine was added as a catalyst which imparted a yellow colour to the solution.

7.5gm (22.38 mmol) of the triphenyl ethelene bromide prepared earlier, was dissolved into minimum amoumt of dry ether and was added in drops slowly from a pressure equalising dropping funnel on the activated magnesium. The initiation occured within a few minutes indicated by the decolourisation of the violet colour iodine of the reaction mixture . The refluxing condition was maintained by the occasional warming of the reaction vessel externally by the use of hot water and also by the controlled rate of the addtion of the bromide. The refluxing condition was maintained even after the addition of the bromide was over till all magnesium was converted into the Grignard reagent.

Then 2.25gm (10.23mmol) of recrystalised dimethyltin dichloride dissolved in 30 ml of dry benzene and the corresponding solution was taken into the pressure equalising funnel under high pressure of nitrogen . As dimethyltin dichloride solution in benzene was added in room temperature , to the Grignard reagent, a visible change took place . The dropwise addition was completed within half an hour . The refluxing condition was continued for more than 2 hours. Then the volatiles were removed at low pressure and the pasty mass obtained was first washed with petroleum ether and then extracted with benzene repeatedly. The benzene extract on concentration gave colourless solid product (yield 70%, m.p. >280°C) which was established to be $[Ph_2C{=}C(Ph)]_2Sn\ Me_2$.

Elemental analysis:Found(calcd.):

C	H	Sn
76.19 (76.49)	5.25 (5.46)	17.73 (18.04)

Relevant Spectral data:

IR:(nujol): 530(m), 565(s), 686(w) 720(w) 790(s), 1030(w), 1070(w), 1195(s), 1370(m), 1390(m), 1450(s), 1620(w), 2568(s), 2580(vs).

^{1}HNMR: δ7.5 (m,30H), 1.5 (3H,s), δ1.7(3H,s).
(*vide* Table 3)

§ 4.4. RESULTS AND DISCUSSION:

§ 4.4.1. INFRARED SPECTRA:

The different absorption bands have been summarised in table.2.

A tentative assignments have been made on the basis of the available literature data. Relative intensities of the bands were expressed as very strong (vs), strong (s), medium (m), variable (v) shoulder (sh).

The unsaturated and aromatic C–H streching frequencies can be distinguished from the saturated C–H absorptions, since the later occurs below 3000cm^{-1}. In the cases containing aromatic ring, $\nu_{=C<}$H(3040–3010cm^{-1}). The C–H out-of-plane deformation vibrations were tentatively assigned to the peaks in the region[17] 840–790 cm^{-1}

The aliphatic tin-carbon streching frequencies were tentatively assigned in the region 450–650cm^{-1} namely, ν_{as}(Sn–C) 500–600cm^{-1} and ν_{s}(Sn–C) 470–530cm^{-1} respectively, where the intesity varied considerably from moderate to weak.[18–21]

$[Ph_2C=C(Ph)]_2SnCl_2$: The two signals for C–H str. vibration of the phenyl ring were characterised at 1586(w) and 1560(m). The moderately strong band below 900 cm^{-1} at 700 cm^{-1} had been attributed to ν_{C-H} out-of-plane bending vibrations[22]. ν_{as}(Sn–C) and ν_{s}(Sn–C) were assigned to 585(s) and 465(w) cm^{-1} respectively.

$[Me_2C=CH]_3SnCl$: Due to the absence of phenyl ring, ν(C=C) frequency can be attributed to the signal at 1600 cm^{-1}(m). The peak for $\nu_{=C<}$H had been attributed to 800(m). The ν (Sn–C) was attributed to the frequencies at ν_{as} 580cm^{-1}, ν_s 530 cm^{-1} respectively.

$[Me_2C{=}CH]_4Sn$:In this compound two peaks at 1600cm^{-1}(m) and 800cm^{-1} could be assigned to the ν (C=C) and ν $(=C<^{H})$ respectively. The two signals at 580 cm^{-1}(s) and 530 cm^{-1}(m) could be attributed to ν_{as}(Sn–C) and ν_s(Sn–C) respectively.

$[Me_2C{=}C(Ph)]_3SnCl$: The frequencies attributed for the phenyl ring signals are 700(s), 750(s), 1065(m), 1580(sh), 1600(m). The ν (Sn–C) peaks came at ν_{as} 585cm^{-1} ν_s 465cm^{-1} respectively.

$[Me_2^aC{=}CH]Sn(Cl)Me_2^b$: The signals at 1620cm^{-1} had been attributed to ν C=C and one strong peak at 790 cm^{-1} could similarly be attributed to ν $(=C<^{H})$. ν (Sn–C) for $Sn{-}CH_3^b$ and $Sn{-}\underset{\underset{H}{|}}{C}{=}C\ (CH_3^a)_2$ have respectively appeared in the range between 600cm^{-1}–500 cm^{-1} which was not possible to identify individually.

$[Me_2C{=}CH]SnPh_3$: The $\nu_{C-H}$of the phenyl rings appeared at 690(vs), 720(vs), 1070(s), 1560(w), 1586(w) and 1600(s)cm^{-1}, as very strong to strong peaks. ν $(=C<^{H}$) was attributed to 780 cm^{-1} as a medium intensity bands.

$[Me_2C{=}CH]Sn\ (\nabla\ C_3H_{11})_3$: Two signals at 1600 cm^{-1} and 790 cm^{-1} had been attributed to streching frequencies of ν (C=C) and ν $(=C<^{H})$ respectively. ν_{as}(Sn–C) and ν_s (Sn–C) appeared at 510 and 430 cm^{-1} both as weak peaks.

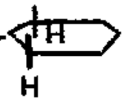
$[Ph_2C{=}C(Ph)]_2Sn\ Me_2$: The aromatic ν (C-H) appeared at 800, 1070, and 1620 cm^{-1} as strong to weak peaks.[23,24]. ν_{as}(Sn-C) could only be assigned at 565 cm^{-1} as strong peak.

§ 4.4.2. ^{1}H NMR DATA:

Comprehensive study on ^{1}H NMR measurements of a number of olefinic tin compounds were done by Leusink and his co-workers.[32] ^{1}H NMR data on a number of tin alkenyls having protons at different environments were also reported [25,26].

The spectra was recorded in $CDCl_3$ downfield to TMS as internal standard in a VA-EM-390; 90 MHz spectrophotometer.

Assignments of each individual signals were not attempted. The aromatic proton signals appeared as a complex multiplet, owing to the change in the electronic distributions of phenyl rings with tin substitutions as well as long range coupling between the ^{119}Sn /^{117}Sn and ortho, meta, para protons of the phenyl ring [33].

In the case of cyclo-hexyl tin derivatives, the bands were found to appear at about δ 0.6 -δ 1.4 downfield to TMS as a very broad resonance peak. This broadness is possibly due to the superposition of a number of signals with close unresolved chemical shifts. Among the three signals of the cyclohexyl protons, one in the higher field may tentatively be attributed to the geminal protons of Sn—C substitutions (Sn— )[31].

The two methyl groups attached to the alkene part ($Me_2C{=}C$ Ph/H) have different chemical shifts owing to the difference in the environments. The Sn-Me peaks appeared at ~ δ 0.06[25].

$[Ph_2C=C(Ph)]_2SnCl_2$: The compound contains only aromatic protons of the phenyl rings. The phenyl protons appeared as a complex multiplet in the range δ 7.0–δ 8.5 (m)[25] which is consistent with literature values[25].

$[Me_2C=CH]_3SnCl$: The signals of methyl groups appeared at δ 1.6 (9H,s) and δ 1.9(9H,s). The signal in the higher field being due to the olefinic proton on C_α carbon $(>C=\underset{\underset{Sn}{|}}{C}-H)$ atom which may unambiguously be located as a singlet at δ 5.4 (3H,s) . The ratio of methyl protons to the olefinic protons found to be 18:4 which is consistent with the stoichiometry.

$[Me_2C=CH]_4Sn$: The signals of methyl groups appeared at δ 1.6 (12H,s) and δ 1.9(12H,s) , the signal in the higher field being due to the olefinic proton on C_α carbon $(>C=\underset{\underset{Sn}{|}}{C}-H)$ atom may be unambiguously be located as a singlet at δ 5.4 (4H,s) . The ratio of methyl protons to the olefinic protons found to be 24:4 which is consistent with the stoichiometry.

$[Me_2C=C(Ph)]_3SnCl$: The two types of protons are present in the compound. The aromatic protons appeared as a complex multiplet in the range δ 6.9– δ 8.3 (15H,m)[25] with a maxima at δ 7.4. The methyl protons appeared as two separate singlet peaks at δ 1.4(3H,s)and δ1.3(3H,s). The ratio of methyl protons to aromatic protons is 18:15, consistent with the required stoichiometry.

$[Me^{a}_{2}C=C(Ph)]Sn(Cl)Me^{b}_{2}$: In this compound the phenyl ring protons appeared as a complex multiplet in the region δ 6.9–δ 8.1 (5H,m) . The two methyl signals of the alkenyl part appeared as two separate singlet peaks at δ 1.6 (3H,s) and δ 1.9 (3H,s) . The two methyl groups (marked b) attached to tin atom appeared at δ 0.06(6H,s). The ratio of the protons , Ph:Me^{a}:Me^{b} was found to be 5:6:6 which agreed well with the desired composition of the compound.

$[\overset{a,b}{Me_{2}}C=CH]Sn(Ph)_{3}$: Three types of proton peaks appeared in this case. The singlet peak at δ 5.8(1H,s) has been attributed to the single proton on C_{α} $(>C=\underset{\substack{|\\H}}{C^{\alpha}}—Sn+)$. The aromatic protons of the phenyl groups attached to tin,appear in the range between δ 6.9–δ 8.4 as a complex multiplet with a maxima at δ 7.5(15H,m). The two methyl peaks on the alkenyl ligand appear at δ1.7(3H,s) and δ 1.9(3H,s) . The ratio of Ph:Me^{a}:Me^{b}:H being 15:3:3:1 which is consistent with the proposed composition.

$[Me_{2}C=CH]Sn(\nabla C_{6}H_{11})_{3}$: The cyclohexyl protons in this case appeared as a complex multiplet in the range between δ 0.6–δ 1.4(33H,m) whereas the two methyl peaks on alkenyl ligand appeared at δ 1.5(3H,s) and δ 1.7(3H,s), The C_{α} proton, $(>C=\underset{\substack{|\\H}}{C^{\alpha}}—Sn<)$ appeared at δ 5.8(1H,s). The ratio of $(\nabla C_{6}H_{11})$:Me^{a}:Me^{b}:H was 33:3:3:1 which was relevant to the stoichiometry of the compound.

$[Ph_2C=C(Ph)]_2Sn\ Me_2$: The spectra consists of phenyl signals in the range δ 7.0–δ 8.5 as complex multiplet (15H,m) and tin-methyl signals at δ 0.06 (6H,s). The ratio of the protons being Ph:Me, being 30:6 which is consistent with chemical composition.

TABLE 2

IR DATA :

Compound		ν_{Phenyl}	$\nu_{>C=C<}$	$\nu_{>C=C<_H}$	ν_{as}(Sn–C)	ν_s(Sn–C)
1.	$[Ph_2C=C(Ph)]_2SnCl_2$	700(vs),740(m) 1070(w),1560(m) 1586(w)		—	585(w)	465(w)
2.	$[Me_2C=CH]_3SnCl$		1600(m)	800(m)	580(s)	530(w)
3.	$[Me_2C=CH]_4Sn$		1600(m)	800(m)	580(s)	530(w)
4.	$[Me_2C=C(Ph)]_3SnCl$	700(s),750(s) 1065(M),1580(sh) 1600(m),3030(w)			585(w)	465(w)
5.	$[Me_2C=CH]Sn(Cl)Me_2$		1620(vw)	790(vs)	560(s)	
6.	$[Me_2C=CH]SnPh_3$	690(vs),720(vs) 1070(s),1560(w) 1586(w)	1600(m)	780(m)	590(s)	
7.	$[Me_2C=CH]Sn(\nabla Cy)_3$		1600(m)	790(s)	510(w)	430(w)
8.	$[Ph_2C=C(Ph)]_2SnMe_2$	700(s),750(s) 1065(M),1580(sh) 1600(m),3030(w)	1620(w)	790(vs)	565(vs)	530(m)

TABLE 3

^{1}H NMR DATA:

Compounds	Chemical Shifts (δ ppm)				
	Ph–	Me	∇Cy	$\genfrac{}{}{0pt}{}{R}{R}\!>\!C{=}C\!<\!\genfrac{}{}{0pt}{}{Sn}{H}$	Sn–Me
$\mathrm{[Ph_2C{=}C(Ph)]_2SnCl_2}$	7.0–8.5 (m)				
$\mathrm{[Me_2C{=}CH]_3SnCl}$		1.6 (9H,s) 2.1 (9H,s)		5.85 (3H,s)	
$\mathrm{[Me_2C{=}CH]_4Sn}$		1.6 (12H,s) 1.9 (12H,s)		5.4 (4H,s)	
$\mathrm{[Me_2C{=}C(Ph)]_3SnCl}$	6.4–8.3 (15H,m)	1.6 (9H,s) 1.9 (9H,s)			
$\mathrm{[Me^{a}_{2}C{=}C(Ph)]Sn(Cl)Me^{b}_{2}}$	6.9–8.1 (5H,m)	1.6 (3H,s) 1.9 (3H,s)			0.06 (6H,s)
$\mathrm{[Me^{a,b}_{2}C{=}CH]Sn(Ph)_3}$	6.9–8.4 (15H,m)	1.7 (3H,s) 1.9 (3H,s)		5.8 (1H,s)	
$\mathrm{[Me_2C{=}CH]Sn(\nabla C_6H_{11})_3}$		1.5 (3H,s) 1.7 (3H,s)	0.6–1.4 (33H,m)	5.8 (1H,s)	
$\mathrm{[Ph_2C{=}C(Ph)]_2SnMe_2}$	7.0–8.5 (5H,m)				0.06 (6H,s)

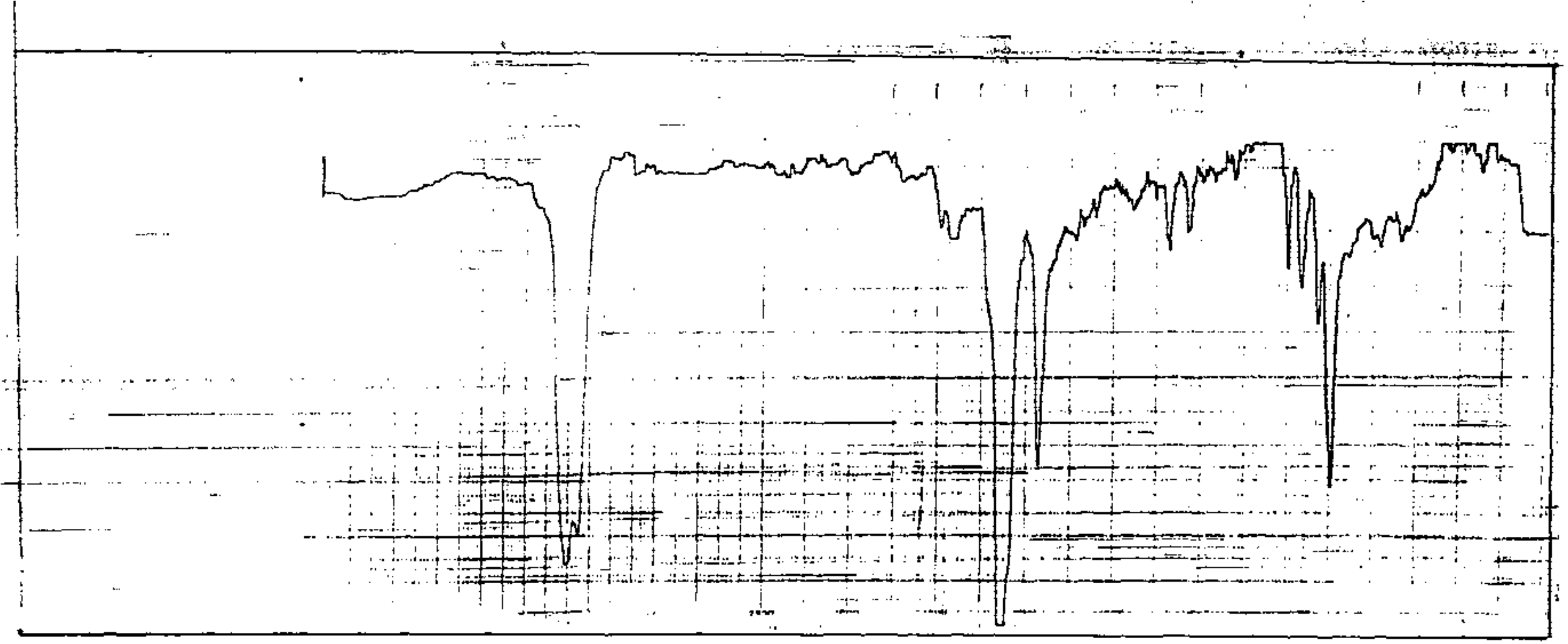


Fig.1 Ir spectrum of $[Ph_2C=C(Ph)]_2SnCl_2$

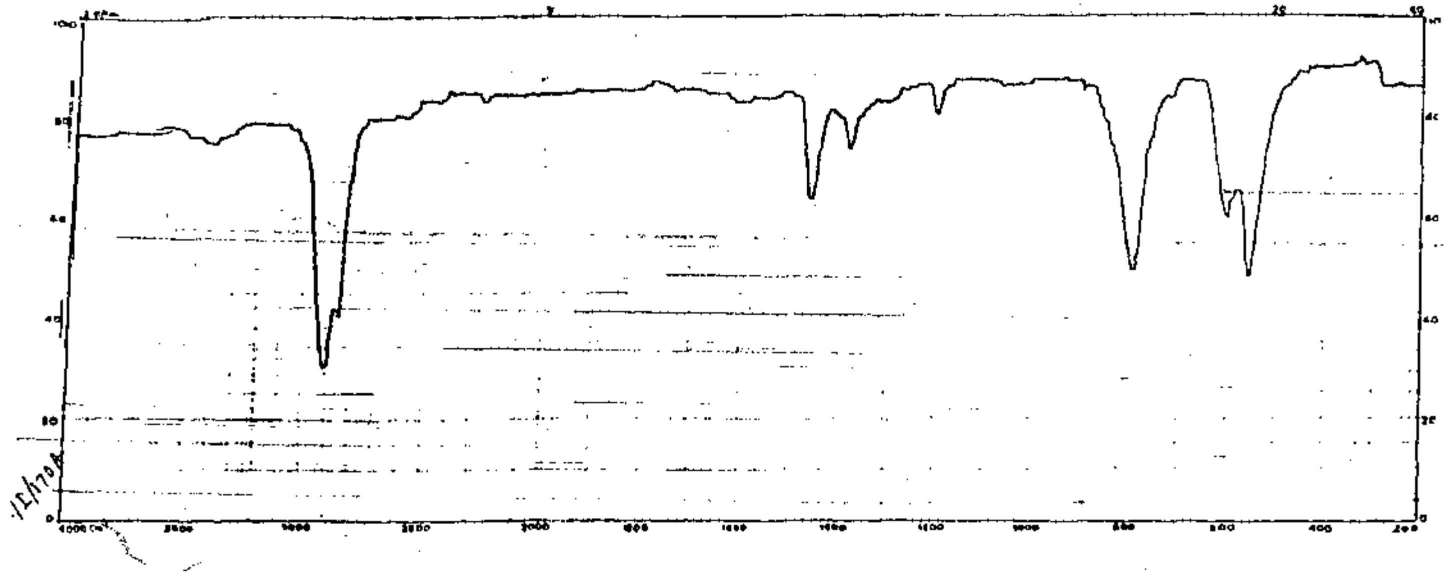


Fig. 2. Ir spectrum of $Me_2C=CH-Sn(Cl)Me_2$

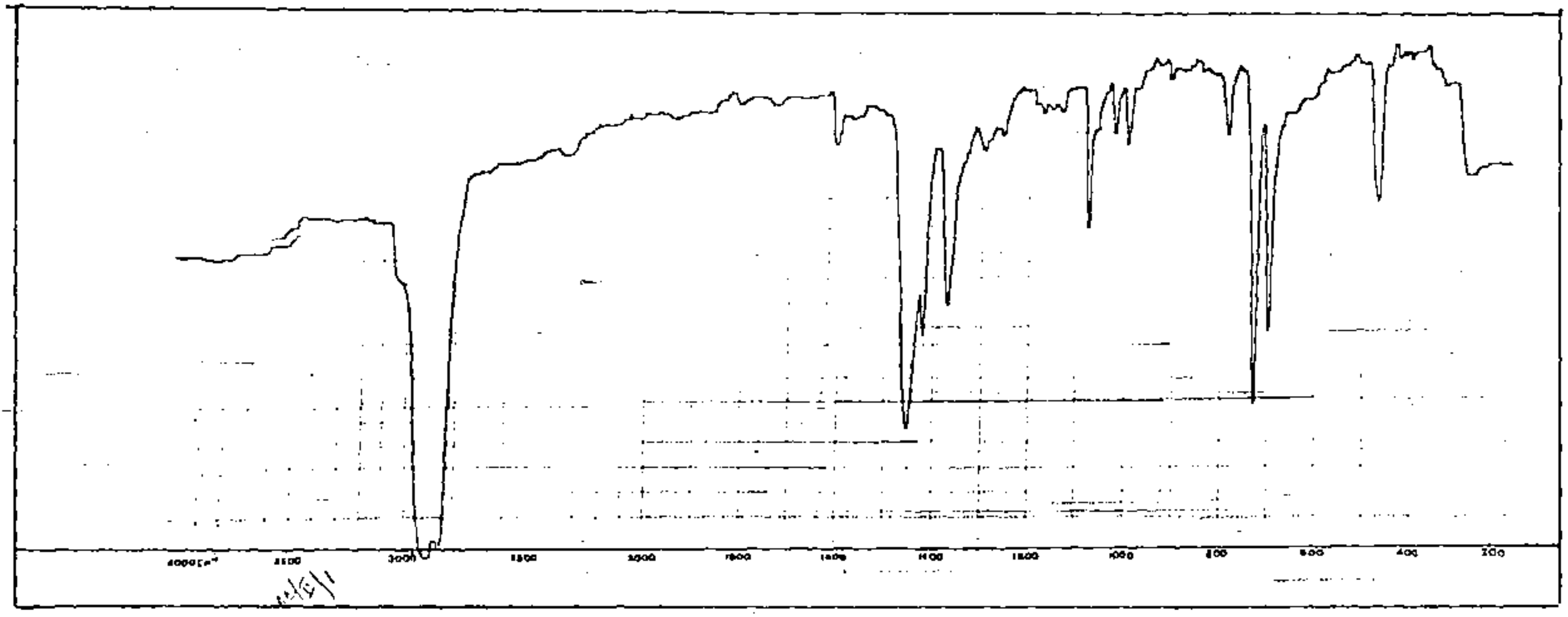


Fig. 3. Ir spectrum of $Me_2C=CH\text{-}Sn\text{-}Ph_3$

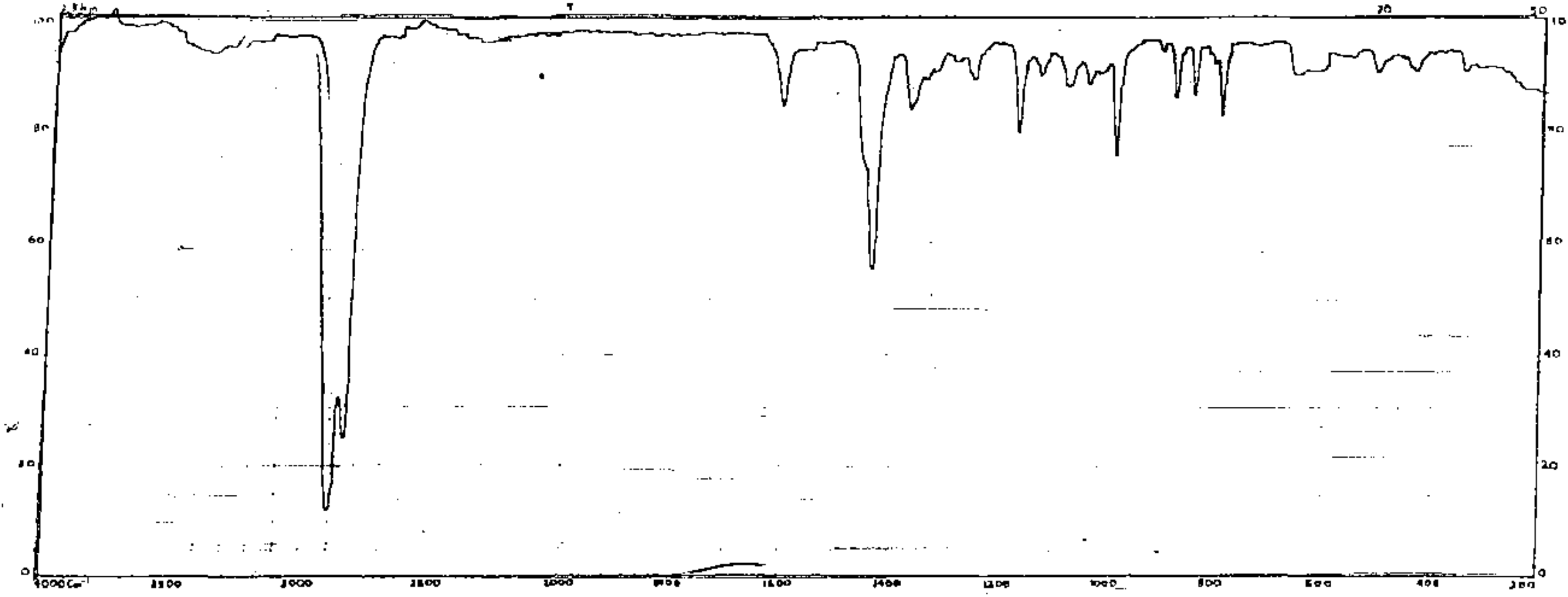


Fig.4. Ir spectrum of $Me_2C=CHSn(\triangledown cy)_3$

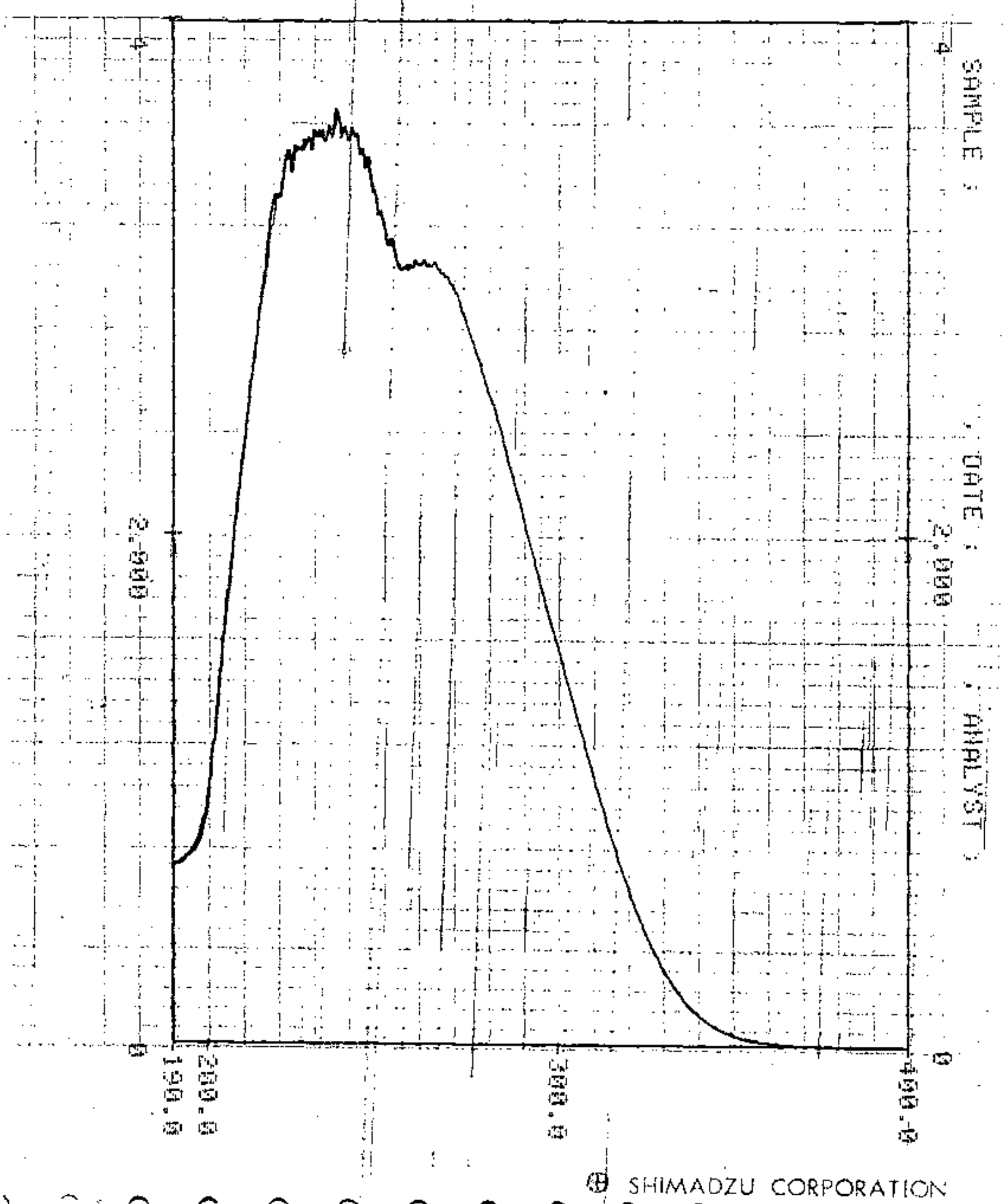


Fig. 5. UV spectrum of $[Ph_2C=C(Ph)]_2SnCl_2$

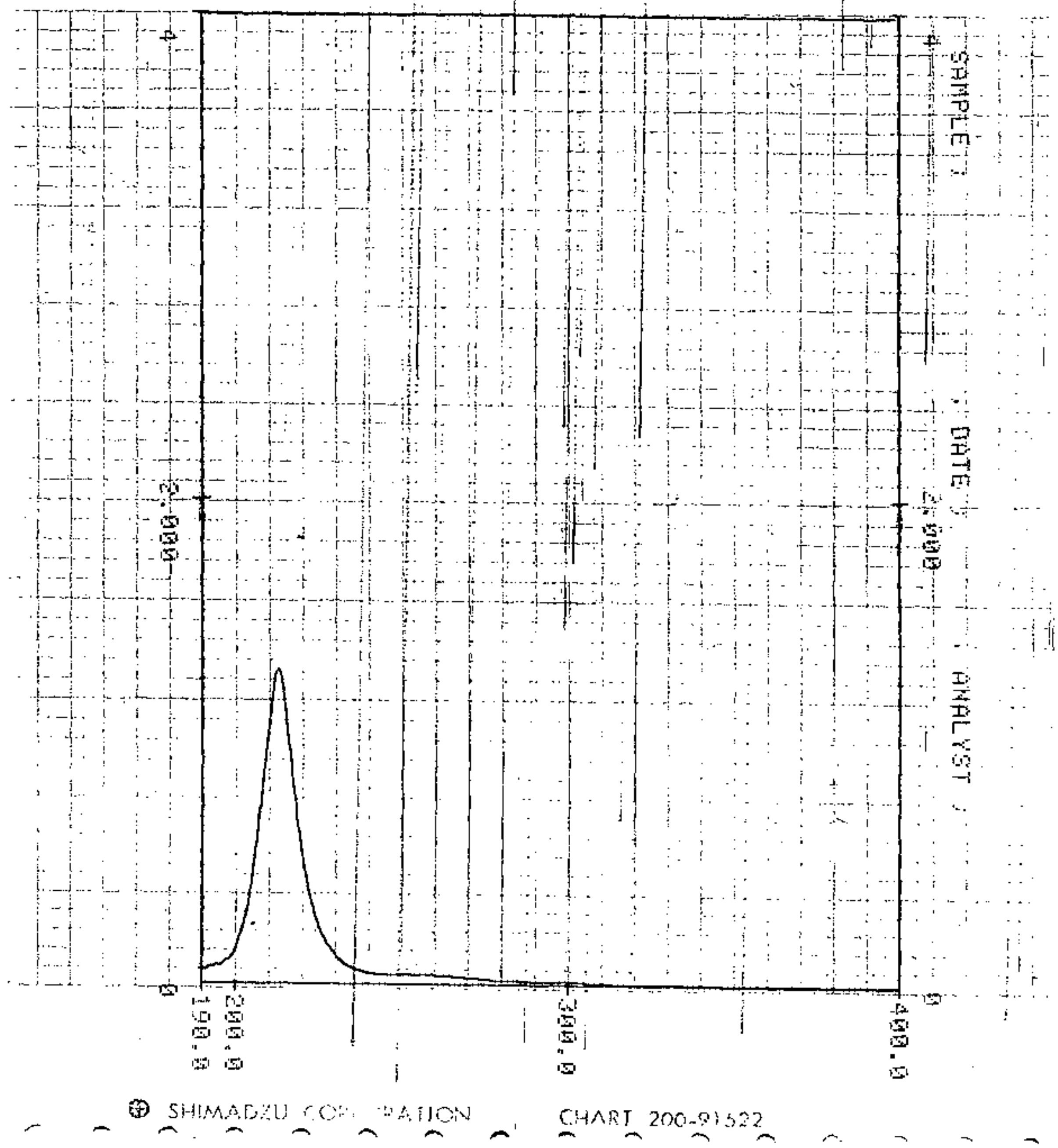


Fig.6 UV spectrum of $[Ph_2C=C(Ph)]_2SnMe_2$

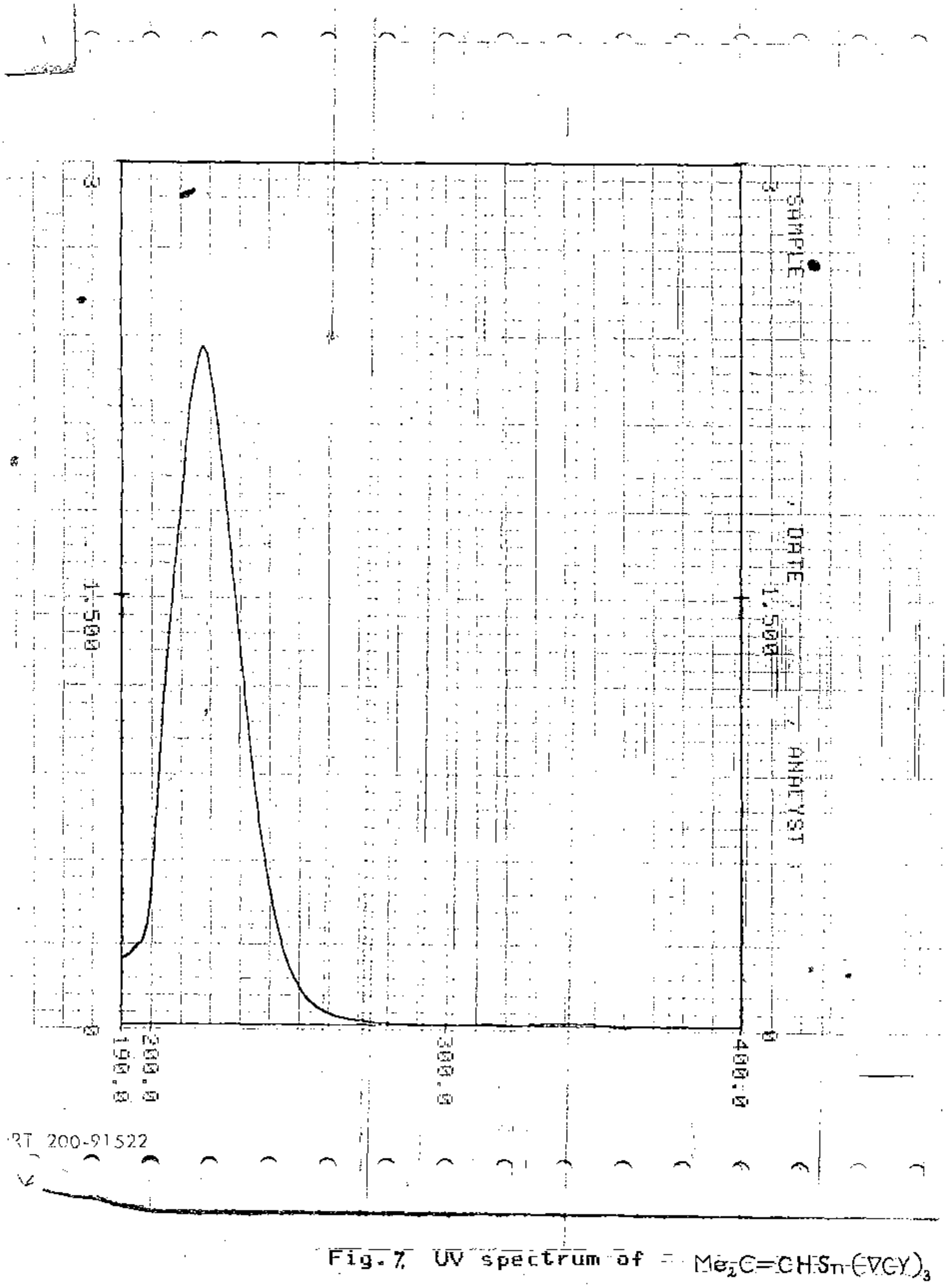


Fig. 7 UV spectrum of $Me_2C{=}CH{-}Sn{-}({-}\nabla C{-}Y)_3$

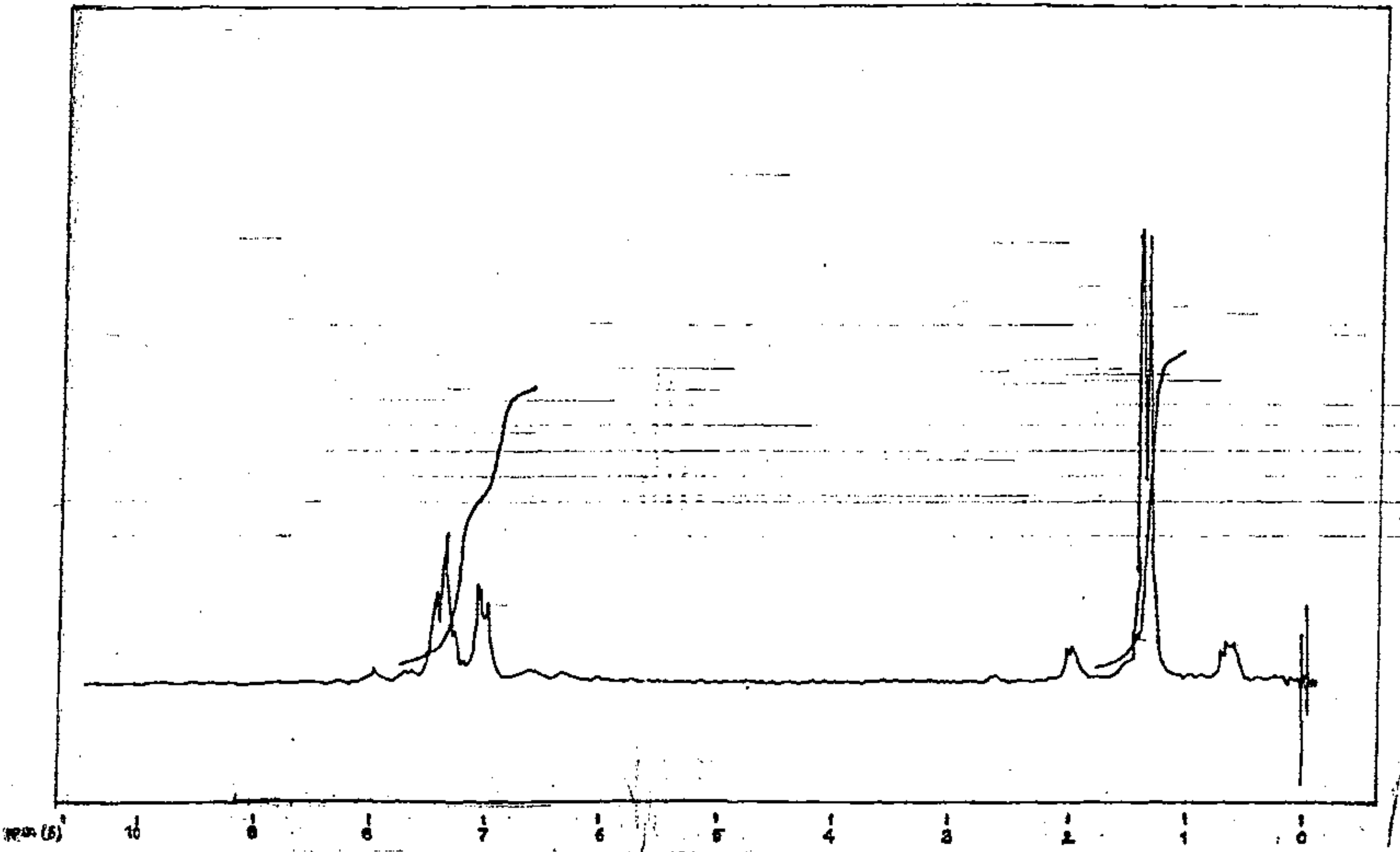


Fig. 8 NMR spectrum of $[Me_2C=C(Ph)]_3SnCl$

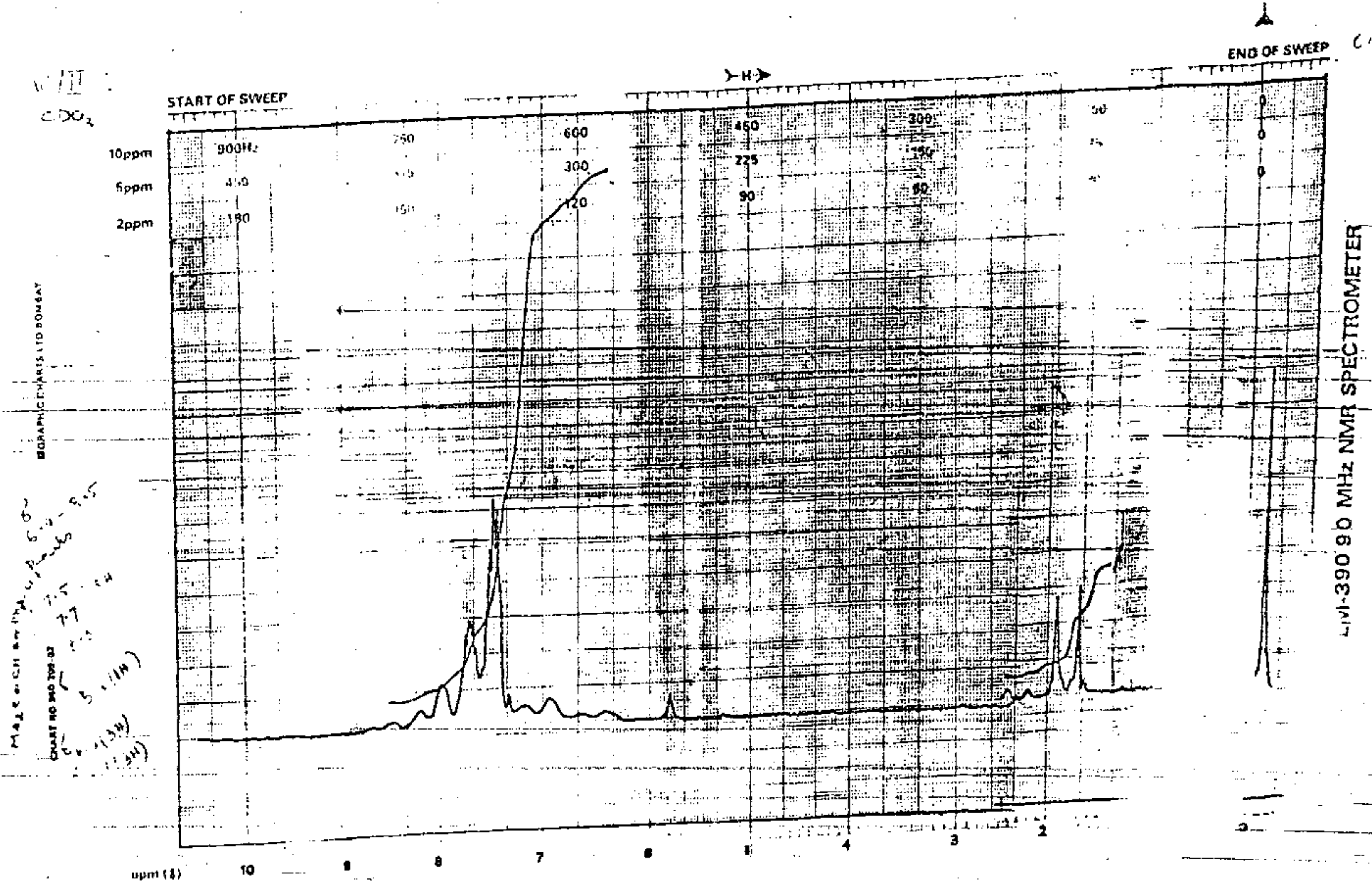


Fig.9 NMR spectrum of $Me_2C=CHSnPh_3$

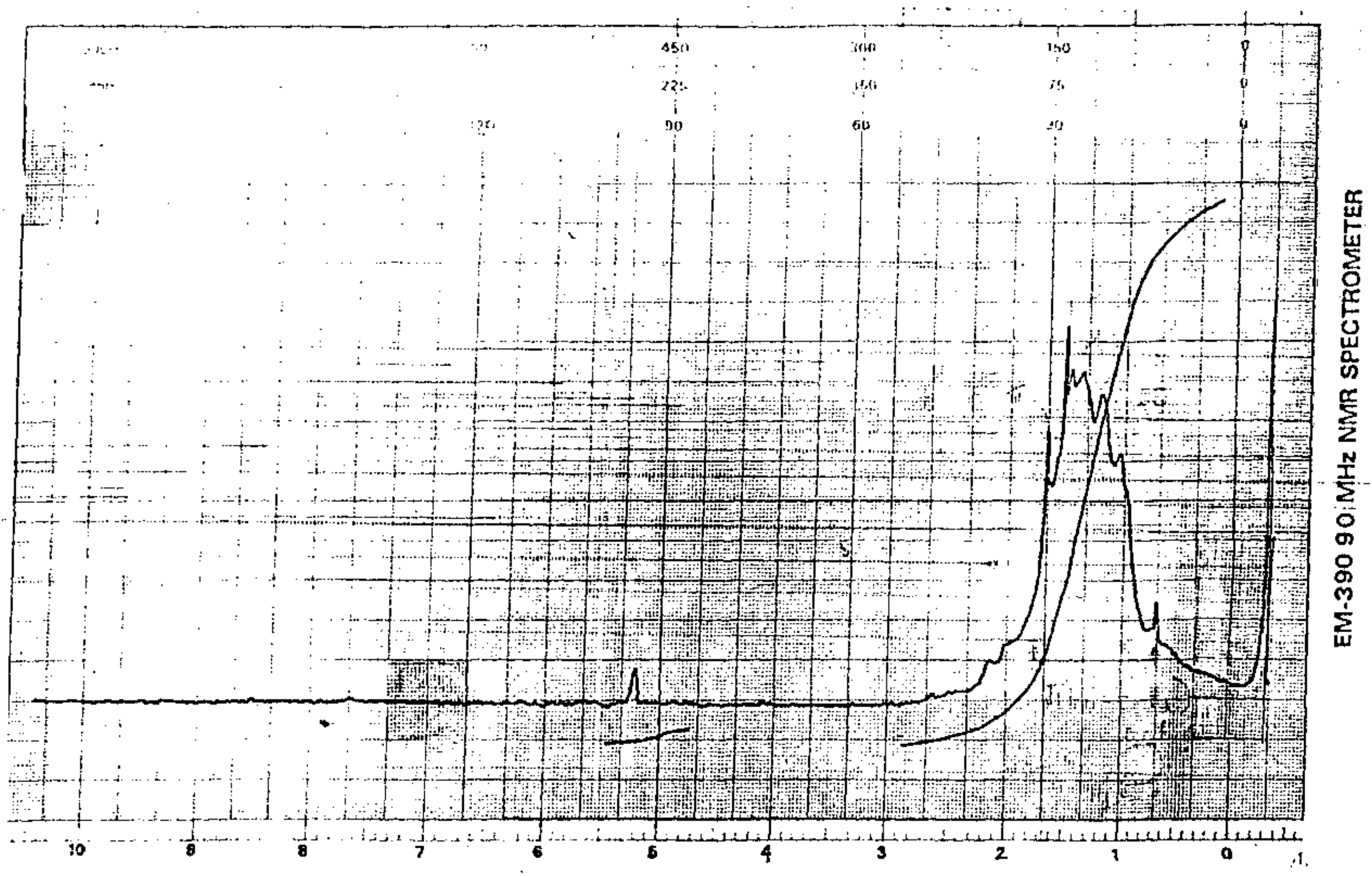


Fig. 10 NMR spectrum of $Me_2C{=}CH\,Sn(\nabla CY)_3$

§ 4.5 REFERENCES:

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