PART II

INTRODUCTION

Lewis acidity of Organotin Compouns:

Tin, the element having atomic number 50, is a member of group IVA of the periodic table with an electronic configuration $[\mathrm{Kr}]4d^{10}5s^{2}p^{2}$ in the ground state (1). The common four covalent state is derived from sp^3 hybridisation. The four covalent state occurs for more fequently than the two covalent state and most of the organotin compounds possess a four covalent tin atom in simple compounds.

Tin differs from the lighter group IVA element in that its d-orbitals are of sufficiently low energy for them to be frequently used in bonding so that tin can readily expand its coordination number above four. As a consequence of this, many organotin compounds exhibit considerable Lewis acid character and can form stable adducts with a number of Lewis bases. Moreover reactions involving nucleophilic attack at tin are facilitated by the formation of coordinated intermediates which, however, unstable, lower the energy of transition state. The coordination chemistry of organotin compounds, was discussed by Poller (2) in 1965 and by Gielen and Sprecher in 1966(3).

Organotins can form a large number of complex compounds with suitable donor and chelating ligands. The presence of an organic group in a molecule usually diminishes the tendency of organometallics to form complexes and hence the observed stability of the complexes should decrease as follows : $MX_4 > RMX_3 > R_2MX_2 > R_3MX > R_4M$. The configuration of the complexes readily follows from the type of metal hybridisation involved. In R_4M complexes sp^3-hybrid orbital exist and tetrahedral configurations are attained. In MX_6^{-2}, the other limiting case, the six sp^3d^2 - hybrid orbitals of the metal are directed towards the ligands so that the resulting complex will be octahedral. When only one monodentate ligand adds to an organotin molecule, a trigonal bipyramidal complex (coordination number five) may be formed through the participation of the sp^3d hybrid orbitals of the metal. A number of compounds have been described by Beletskaya, Butin, Ryabtsev and Reutov (4) which show agreement with these simple rules, although in many cases, the structures mentioned are often distorted, due to the different nature of the ligands in an organometallic complex.

Organotin adducts and related compounds:

The readiness with which the stannic halides form thermodynamically stable adducts of the type $SnX_4.2L$ (L = ligand) with Lewis bases is well known (5). Organotin compound acts as a Lewis acid to react with electron pair donor i.e., Lewis base to form addition compound. Mono-, di- and triorganotin compound can form adducts with mono-, di- and polydentate ligands. The acceptor strength of organotin compounds is dependent on many factors, viz., the nature of the ligands, the organic groups, the substituents attached to tin etc. As pointed out earlier, the stability of organotin halides to form adducts increases in the order $R_3SnX < R_2SnX_2 < RSnX_3$ (6,7) . The acceptor strength of a series of $(CH_3)_3SnX$ compounds is found to be proportional to the electronegativity of the substituent bonded on tin (8). The stronger the electron attracting power of the substituent, the less the electron density around tin and the acceptor strength increases accordingly. Thus the order of acceptor strength of the $(CH_3)_3SnX$ moiety is F^- Cl^- Br^- I^-. The apparent acceptor strength depends also on the nature of the donor (7).

It is widely accepted that tin (IV) is a class A acceptor (8) and using the "Hard and Soft Acids and Bases" (HSAB) concept (9), it is a hard acid. The presence of organic groups on tin may confer some softness (10) and organotins sometimes show characteristics of class B acceptors towards certain ligands (3) but generally it is believed that in organotin complexes tin retains its class A (hard acid) character. Thus, trimethyl tin chloride forms more stable adducts with oxygen or nitrogen donors than it does with corresponding sulphur or phosphorous compounds (11). However, in our laboratory, reaction of the following type were carried out.

$$RSnL + L' \longrightarrow R_3SnL' + L$$

(where L = Diphenyl carbazone, substituted hydroxamic acids, 8-hydroxyquinoline and L' = Dithizone) indicating the soft acid character of the organotin compound. Organotin compounds may, therefore, be considered better as a border line case between hard and soft acid.

1:1 adduct of HMPA (hexamethyl phosphoric triamide), DMSO (Dimethyl sulphoxide), Phen (1,10 phenanthroline) with R_3SnX (R = CH_3, C_6H_5, X = Cl, Br, I, N_3, CN, NO_3) have been prepared by several workers (12-14). $(C_6H_5)_3SnNO_3L$ (L = HMPA, DMSO, Phen) adducts were found good electrolytes in absolute alcohol. Evidence for coordinated nitrate group in these complexes comes from IR data and these compounds have been suggested to be penta coordinated from the Mossbauer Spectra (14). A large number of 1:1 adducts of $(C_6H_5)_3SnCl$ with substituted pyridine -N-oxide are known (15) and the stability constants of $Me_3SnCl.L$ adducts have also been measured (16). Triphenyl phosphine oxide, triphenyl arsine oxide can also form adducts with R_3SnX (R = CH_3, C_6H_5; X = Cl, Br, I) (17,18,19).

The complexation of $(CH_3)_3SnX$ (X = Cl, Br, I) in donor solvents e.g. acetone, dioxan, dimethyl ether, pyridine, DMF, DMSO and tetramethyl ethylene diamine (20) and also its adduct formation with 2,2'-bipyridyl or 1,10-phenanthroline in inert solvents like benzene have been studied (21-23). Among these the structure of $Me_3SnCl.bipy$ was studied by Rechie et al (24). Smith (25) also reported the

$(C_6H_5)_3SnCl$ complexes with 2,2'-bipyridyl and 1,10-phenanthroline. Srivastava et al reported $(C_6H_5)_3SnNCS.L$ (L = $H_2NCH_2CH_2NH_2$, 1-methyl 1-2-pyrrolidinone, 2-aminothiazole etc) (26) and $Ph_3SnNCO.L$ (27) (L = phenanthroline, DMF, $(C_6H_5)_3PS$ etc) adducts. They also prepared $R_4SnX_{4-n}.mL$ (R = CH_3, C_6H_5, X = Cl, Br; n = 1-3, m = 1-2; L = urea, tetramethyl urea) compounds (28). Narula et al (29) reported the 1:1 adduct formed by SO_3 and $(R_3Sn)_2O$ (R = C_6H_5, C_3H_7, C_4H_9).

Smith and Liengme (30) prepared and studied the crystalline solid adducts $(CH_3)_3SnCl.L$; $(C_6H_5)_3SnCl.L$ (L = I and II); $(C_6H_5)_3Sn(NCS).L$ (L = I) where

I = 3- /‾2-(1,10-phenanthrolyl) _7-5,6-diphenyl 1,24-triazine.

II = 3- /‾2-(1,10-phenanthrolyl) _7-5,6-dimethyl 1,2,4-triazine.

Diorganotin dihalide also form adducts with a number of ligands viz. pyridine (py), bipyridyl (bipy), phenanthroline (phen), terpyridyl (terpy) etc. (23,31,32). Although with diorganotin dihalides and diisothiocyanates, 1:1 adducts are formed with 2,2'-bipyridyl, diphenyltin diisothiocyanate forms 2:1 adduct. /‾$Ph_2Sn(NCO)_2$ _7 bipy (33). By contrast to the ion pair product from dimethyl tin dichloride (34,35), dimethyl tin diisothiocyanate forms a seven coordinated adduct with terpyridyl (36).

The adducts of diorganotin compounds with a number of donor ligands like pyrazine (37), terpyridyl amine (38), bipy.O_2 and diphoϕs.O_2 (14), dimethyl formadide (39), $(C_6H_5)_3PO$ (18), phenanthroline (40) etc. have been reported.

The oxygen donor ligand, DMSO forms 1:2 adducts with dimethyl (41) and diphenyltindichloride (42,43) in which the diorganotin group is in a trans, or cis-octahedral arrangement. Srivastava et al (44) have reported adducts $Ar_2SnCl_2.nI$ /‾Ar = C_6H_5, o-, m- and p-tolyl; I = mono- , di- and triethanol amine (MEA, DEA and TEA); n = 1 for MEA and DEA and n = 2 for TEA. Adducts of the type $RPhSnCl_2.L$ (R = CH_3, C_2H_5, n-C_4H_9, Benzyl and L = bipyridyl and phenanthroline) was reported by Jaura et al (45). Smith et al reported compounds of R_2SnX_2 with 1,10-phenanthroline, 2-2'-bipyridyl and triazine (46) which were shown to be octahedral structure with trans groups.

The adduct of $RSnX_3$ with a number of ligands like $(C_6H_5)_3PO$, C_6H_5N and DMSO (47) and bipy, phen and tetrapyridyl (21,23,48,49) have been reported by several workers.

Narula et al (50) reported the adducts of the type $C_2H_5SnCl_3.L'$, $C_2H_5SnCl_3.LL'$, $SnCl_4.L''$ and $SnCl_5.L''$ (where L' = $(Ph_3Sn)_2O$, $(Bu_3Sn)_2O$ and L" = Bu_2SnO). Tanaka et al (51) and Cunningham et al (52) prepared and studied the structure of several other organometallic compounds.

Organotin coordination compounds with bi and polydentate ligands.

In last three decades or so, extensive work have been carried out in this area. The ligands which formed coordination compounds with organotin moieties were of diverse types. These included β-diketone, substituted hydroxamic acid, diphenyl carbazone, tropolonic acid, kojic acid, amino acid, 8-hydroxy quinoline, substituted hydroxyquinoline, diphenyl thiocarbazone, dithiocarbamic acid, oxine etc. As illustration of the above type of compounds we would briefly discuss only few types of the above ligands.

1,5-diphenyl thiocarbazone (Dithizone) has been used as a colorimetric reagent for organometallic compounds (53,54) for a number of years and the isolation of several solid organotin dithizonates with mono-, di- and tri organotin moiety have been reported (55,56). The organotin dithizonates, $R_3Sn(HDz)$, $R_2Sn(HDz)_2$, $R_2Sn(HDz)X$ and $RSn(HDz)XY$ ($R = CH_3$, C_6H_5, C_4H_9, C_3H_7, P-tolyl, Bz; X = Cl, Br, I, NCS; Y = substituted benzohydroxamic acids; H_2Dz = Dithizone) have been isolated and characterised. Test of triphenyl and tributyl tin dithizonates as fungicides showed excelletn activity against a number of plant pathogenic fungi (57). The oxygen analogue of dithizone, 1,5-diphenyl-carbazone was also reported (58) to form organotin complexes of the type R_3SnL, R_2SnL_2, $RSnL_3$,

R_2SnLX (R = CH_3, C_4H_9, C_6H_5, p-tolyl, cyclohexyl, C_3H_7; X = Cl, Br, SCN and LH = diphenyl carbazone). Some of these triorganotin compounds showed excellent fungitoxicity (57).

Organotin oxinates of the type $R_{4-n}SnOx_n$ (R = organic group, OxH = 8-hydroxyquinoline, n = 1, 2, 3) (59,60-63) are prepared either from the organotin halides and soidum/thalium (I) oxinate (59,60) or from organotin halides and oxine itself, the hydrogen halide formed is removed by a base such as ammonia (64) and also by reacting organotin oxide with oxine (65,66). Triorganotin oxinates have also been prepared by reacting triorganotin chloride with a mixture of oxine and sodium methoxide (213). Preparation of bis-(penta-fluorophenyl)tin bis-oxinates have also been reported (67).

In the crystal structure of dimethyl bis (8-hydroxy oxinate) which assumes a cis-dimethyl tin groups, the oxygen atoms appear trans and the nitrogen atoms are cis. (68).

During the reaction of diorganotin dihalide and oxine in the molar ratio 1:1 in the absence of a base, the halooxinate has been reported to form (69,70). These compounds can also be prepared through disproportionation of a halide and a dioxinate, refluxing in benzene or ethanol (60,63,71-74) or by the reaction between a dioxinate and a silver halide (71). The halogen in halooxinate can be substituted by other groups like NCS^-, $SO_4^{=}$, NO_3^- or I^- etc.

The halogen atom of penta coordinated halooxinate undergoes exchange with groups like such as butyl, alkoxy or with chelates like acetylacetonates (60,74) which may disporportionate into the diorganotin dioxinates.

Organotin halide bis oxinate, $RSnX(Ox)_2$ ($R = CH_3$, $n\text{-}C_4H_9$, C_6H_5; $X = Cl, Br$) have been prepared by reacting organotin trihalides with oxine (1:2 mole) in ethanol followed by neutralisation with aqueous ammonia or sodium acetate (60,75). Datta (76) has prepared phenyl tin halo oxinate by reacting diphenyl tin dioxinate with mercuric halides in ether at room temperature. A compound, $[n\text{-}C_4H_9Sn(Ox)_2]S$ was prepared from n-butyl tin sesquisulphide and oxine in boiling toluene (77).

Some of the organotin trioxinates have been prepared by using either of the following reactions (63,66).

$$R_2Sn_2O_3 + 6OxH \xrightarrow[\text{benzene}]{\text{boiling}} 2RSnOx_3 + 3\ H_2O$$

$$RSnCl_3 + 3NaOx \longrightarrow RSn(Ox)_3 + 3NaCl$$

$$(R = C_2H_5,\ C_4H_9,\ C_6H_5)$$

Mehrotra et al (78) prepared butyltin isopropoxide oxinate by reacting butyltin tris isopropoxide with oxine.

The ~~analytical report of~~ spectrophotometric data on triphenyl tin oxinate in 95% ethanol (79) and in methanol and benzene/methanol mixture has been reported (80). The reactions of mercuric halides with some organotin oxinates have also been studied.

Srivastava et al (81) have prepared some diaryl tin bis oxinates/2-methyl oxinates and diaryl tin chloride oxinates/2-methyl-oxinates. Barsode et al (82a, 82b) have synthesised and studied several other derivatives of substituted oxines. These were of the type R_2SnL_2 where R = CH_3, C_2H_5, C_4H_9 and LH = 5-nitro oxine; 5,7-dichlorooxine, 5,7-dibromooxine, 5-nitro-7-bromo oxine, 5,7-diiodo oxine, 5,7-dinitro oxine etc. Not only these, they also reported (83) the formation of mono- and triethyl tin (IV) and triphenyl tin (IV) chelates with substituted 8-quinolinols. The compounds are of the type $RSnL_3$, $RSnL_2X$, R_3SnL (where R = C_2H_5, C_6H_5; LH = 5 nitro oxine, 5,7- dinitro oxine; 5,7-dichloro oxine, 5,7-dibromo oxine, 8-mercapto oxine etc; X = Cl), (8-quinolinato) (1,3-diphenyl-propanedionato) diethyltin (IV) have also been reported.

The complexes of the type RR'SnLL' (R = R' = Me, Ph, Bu; R = Bu, R' = Ph; L, L' = 8-quinolinates, 2-methyl-8-quinolinate etc) have been synthesised and studied by Smith et al (84). Majee et al (85) prepared and studied the compound of the type $R'_2Sn(LSnR_3)_2$ [R = C_6H_5, C_4H_9; R' = C_6H_5, C_4H_9; LHH' = 5-(2'-carboxy phenyl) azo-8-quinolinol of which H and H' represent the carboxyl and hydroxyl hydrogen respectively], R_3SnLH and $R'_2S(LH)_2$.

They also prepared some organotin-copper mixed complexes (86). Metal and organometal complexes of ortho-carbazoxines have also been reported (87).

The Lewis acidity of esterin chlorides $Cl_3SnCH_2CH_2COOR$ (R = CH_3, iso-C_3H_7, C_6H_5 and H) and $Cl_2Sn(CH_2CH_2COOR)_2$ (R = CH_3 and iso-C_3H_7) has been investigated by Maughan, Wardell and Burley (88). From the stability constants determination for adducts of these Lewis acids with nitrogen donors e.g. D = bipyridyl, phenanthroline, pyridine quinoline and aniline, it was concluded that (i) $CH_3SnCH_2CH_2COOCH_3$ appears as a strong Lewis acid as CH_3SnCl_3 towards bidentate ligands and a single pyridine molecule, (ii) $Cl_3SnCH_2CH_2COOCH_3$.D (D = mono-dentate ligand) is a better acceptor than CH_3SnCl_3.D but comparable to $(CH_3)_2SnCl_2$ towards D and (iii) $Cl_2Sn(CH_2CH_2COOR)_2$ is weaker acceptor than $Cl_2Sn(CH_3)_2$ towards phenanthroline and bipyridyl. For $Cl_3SnCH_2CH_2COOR$ the sequence of acidity was established as R = C_6H_5 CH_3 iso-C_3H_7 H towards bipyridyl. Adducts of $Cl_3SnCH_2CH_2COOCH_3$ and $Cl_2Sn(CH_2CH_2COOCH_3)_2$ with phenanthroline and bipyridyl showed similar Mossbauer parameters to those for other phenanthroline and bipyridly adducts of organotin trichloride and diorganotin dichloride. Howie et al (88a and 88b) studied Lewis acidity and crystal structure of few esterin trichlorides.

Gopinathan et al (89) reported the chelated compounds of Bis- (β-carbomethoxy ethyl) tin dichloride with various bi- and tridentate chelating ligands like acetylacetone, salicylaldehyde, 8-hydroxyquinoline, dibenzoylmethane, benzoyl phenyl hydroxylamine, 2-hydroxy benzophenone, 2-hydroxy 4-methoxy benzophenone and salicylaldazine. They also reported (90) molecular addition complexes of β-carboalkoxy ethyltinchlorides with neutral ligands such as pyridine, triphenylphosphine, hexamethylphosphoramide, triphenylphosphineoxide, tri n-octylphosphine oxide, 1,10-phenanthroline and 2,2'-bipyridyl. Kumar Das et al (91) prepared and studied the complexes of bis (β-carbomethoxy ethyl)tin dichloride $(Me_2O_2CCH_2CH_2)_2SnCl_2L_2$ [L = Ph_3AsO, Ph_3PO, L_2 = 1, 10-phenanthroline, 1,1'-bipyridyl, [$Ph_2P(O)_2CH_2$], $(MeO_2CCH_2CH_2)_2SnL'_2$ [where L' = oxinate), S_2CNMe_2, S_2CNEt_2] and $(MeOCCH_2CH_2)_2SnClL'_2$. The compound $(CH_3COOCH_2CH_2)_2Sn(Ox)_2$ (OxH = 8-hydroxyquinoline) was reported by Gopinathan et al (89,90) in 1980 and by Kumar Das et al in 1981 (91). Wassef and Hessin (92) prepared the compound of the composition type $(C_6H_5)_2SnCl_3.HL$ where L = $(C_6H_5)_3P$, 2,9-dimethyl-o-phenanthroline, o-phenanthroline, 4,4'-dimethyl-2,2'-bipyridyl. In the same year (1981) the adducts of diphenyltin dichloride with some organic donors like o-phenanthroline, 2,9-dimethylphenanthroline, 2,2'-bipyridyl, 4,4'-dimethylbipyridyl, 2,2',2" - tripyridyl etc were reported by Wassef et al (93). Some addition compounds of the type R_2SnX_2L and $R_2SnX_2L_2$ (R = methyl, butyl; X = Cl, CH_3COO; L = pyrrolidine, acridine, 1,10-phenanthroline, 2,2'-bipyridyl, piperazine) were prepared by Siddiqui and his co-workers (94) in 1983. In the same year Otera (95) reported the preparation of $[(CH_3)_3C]_2SnL_2$ where L = oxinate or 2-methyloxinate. Some novel chelated compounds of β-carbobutoxyethyltin trichloride were prepared by Garad (96) in 1984. In the same year Gabe et al (97) studied the outer sphere coordination in the 1,10-phenanthroline and 2,2'-bipyridyl complexes of triphenyltin chloride. In 1986 Bonire (98) synthesised and studied few acylpyridine adducts of organotin and stannic chloride. Spencer et al (99) studied the Lewis acidities of tri-alkylhalostannanes. Trehan et al (100) reported the synthesis and spectroscopic investigation of the adducts of some diorganotin dichloride using pyridine, piperadine, α-, β- or γ- picolines, isoquinoline, morpholine, 2,2'-bipyridyl, 1,10-phenanthroline as ligands.

A number of β-alkoxy carbonyl ethyltin dithizonate of the type R_2SnL_2, R_2SnLX and $RSnL_2X$ where R = $CH_3OCOCH_2CH_2$, $C_4H_9OCOCH_2CH_2$, $CH_3OCOCH(CH_3)CH_2$; X = Cl, SCN, and L = Dithizone (i.e. 1,5-diphenyl thiocarbazone) and one complex $(CH_3OCOCH_2CH_2)_2SnL'Cl$ where L' = Diphenyl carbazone was prepared and characterised by elemental analyses, electronic, IR and PMR spectral data by Deb and Ghosh (101).

Also the complexes of the types - R_2SnL_2, R_2SnLX, $RSnL_2X$ and $RSnL_3$ where R = $CH_3CO_2CH_2CH_2$, $C_4H_9CO_2CH_2CH_2$, $CH_3CO_2CH(CH_3)CH_2$, $CH_3COCH_2C(CH_3)_2$; X = Cl, SCN; and L = oxine, 5,7-dichloro oxine or 5,7-dibromo oxine was reported along with their proper characterisation by elemental analyses, electronic, IR and PMR spectral data by same set of workers (102).

Beside these a number of complexes of the type R_2SnL_2, $RSnL_2Cl$, R_2SnLCl, $R_2Sn(L'H')_2$, $R_2SnL''H$ and $RSnL''Cl$ (where R = $CH_3OCOCH_2CH_2$, $C_4H_9OCOCH_2CH_2$, $CH_3OCOCH(CH_3)CH_2$; LH = 5-phenylazo-8-quinolinol, 1-nitroso-2-naphthol; L'HH' = 5-(2'-carboxy phenylazo)-8-quinolinol and $L''H_2$ = 1,2-hydroxy anthaquinone) characterised by elemental analyses, electronic, IR and ^1H NMR spectra and studied ~~them~~ in somewhat detail by Deb and Ghosh (103). In the same year Kumar Das and his co-workers (104) synthesised and studied the complexes of the type $RR'SnX_2.L_2$ and $RR'SnL'_2$ /RR' = biphenyl, bis(p-tolyl), bis(m-chlorophenyl), bis(p-chlorophenyl), propane, n-pentane; X = Cl, NCS; L = neutral monodentate oxygen donor e.g. hexamethylphosphorictriamide, $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$, or half bidentate donor (2,2'-bipyridyl, 4,4'-dimethyl-2-2'-bipyridyl, 1,10-phenanthroline, 3,4,7,8-tetramethyl-1, 10-phenanthroline); L' = 8-quinolinolato, 2-methyl-8-quinolinolato/. The synthesis and ^{119}Sn Mossbauer spectra of a series of organotin complexes of general molecular formula $R_2SnCl_2L_2$ (R = 4-R'C_6H_4; R' = CH_3, CF_3, F, Cl, OCH_3; L_2 = 2,2'-bipyridyl, 1,10-phenanthroline, 2-aminomethylpyridine were reported by Biddle et al (105) in the same year.

Cleavage reactions involving tin-carbon bond

Although the reactivity of tin-carbon bond depends largely upon molecular environment, yet they are susceptible to attack by a wide variety of reagents. There are so many examples of cleavage of tin-carbon bond brought about by different neutral molecules, acids and bases and also by different physical methods such as heating etc. Poller discussed several of such typical cleavage reaction (106).

Halogen cleavage reaction of organotin compounds is used particularly for the preparation of organotin mono- and di- halides. Many investigators carried out such reactions mainly for preparation of different organotin compounds and some of them studied thoroughly such reactions.

$$R_4Sn + X_2 \longrightarrow R_3SnX + RX$$

$$R_3SnX + X_2 \longrightarrow R_2SnX_2 + RX$$

where X = Cl, Br, I

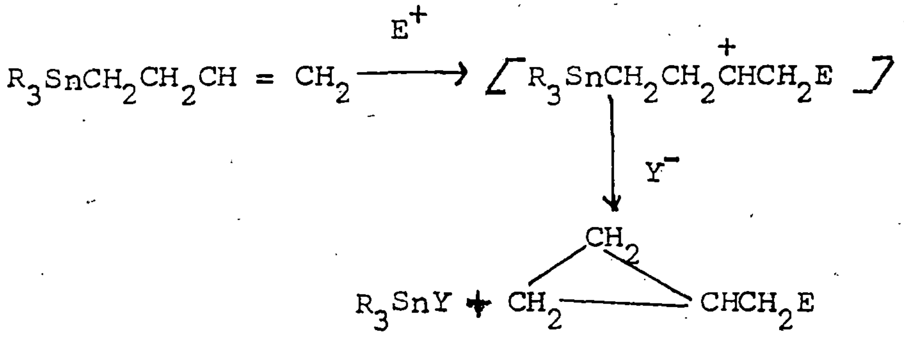
R = alkyl or aryl group (107).

Ditin compound $(C_6H_5)_3Sn(CH_2)_4Sn(C_6H_5)_3$ on treatment with iodine formed $(C_6H_5)_2ISn(CH_2)_4SnI(C_6H_5)_2$ (108).

There are some other type of tin-carbon bond cleavage reactions which are effected by halogen molecules. Wardell et. al studied reactions of the following type, e.g.

$$(C_6H_5)_3SnCH_2CH_2SR' + Ey \longrightarrow (C_6H_5)_3SnY + CH_2 = CH_2 + R'SE$$

$R' = p\text{-}MeC_6H_4$, $Ey = Br_2$ (109)



where $EY = Cl_2, Br_2, I_2$, ArSCl;

$R = -CH_3, -C_4H_9$ (110)

Wardell et al in 1983 also reported the phenyl tin bond cleavage during the reaction of $(C_6H_5)_3Sn(CH_2)_nSOC_6H_4(CH_3)$-p. ($n = 3$ or 4) with iodine, or bromine (111).

In 1984 several other tin-carbon bond fission reactions were studied by Olszowy and his co-workers. Among these brominolysis of <u>cis</u> and <u>trans</u>-(4-methylcyclohexyl)- and cis and trans-(4-tert-butylcyclohexyl) triphenylstannanes was also reported by them (112).

Electrophilic cleavages in $(CH_3)_3SnCH_2M(CH_3)_3$ (M = Sn, Ge, Si, C) were studied by Hawker and Wells in 1985 (113). The effect of solvent and nature of M were also found to be important.

Bromination of some organotin bromide to prepare new organotin bromide by Medvedev and his co-workers in 1986 was also effected by tin-carbon bond fission (114).

A variety of acids effect tin-carbon bond and for example, hydrochloric acid is sometimes used to prepare organotin chlorides. Of course in many cases gaseous hydrogen halide is used instead of its aqueous solution.

$$R_4Sn + HX \longrightarrow R_3SnX + RH$$

where X = Cl, Br, I

R = alkyl or aryl group (107).

Buchmann et al (115) made an extensive investigation on the reaction kinetics of the tin-carbon bond cleavage in aryltin compounds by hydrogen chloride.

A selective cleavage of tin-carbon bond was studied and was used to prepare some new organotin halides from tetraorganotin compounds by using hydrogen bromide in methylene chloride in 1983 by Laosooksathit (116).

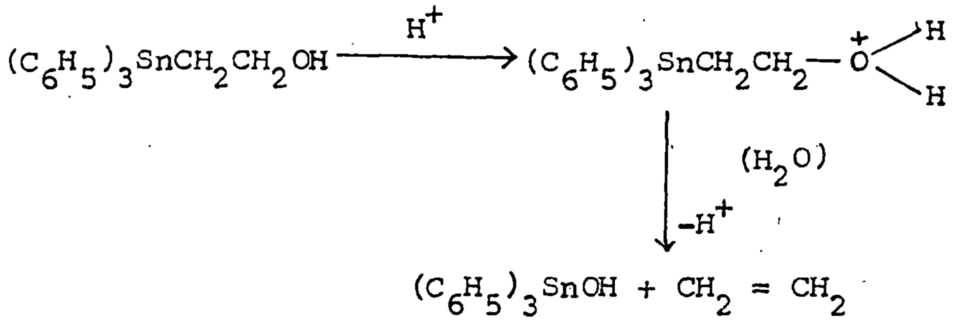
Similarly 100% sulphuric acid reacts with tetramethyltin to give the reaction

$$(CH_3)_4Sn + H_2SO_4 \longrightarrow (CH_3)_3SnHSO_4 + CH_4$$

With tetraphenyltin all the tin-carbon bonds are broken giving $H_2Sn(HSO_4)_6$ (117).

Acid cleavage of an organic group from tin is essentially an electrophilic substitution at carbon and readiness with which it occurs depends on several factors. A phenyl group carrying electron releasing substituents is more readily attacked than unsubstituted phenyl group, i.e. $p\text{-}MeOC_6H_4SnR_3 > C_6H_5SnR_3$ (118). The rate of acid cleavage of the aryl group in $C_6F_5Sn(CH_3)_3$ is greater than usual expectation due to inductive effect of five fluorine atoms in the phenyl ring (119). Similarly tin tetracarboxylates have been made by the reaction between carboxylic acids and tetravinyltin (120).

Wardell showed the following acid cleavage wherein the ultimate reaction product, there was one appropriate alkene.



$$(C_6H_5)_3SnCH_2CH_2OH \xrightarrow{H^+} (C_6H_5)_3SnCH_2CH_2-\overset{+}{O}H_2 \xrightarrow[-H^+]{(H_2O)} (C_6H_5)_3SnOH + CH_2=CH_2$$

(109).

Chandrasekhar et al in 1983 studied several replacement reactions of $Sn(C_6H_5)_3$ group by CCl_3 where tin-carbon bond fission took place by electrophilic reagents (121).

The reactions of tris (trimethyl stannyl) and tetrakis(trimethyl stannyl) methane were studied by Hawker and his co-workers in 1984. The tin-methyl bonds were found to cleave successively with electrophilic reagents (122).

Trifluoroacetolysis of cyclohexyltin bond was studied by Olszowy and others in 1984 (112).

The reactivity of the tin-carbon bond towards an internal cationic carbon was studied by Murayama et al in 1985 (123).

In all these cleavage reactions, the extent of reactivity depends on several factors (124,125,126,127).

There are also many examples of base cleavage of organic group from tin. Phenyltin compounds undergo tin-carbon bond fission when heated with 8-hydroxyquinoline (oxine) as follows.

$$(C_6H_5)_2SnCl_2 + 2HOx \longrightarrow Cl_2SnOx_2 + 2C_6H_6$$

$$(C_6H_5)_2SnOx_2 + 2HOx \longrightarrow SnOx_4 + 2C_6H_6$$

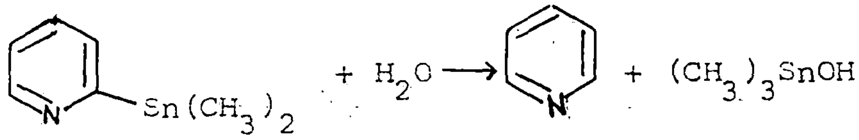
where HOx = oxine (128-130).

The β-diketones and β-ketones effect tin-carbon bond cleavage in stannylacetones (131)

$$R_3SnCH_2COCH_3 + CH_3COCH_2COR' \longrightarrow$$
$$\longrightarrow R_3SnOC(CH_3) = CHCOR' + CH_3COCH_3$$

where R' = alkyl or alkoxyl group.

Another example of nucleophilic attack by the ligand molecule to tin centre is



Another example of the similar type was the formation of $K_2Sn(NH_2)_6$ and benzene from tetraphenyltin and potassium amide in liquid ammonia at 0^oC (132). There are many examples of base cleavage of tin-carbon bond which proceed with neucleophilic attack by the ligand molecules (133-135).

In 1983 Dembech and his co-workers determined the rate of base cleavage of tin-carbon bond in

$$RC_6H_4Sn(CH_3)_3 \text{ by } (CH_3)_2SO - \text{aq KOH}$$

where R = p-$N(CH_3)_2$, p-OCH_3, p-CH_3, H, p-SCH_3, p-Cl, m-Cl, m-CF_3, p-$N(CH_3)_3{}^+I^-$, p-NO_2)

(136)

Several metals, metal alkyls and some compounds are also found active in cleaving the tin-carbon bonds.

Vinyllithium prepared by treating tetravinyltin with phenyllithium in ether or petroleum ether (137). Tetrapropenyltin was cleaved by metallic lithium in diethyl ether (138). The reactions of $R_3SnCH_2CH = CHR$ with R'Li where R' = C_4H_9, CH_3, C_6H_5 were tin-carbon bond cleavage reactions (139-141). Metallic sodium was used to cleave aryl-tin bond in (4-biphenylyl)trimethyltin (142).

Lead tetraacetate may also bring about the similar type of reaction.

$$\text{e.g.}\quad (C_4H_9)_3SnCH = CHR \xrightarrow{Pb(OCOCH_3)_4}$$

$$\longrightarrow (C_4H_9)_3SnOCOCH_3 + RCH = CHPb(OCOCH_3)_3$$

(143)

Several of such cleavage reactions were carried out successfully by using boronhalides, substituted boronhalides, germenium halide, siliconhalide, substituted silicon halide, phosphorus halide, substituted phosphorus halide, mercuric halide, zinc halide, tin halide, bismuth trichloride, antimonytrichloride etc compounds (144-182)

$$\text{e.g.}\quad R_4Sn + 2BCl_3 \longrightarrow R_2SnCl_2 + 2RBCl_2$$

(144)

$$(C_2H_5)_3SnC\quad CCH = CH_2 + (C_4H_9O)_2BCl \longrightarrow$$

$$\longrightarrow (C_2H_5)_3SnCl + (C_4H_9O)_2BC \equiv CCH = CH_2$$

(145)

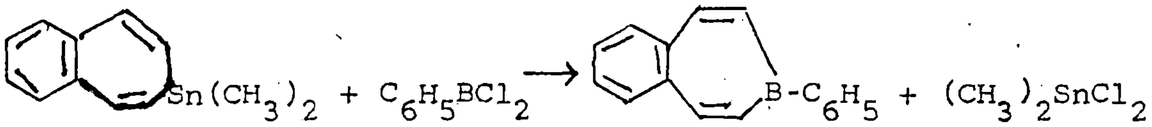
$$(CH_3)_3SnCCl_3 + BCl_3 \xrightarrow{25^\circ C} (CH_3)_2Sn(Cl)CCl_3 + CH_3BCl_2$$

(146)

$$(CH_3)_3SnC_6H_5 + 2BCl_3 \longrightarrow (CH_3)_2SnCl_2 + CH_3BCl_2 + C_6H_5BCl_2$$

(X = F or Cl)

(146, 147)



(148)

$$HgX_2 + (C_6H_5)_4Sn \longrightarrow (C_6H_5)_3SnX + C_6H_5HgX$$

$(X = Cl,\ Br)$ (149)

Wardell etal in 1983 reported to cleave the phenyltin bond in $(C_6H_5)_3Sn(CH_2)_nSOC_6H_4(CH_3)$-p (n = 3 or 4) by mercuric chloride (111).

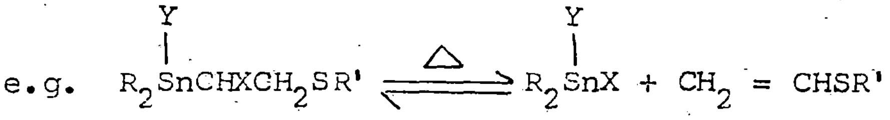
In presence of suitable catalysts organic halides can cause tin-carbon bond fission.

A number of oxidation reactions of tetraalkyltin compounds brought about by irradiation with ultraviolet light (183,184) or by treatment with peroxides (185) leading to cleavage of tin-carbon bond.

The reaction mechanism for the homolytic substitution of trialkyltin iodides by photochemically generated iodine atoms was determined by De Ryck et al in 1985. The propagation step was the cleavage of tin (IV) - carbon bond by radical attack of the iodine atom, followed by the formation of a new tin (IV)-iodine bond (186).

Soundararajan and Platz in 1987 studied the photochemical cleavage of benzylic stannanes $(C_4H_9)_3SnR$ (R = $C_6H_5CH_2$, 1-naphthyl-methyl, $(C_6H_5)_2CH$ to form benzylic and stannyl radicals (187).

A number of cleavage reactions with electrophilic reagents and a number of thermal decomposition leading to fission products involving tin-carbon bond cleavage is also known in some cases.



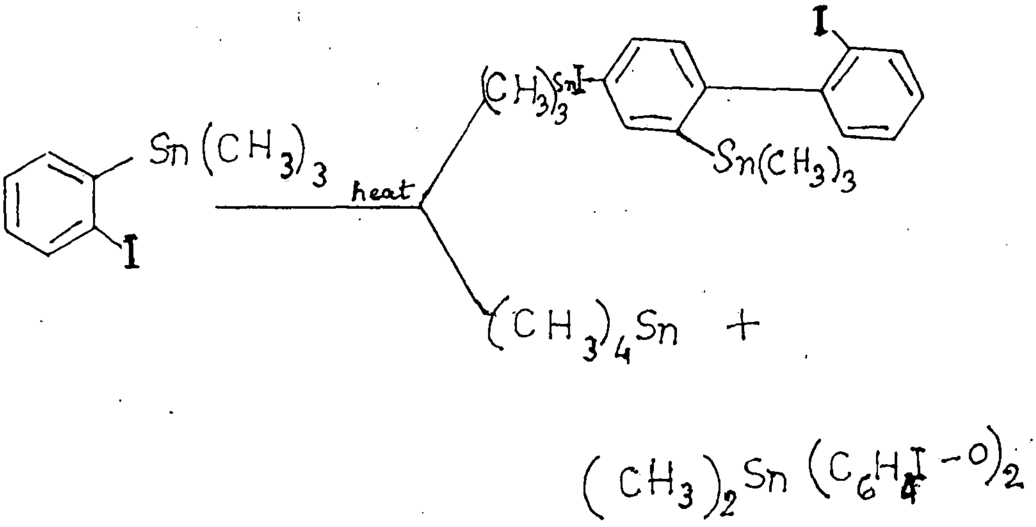
$$\text{e.g.}\quad R_2\overset{\overset{\displaystyle Y}{|}}{Sn}CHXCH_2SR' \overset{\triangle}{\rightleftharpoons} R_2\overset{\overset{\displaystyle Y}{|}}{Sn}X + CH_2 = CHSR'$$

where Y = R, Cl, Br, I, SCN (188)

R, R' = alkyl or aryl group

$$(CH_3)_3SnCF_3 \xrightarrow{150^{\circ}C} (CH_3)_3SnF + :CF_2$$

(189)



In 1984 few organotin halides were prepared by Buschhoff and others where such cleavage reactions took place among tin-carbon bond (191).

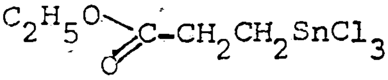
Halogenodephenylation of triphenyltin pseudohalides was reported by Srivastava et al (192) in 1985 and halodealkylation was carried out successfully in few trialkylstannyl substituted esters by Podesta and his co-workers (193) in 1987.

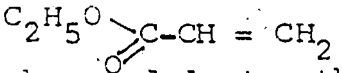
Beside these other miscellaneous cleavage reactions of tin-carbon bond were carried out and studied time to time by different investigators (189, 194-205).

Very recently Wang and Cheng (206) have published a review on cleavage reaction of tin-carbon bond for the transfer of functional groups.

SCOPE AND OBJECTIVES

Scope and Objectives

Recent works have established the Lewis acid character of estertin chlorides with different Lewis bases in the formation of stable adducts and chelate compounds. But stronger base like 1,2 diaminopropane can cleave the Sn-C bond of  $C_2H_5O-\underset{O}{\underset{\|}{C}}-CH_2CH_2SnCl_3$ with liberation of

 $C_2H_5O-\underset{O}{\underset{\|}{C}}-CH=CH_2$, $SnCl_2$ and $NH_2CH_2CH_2CH_2NH_2{\cdot}2HCl$ as observed during the current investigation. Hence, the study of Lewis acid character of the new organotin chlorides obtained from above mentioned reactions will be of interest. The possibility of Sn-C bond fission of the new organotin chlorides obtained from aromatic unsaturated ketones was explored. It was found that Sn-C bond fission, took place rather easily even with moderate bases, so that no adduct or chelate compounds could be isolated with these new organotin chlorides.

Tentative mechanisms for the formation of new organotin chlorides and their interaction with Lewis bases have been attempted. The current investigations have opened up quite a number of interesting possibilities, of which, it has been possible to study only a part of these possibilities.

EXPERIMENTAL

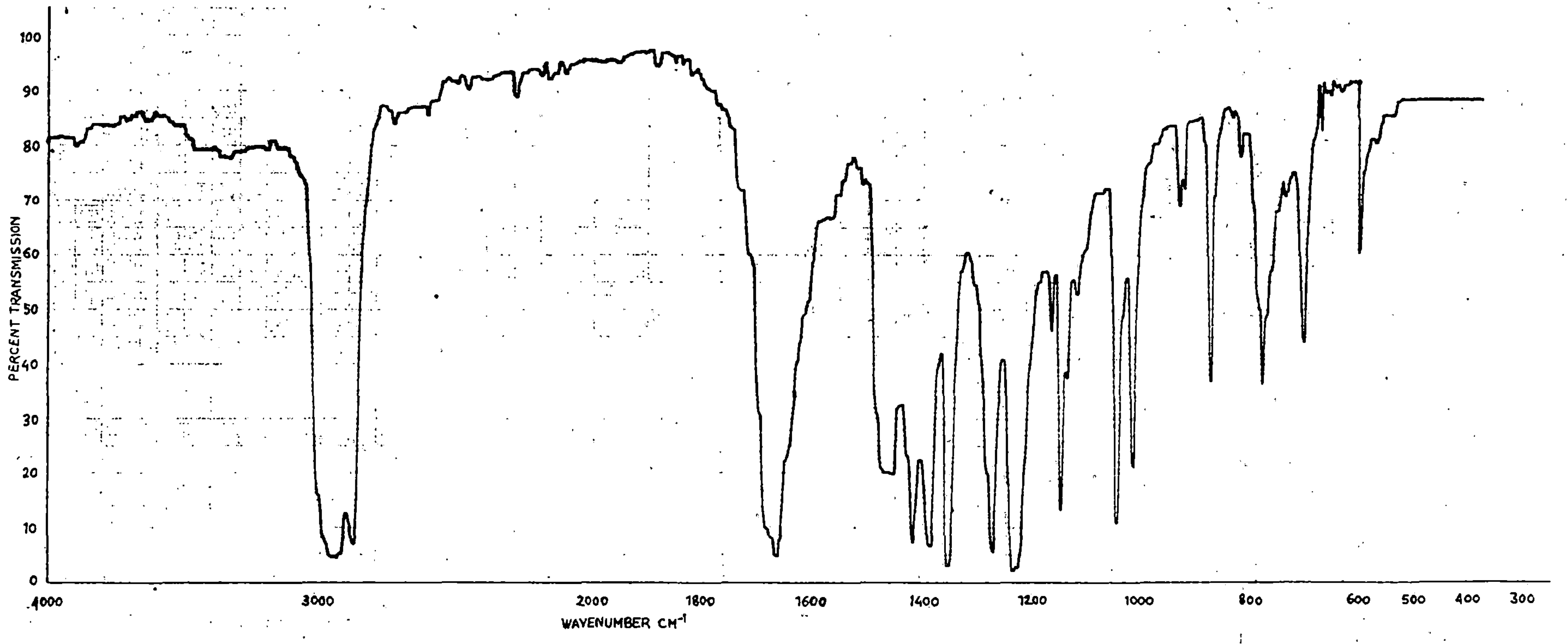


Fig. 18 IR spectrum of β-carboethoxyethyltin trichloride

Elemental analyses and spectral recordings, purification of solvents, use of abbreviations remain the same as mentioned in Part I of the thesis. Digital P_H meter 331 Systronics (India) was used to measure the P_H of the solution of β-keto-organotin chlorides.

Preparation of starting material

Preparation of β-carboethoxyethyltin trichloride (207)

Dry hydrogen chloride was passed into the ether solution of ethylacrylate (5 gm) and anhydrous stannous chloride (9.5 gm) (i.e. in the molar proportion 1:1) at 20°C temperature for two hours. The reaction mixture was worked up following the literature method. The melting point of the final crystals was 68°C. The compound was characterised by elemental analyses and IR spectrum.

% Analysis for $C_5H_9O_2SnCl_3$

Found	C	18.00	H	2.61	Sn	36.74
Calculated	C	18.38	H	2.76	Sn	36.45

IR spectral data (cm^{-1}) (Fig. 18)

2880-3000 vs(b), 1665 vs, 1460 vs, 1420 s, 1385 s, 1355 s, 1275 s, 1235 vs, 1170 w, 1150 s, 1120 w, 1045 s, 1015 s, 930 m, 920 m, 870 s, 820 w, 780 s, 740 w, 700 s, 670 w, 600 m.

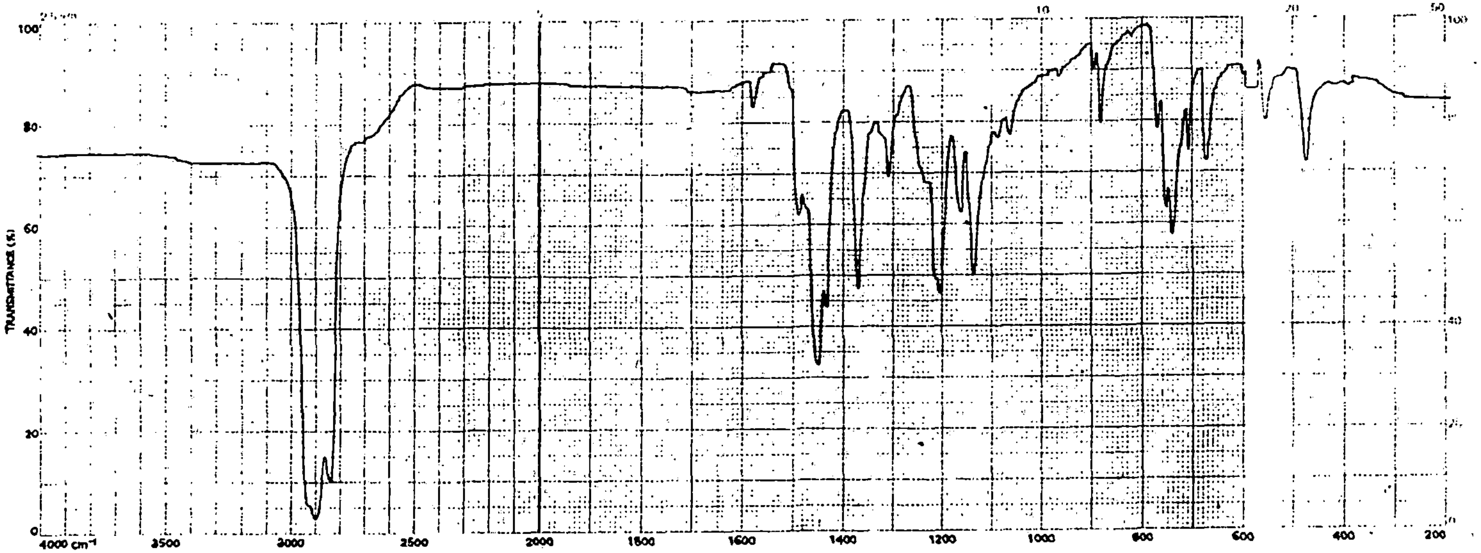


Fig. 19a IR spectrum of 1,5-diphenylthiocarbazone

Reactions of β-carboethoxyethyltin trichloride

(a) With 1,5-diphenyl thiocarbazone (dithizone)

The compound β-carboethoxyethyltin trichloride (653 mg) and pure diphenyl thiocarbzone (1024 mg) were taken in chloroform (150 ml). The reaction was carried out with the molar proportion of the reactants as 1:2. The reaction mixture was heated on a steam bath for about ten minutes. It was then cooled to room temperature and few drops of ammonia solution was added with constant shaking. The colour of the solution changed sharply from green to dark red along with the deposition of ammonium chloride (confirmed by chemical test). Filtering off the deposited ammonium chloride the filtrate was refluxed for two and half hours. During the reflux some more ammonium chloride was deposited, which was filtered off. The filtrate was concentrated to one tenth of its original volume (15 ml) over a steam bath. Few drops of pet ether was added to the concentrated filtrate. On standing overnight, greenish fluorescent red crystal separated . The solid was recrystallized twice from chloroform containing few drops of methanol. The melting point of the final crystals was 161°C.

(Yield 55%)

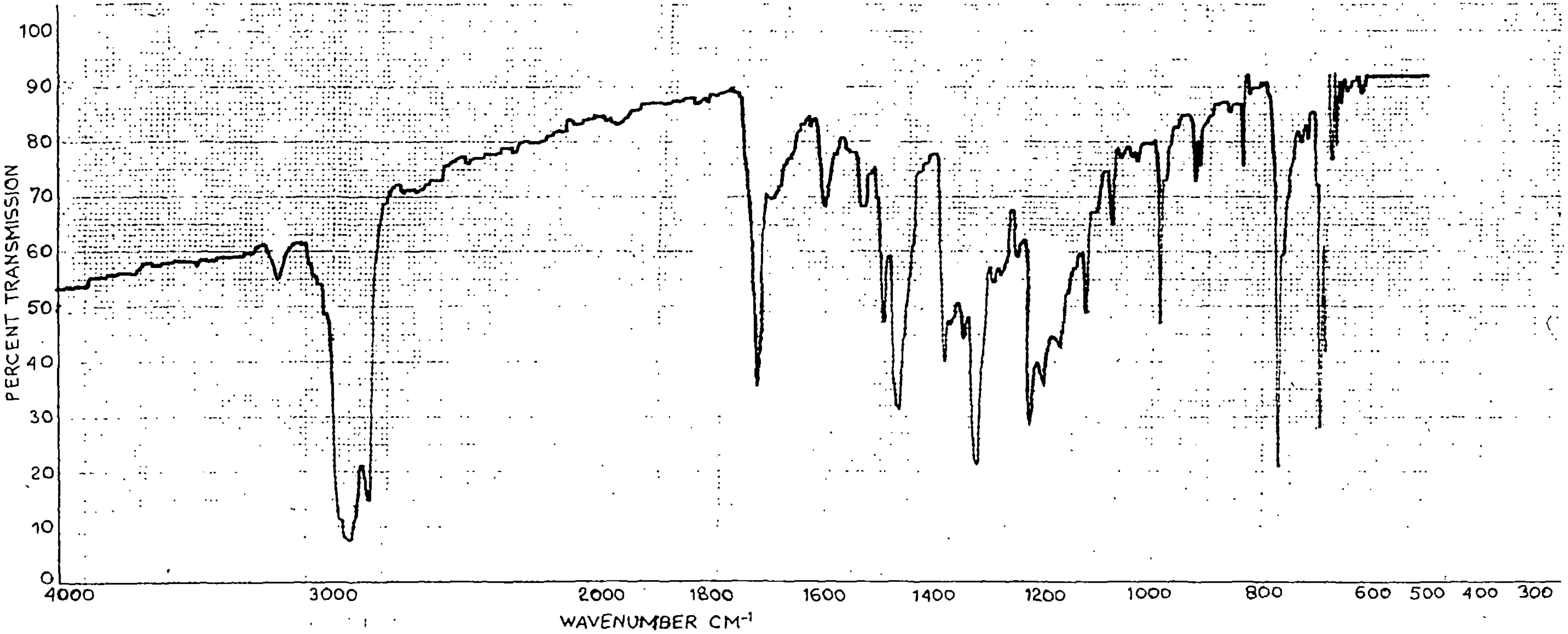


Fig. 19 IR spectrum of β-carboethoxyethyl chlorotin bis-dithizonate

% Analysis for $C_5H_9O_2Sn(C_{13}H_{11}N_4S)_2Cl$

Found	C	48.21	H	3.95
	N	14.24	Sn	15.85
Calculated	C	48.60	H	4.05
	N	14.63	Sn	15.55

Infrared spectral data (cm^{-1}) (Fig.19)

3200 w, 2860-3000 vs (B), 1720 s, 1700 sh, 1605 m, 1535 m, 1495 m, 1465 s, 1385 m, 1350 w, 1325 s, 1295 w, 1285 w, 1255 w, 1230 s, 1200 m, 1165 m, 1125 m, 1110 sh 1080 m, 990 s, 980 sh, 925 w, 915 w, 840 w, 770 s, 700s, 690 s, 685 s, 680 w, 670 w, 620 w.

(b) With 8-hydroxy quinoline (oxine)

The compound β-carboethoxy ethyltin trichloride (653 mg) and pure 8-hydroxy quinoline (580 mg) were taken in chloroform (150 ml). The reaction was carried out with the molar proportion of the reactants as 1:2. The reaction mixture was heated on a steam bath for about ten minutes and then cooled to room temperature after which few drops of ammonia solution was added with constant shaking. The colour of the solution changed to intense yellow along with the deposition of ammonium chloride (confirmed by chemical tests), which was filtered off. The filtrate was refluxed for two and half hours, during which more ammonium chloride was deposited. It was again filtered. The filtrate was concentrated to one tenth of its original volume

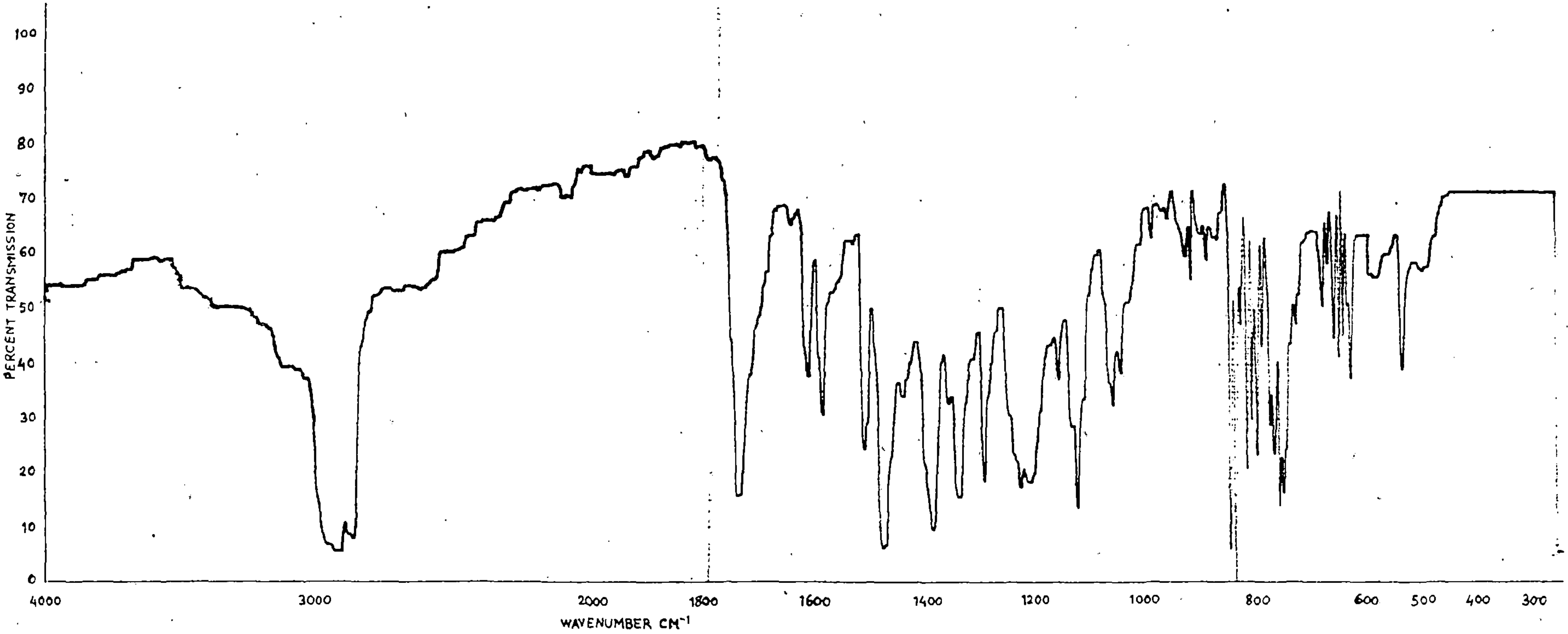


Fig. 20 IR spectrum of β-carboethoxyethyl chlorotin bis-oxinate

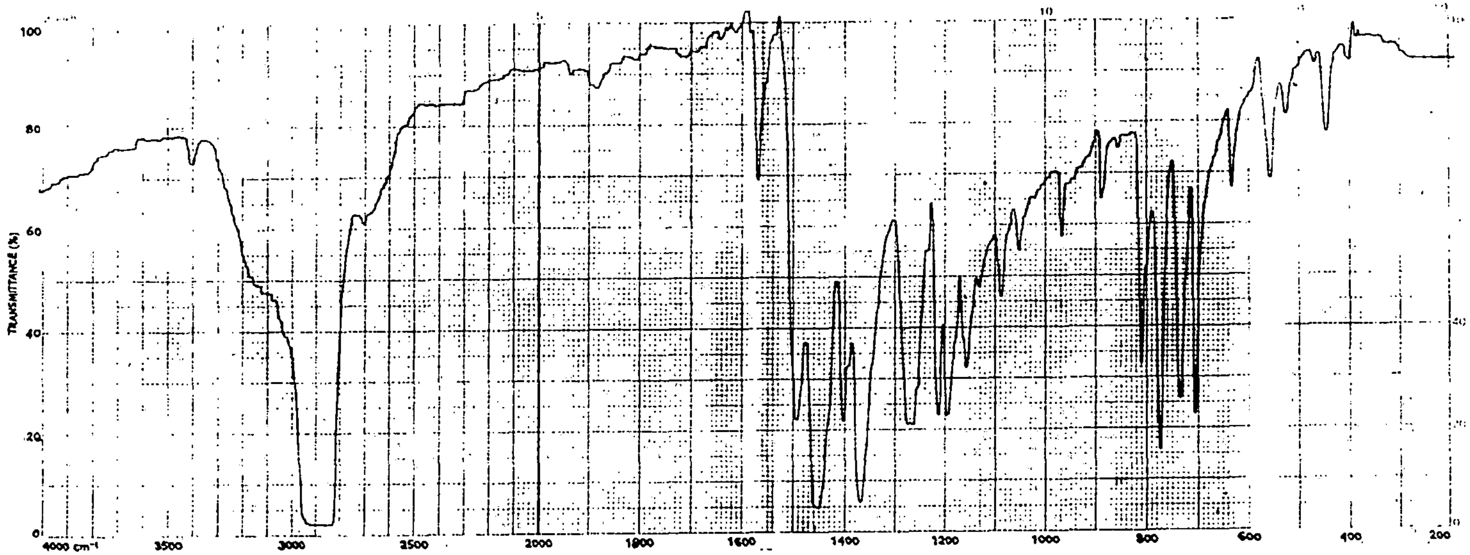


Fig. 20a IR spectrum of 8-hydroxyquinoline (oxine)

(15 ml) by heating on a steam bath. Few drops of pet ether was added to the concentrated filtrate. On standing overnight yellow cyrstalline solid separated out. The solid was recrystallized from chloroform. The melting point of the final crystals was 181° C.

(Yield 50%)

% Analysis for $C_5H_9O_2Sn(C_9H_6O)_2Cl$

Found	C	50.19	H	3.47
	N	4.78	Sn	22.23
Calculated	C	50.78	H	3.86
	N	5.15	Sn	21.90

Infrared spectral data (cm^{-1}) (Fig. 20)

2860-2990 vs(b), 1735 vs, 1610 s, 1585 s, 1510 s, 1475 vs, 1440 w, 1385 vs, 1360 w, 1340 s, 1290 s, 1230 s, 1210 s, 1160 w, 1125 s, 1060 s, 1045 m, 1030 sh, 1010 sh, 990 w, 930 w, 905 w, 870 w, 850 s, 840 s, 810 m, 805 m, 800 m, 790 w, 780 w, 770 m, 760 s, 750 s, 730 w, 680 m, 675 w, 660 m, 650 m, 640 m, 630 m, 590 m, 585 s, 560 sh, 500 m, 480 sh.

(c) With pyridine

The compound β-carboethoxyethyltin trichloride (980 mg) was dissolved in chloroform. Pyridine (237 mg i.e. approximately 0.25 ml) was mixed with little chloroform

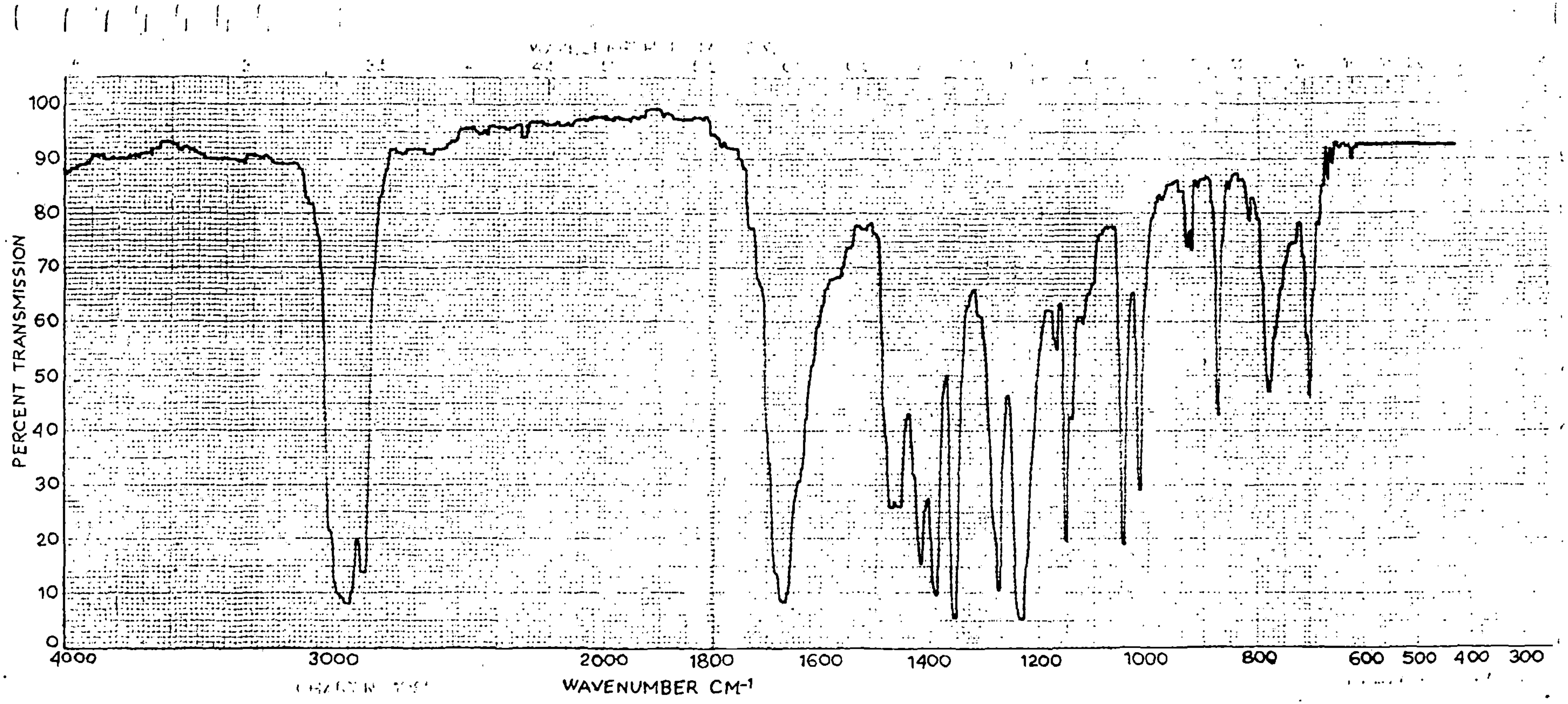


Fig. 21 IR spectrum of pyridine adduct of β-carboethoxyethyltin trichloride

and this mixture was added to the solution of the estertin compound dropwise with constant shaking (The reaction was carried out with the molar proportion of the reactants as 1:1). The mixed solution was concentrated on a steam bath to about one fifth of its original volume. On standing overnight white crystals separated out. The solid was recrystallized chloroform and the melting point of the final crystals was 91°C.

(Yield 85%.)

% Analysis $C_5H_9O_2SnCl_3.C_5H_5N$

Found	C	30.01	H	3.63
	N	3.78	Sn	29.91
Calculated	C	29.51	H	3.45
	N	3.45	Sn	29.35

Infrared spectral data (cm^{-1}) (Fig. 21)

2880-3020 vs(b), 1740(sh),1720(sh), 1665 vs, 1580 sh, 1500 sh, 1475 s, 1455 s, 1420 s, 1390 s, 1355 s, 1275 s, 1240 vs, 1170 m, 1150 s, 1140 sh, 1120 w, 1100 sh, 1045 sh, 1015 sh, 935 m, 920 m, 875 s, 820 w, 780 s, 730 sh, 700 s.

(d) With picolines

The compound β-carboethoxyethyltin trichloride (980 mg) was dissolved in chloroform and picoline (0.30 ml) was mixed with little chloroform and the mixture was added to the solution of the estertin compound dropwise

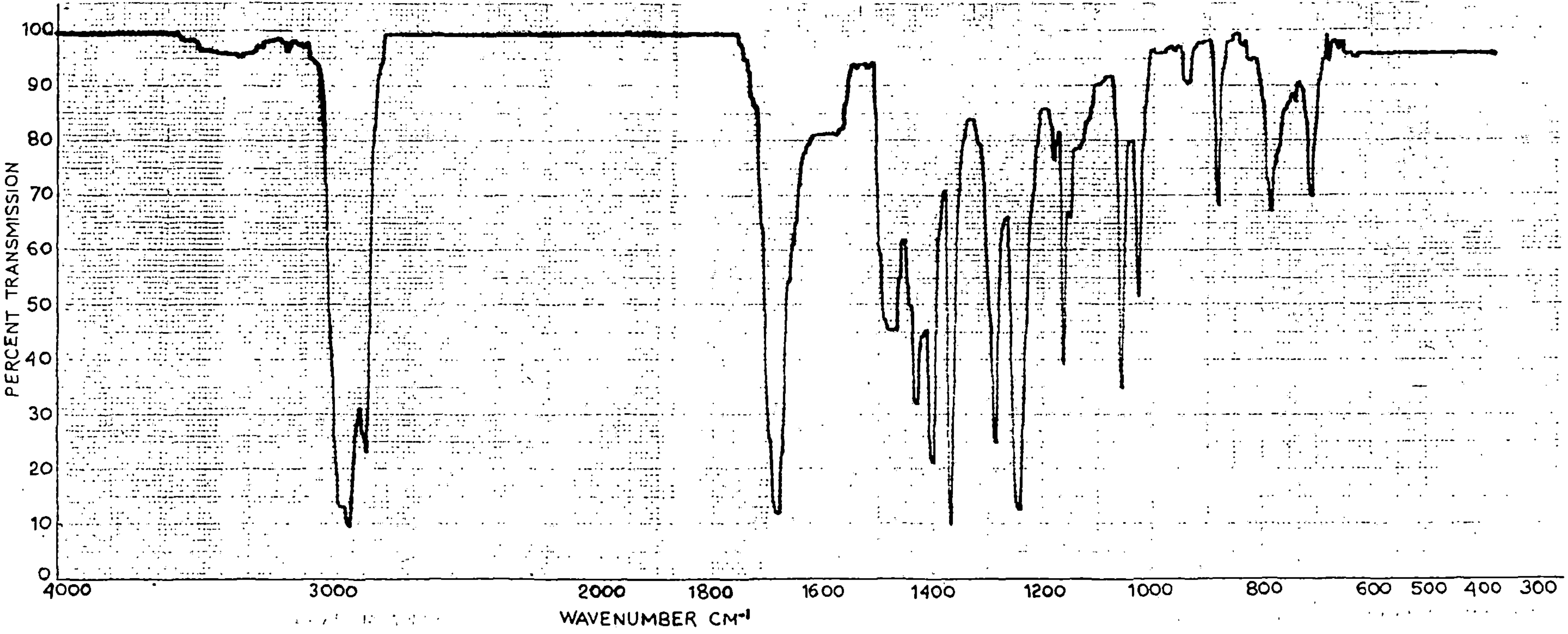


Fig. 22 IR spectrum of β-picoline adduct of β-carboethoxyethyltin trichloride

with constant shaking (The reaction was carried out with the molar proportion of the reactants as 1:1). The mixed solution was concentrated on a steam bath to about one fifth of its original volume. On standing overnight white crystals separated out. The solid was recrystallized from chloroform.

(i) With β-picoline

The melting point of the final crystals was 81°C. (Yield 80%)

% Analysis for $C_5H_9O_2SnCl_3.C_6H_7N$

Found	C 31.33	H 4.01	N 3.64
	Sn 28.78		
Calculated	C 31.47	H 3.81	
	N 3.34	Sn 28.37	

Inrared spectral data (cm^{-1}) (Fig. 22)

2870-2990 vs(b), 1680 vs, 1565 sh, 1470 s, 1435 s, 1405 s, 1370 s, 1295 s, 1245 vs, 1185 w, 1160 s, 1150 sh, 1055 s, 1025 s, 940 m, 885 s, 785 s, 740 w, 710 s, 680 w.

(ii) With γ-picoline

The melting point of the final crystals was 85°C. (Yield 82%)

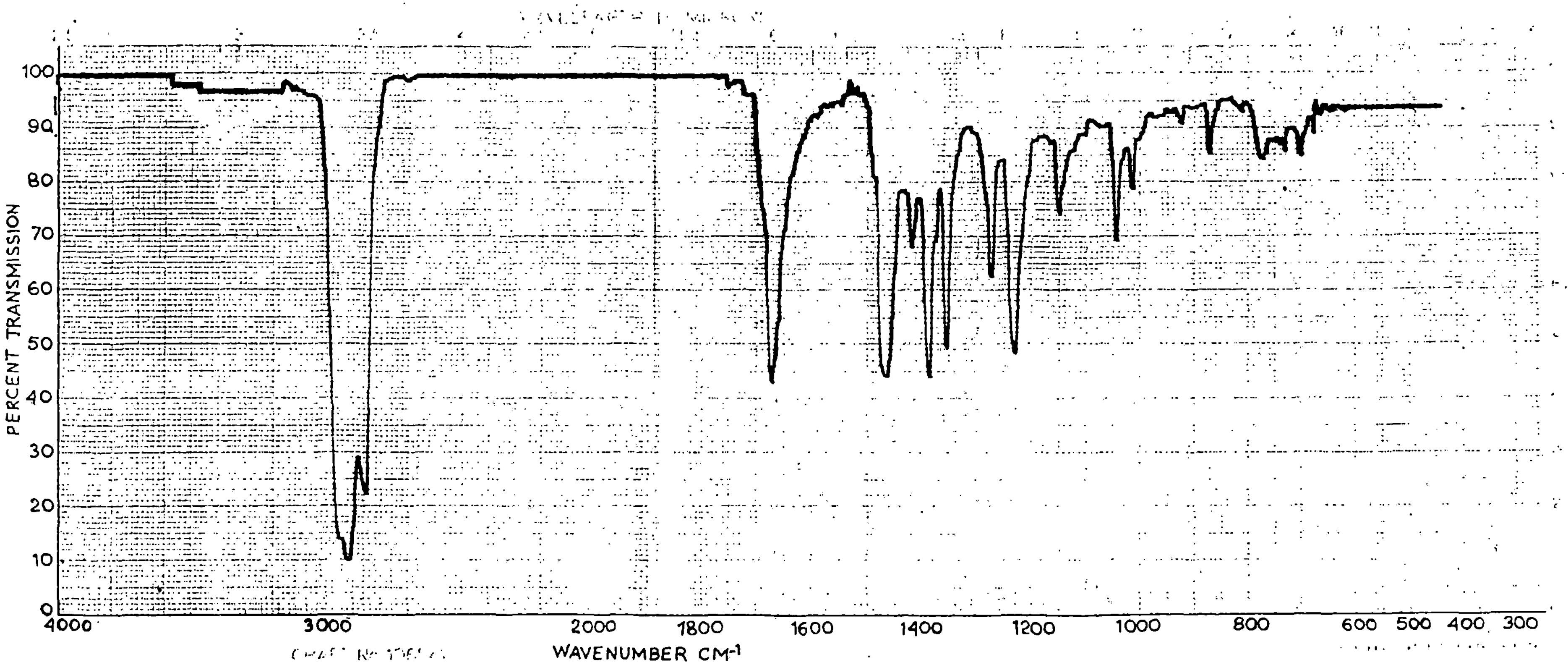


Fig. 23 IR spectrum of γ-picoline adduct of β-carboethoxyethyltin trichloride

% Analysis for $C_5H_9O_2SnCl_3.C_6H_7N$

Found	C 31.68	H 3.56	N 3.73
	Sn 28.81		
Calculated	C 31.47	H 3.81	N 3.34
	Sn 28.37		

Infrared spectral data (cm^{-1}) (Fig. 23)

2850-2980 vs(b), 1670 vs, 1465 vs, 1420 m, 1385 s, 1355 s, 1275 s, 1230 s, 1150 s, 1045 s, 1015 s, 920 w, 870 m, 775 w, 730 w, 700w.

(e) With isoquinoline

The compound β-carboethoxyethyltin trichloride (980 mg)was dissolved in chloform and isoquinoline (387 mg) mixed with little chloroform was added to the solution of the estertin compound dropwise with constant shaking (The reaction was carried out with the molar proportion of the reactants as 1:1). The mixed solution was heated on a steam bath to concentrate to about one fifth of its original volume. On standing overnight and then adding few drops of pet ether to the solution with vigorous shaking, colourless crystals separated after scratching the glass wall of the container in contact with the solution. The solid was crystallized twice more from chloroform. The melting point was found 87°C.

(Yield 78%)

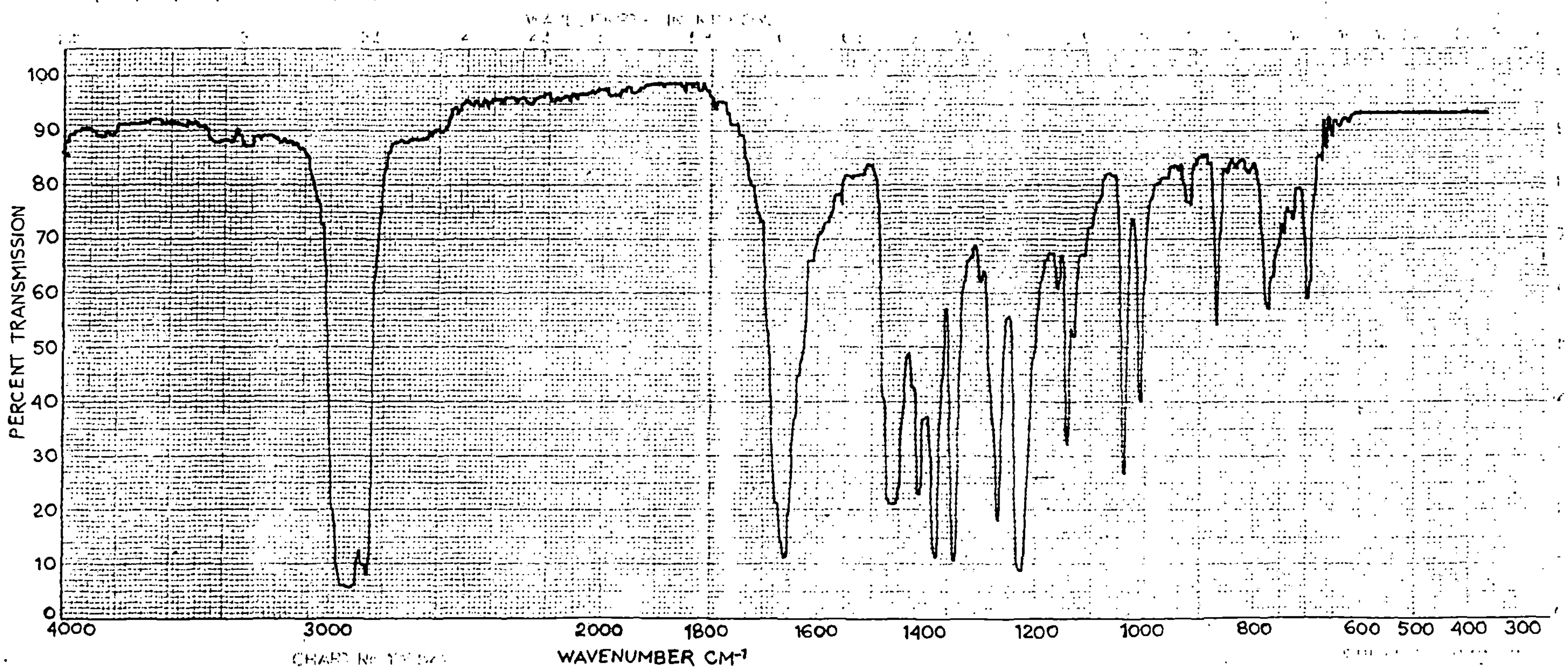


Fig. 24 IR spectrum of isoquinoline adduct of β-carboethoxyethyltin trichloride

% Analysis for $C_5H_9O_2SnCl_3.C_9H_7N$

Found	C 36.38 Sn 25.88	H 3.46	N 3.29
Calculated	C 36.88 Sn 26.12	H 3.51	N 3.07

Infrared spectral data (cm^{-1}) (Fig. 24)

2850-2980 vs(b), 1660 vs, 1465 vs, 1415 s, 1380 s, 1350 s, 1305 w, 1270 s, 1230 vs, 1160 w, 1145 s, 1135 sh, 1105 sh, 1090 sh, 920 m,870 s, 770 s, 760 sh, 740 w, 725 w, 695 s, 670 sh.

(f) With triphenyl phosphine

The compound β-carboethoxyethyltin trichloride (980 mg) was dissolved in chloroform and a pure sample of triphenyl phosphine (786 mg) was dissolved separately in minimum volume of chloroform. The reaction was carried out with the molar proportion of the reactants as 1:1 The solution of triphenyl phosphine was added to the solution of the estertin compound dropwise with constant shaking. The mixed solution was heated on a steam bath to concentrate to about one fifth of its original volume. On standing overnight white crystals separated out. The solid was recrystallized from chloroform. The melting point of the final crystals was 60°C.

(Yield 85%)

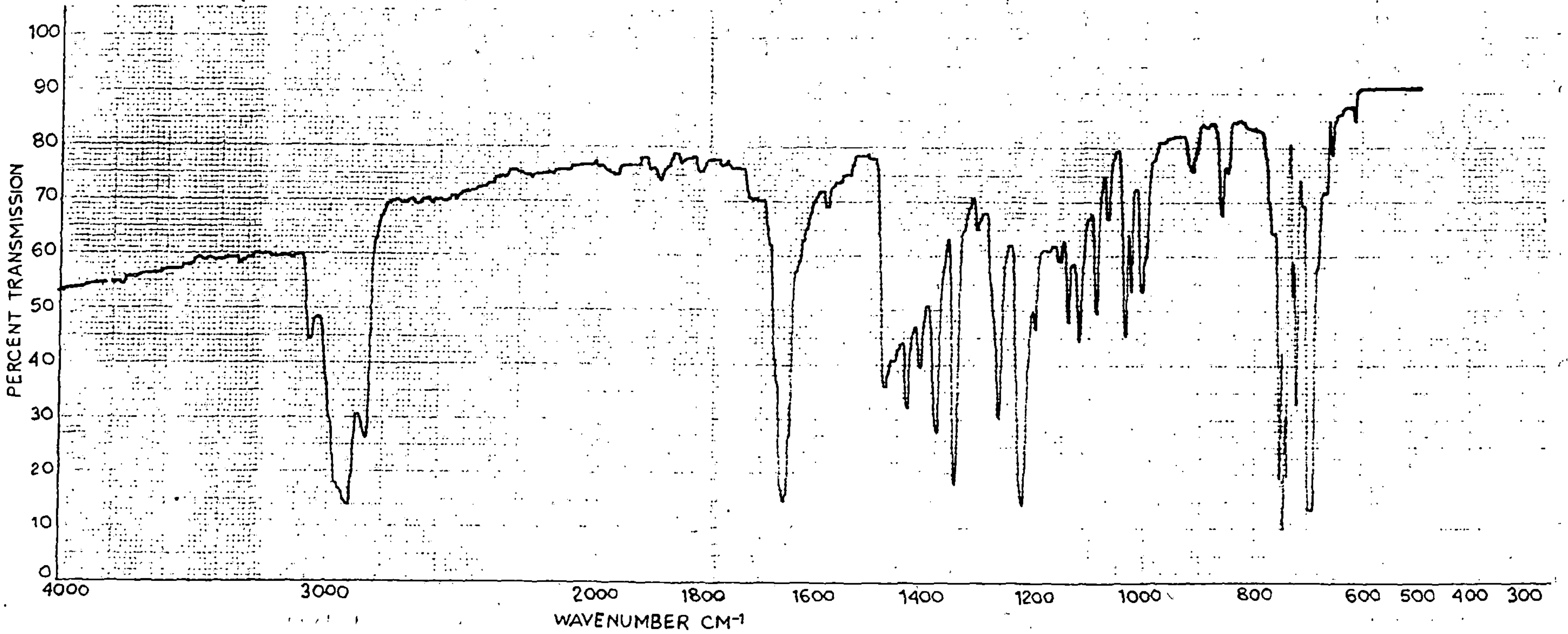


Fig. 25 IR spectrum of triphenylphosphine adduct of β-carboethoxyethyltin trichloride

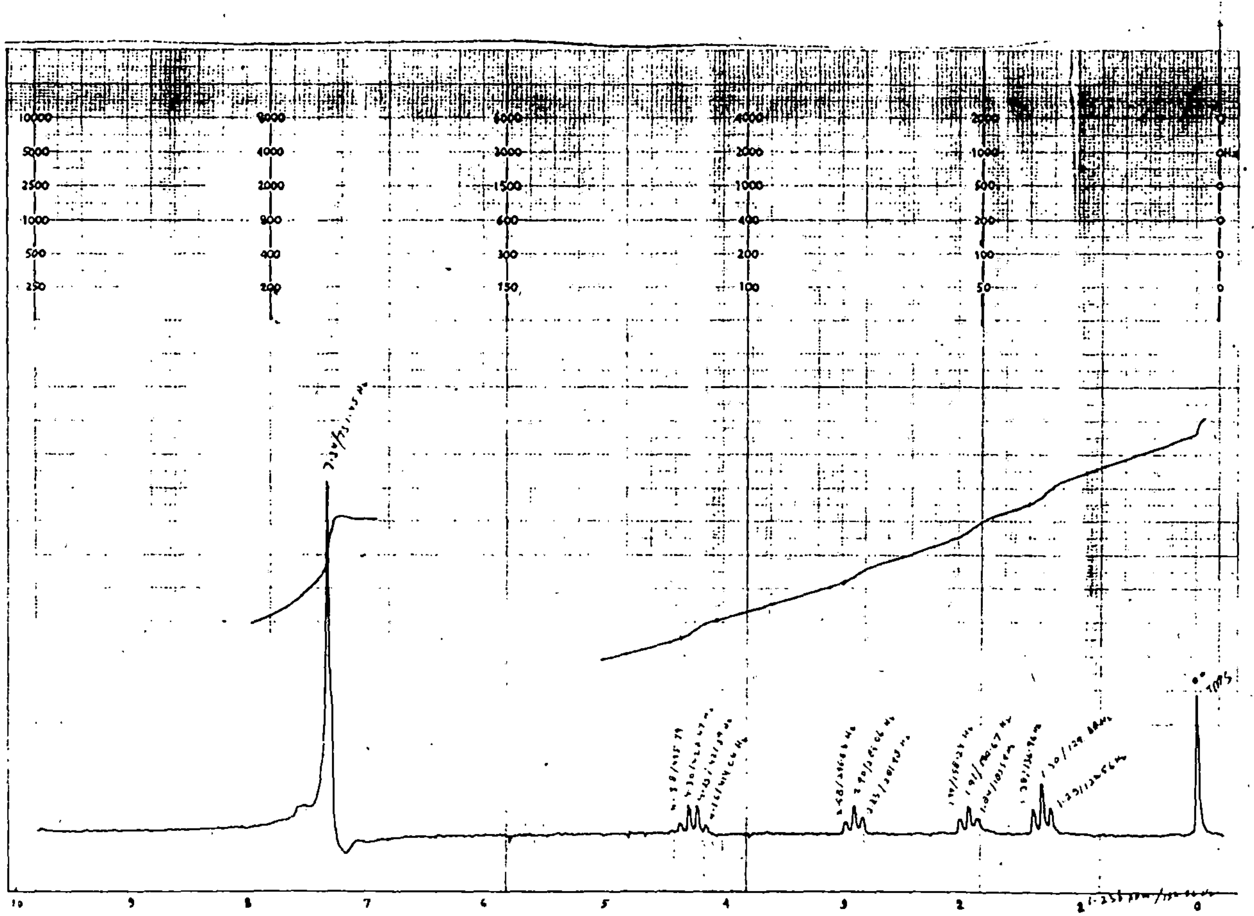


Fig. 25a ^{1}H NMR psectrum triphenylphosphine adduct of β-carboethoxyethyltin trichloride

% Analysis for $C_5H_9O_2SnCl_3.P(C_6H_5)_3$

Found	C 46.33	H 4.27	Sn 20.48
Calculated	C 46.9	H 4.08	Sn 20.22

Infrared spectral data (cm^{-1}) (Fig. 25)

2860-3065 vs(b), 1660 vs, 1585 w, 1435 m, 1410 m, 1380 s, 1345 s, 1310 w, 1270 s, 1225 s, 1220 vs, 1200 w, 1140 m, 1120 m, 1080 m, 1070 w, 1035 s, 1025 m , 1005 m, 915 w, 860 m, 755 vs, 745 vs, 740 vs, 720 s, 695 vs, 655 w, 610 w.

(g) With 1,10-phenanthroline (monohydrate)

The compound β-carboethoxyethyltin trichloride (980 mg) was dissolved in chloroform and 1,10 phenanthroline monohydrate (594 mg) was dissolved separately in minimum volume of chloroform. The reaction was carried out with the molar proportion of reactants 1:1. The solution of phenanthroline was added to the solution of the stertin compound dropwise with constant shaking. The mixed solution was then heated on a steam bath to concentrate to about one fifth of its original volume. Few drops of diethyl ether was added to this concentrated solution. On standing overnight light orange pink crystals separated out. The solid was recrystallized from chloroform. The melting point of the final crystals was 97°C.

(Yield 80%)

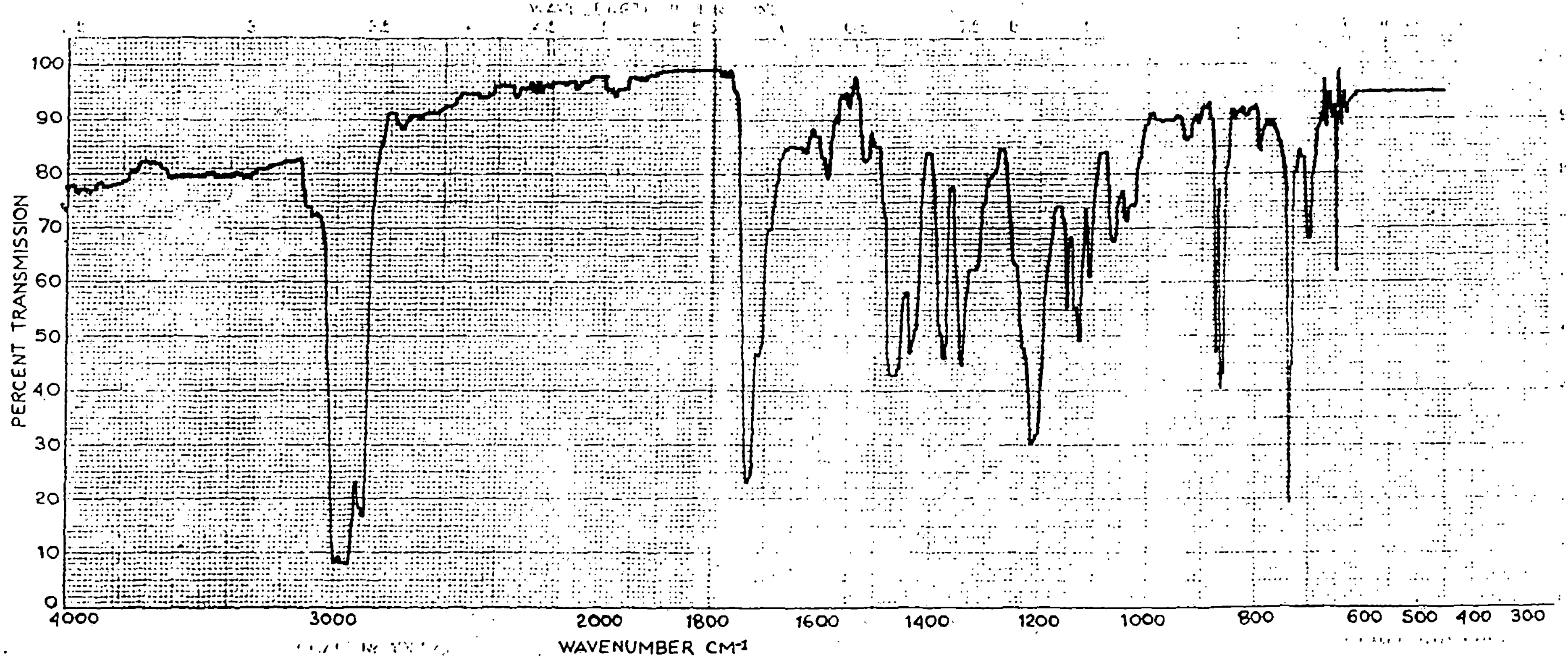


Fig. 26 IR spectrum of 1,10-phenanthroline chelate of β-carboethoxyethyltin trichloride

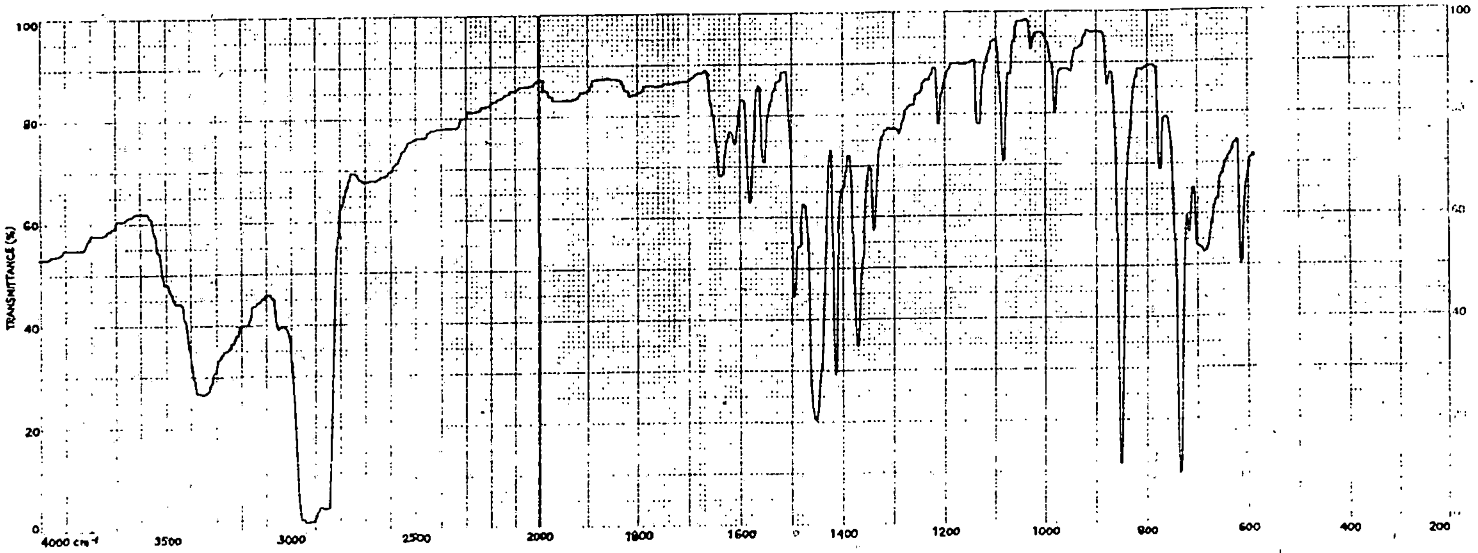


Fig. 26a IR spectrum of 1,10-phenanthroline (monohydrate)

% Analysis for $C_5H_9O_2SnCl_3.C_{12}H_8N_2$

Found	C 40.56	H 3.78	N 5.88
	Sn 23.98		
Calculated	C 40.28	H 3.36	N 5.53
	Sn 23.49		

Infrared spectral data (cm^{-1}) (Fig. 26)

2890-3000 vs(b). 1735 vs, 1710 sh, 1590 w, 1520 w, 1470 vs, 1435 s, 1375 s, 1345 s, 1330 sh, 1215 vs, 1150 w, 1130 m, 1110 w, 1065 w, 1040 w, 1030 sh, 930 w, 875 m, 865 m, 860 sh, 790 w, 740 s, 700 m, 650 m.

(h) With 2,2'-bipyridyl

The compound β-carboethoxy ethyltin trichloride (980 mg) was dissolved in chloroform and then a pure sample of 2,2'-bipyridyl (468 mg) was dissolved separately in minimum volume of chloroform. The reaction was carried out with the molar proportion of the reactants as 1:1. The solution of bipyridyl was added to the solution of the estertin compound dropwise with constant shaking. The mixed solution was heated on a steam bath to concentrate to about one fifth of its original volume. Few drops of methanol was added to this concentrated solution. On standing overnight light pink crystals separated out. The solid was crystallized twice more from chloroform. The melting point of the final crystals was 88°C.

(Yield 80%)

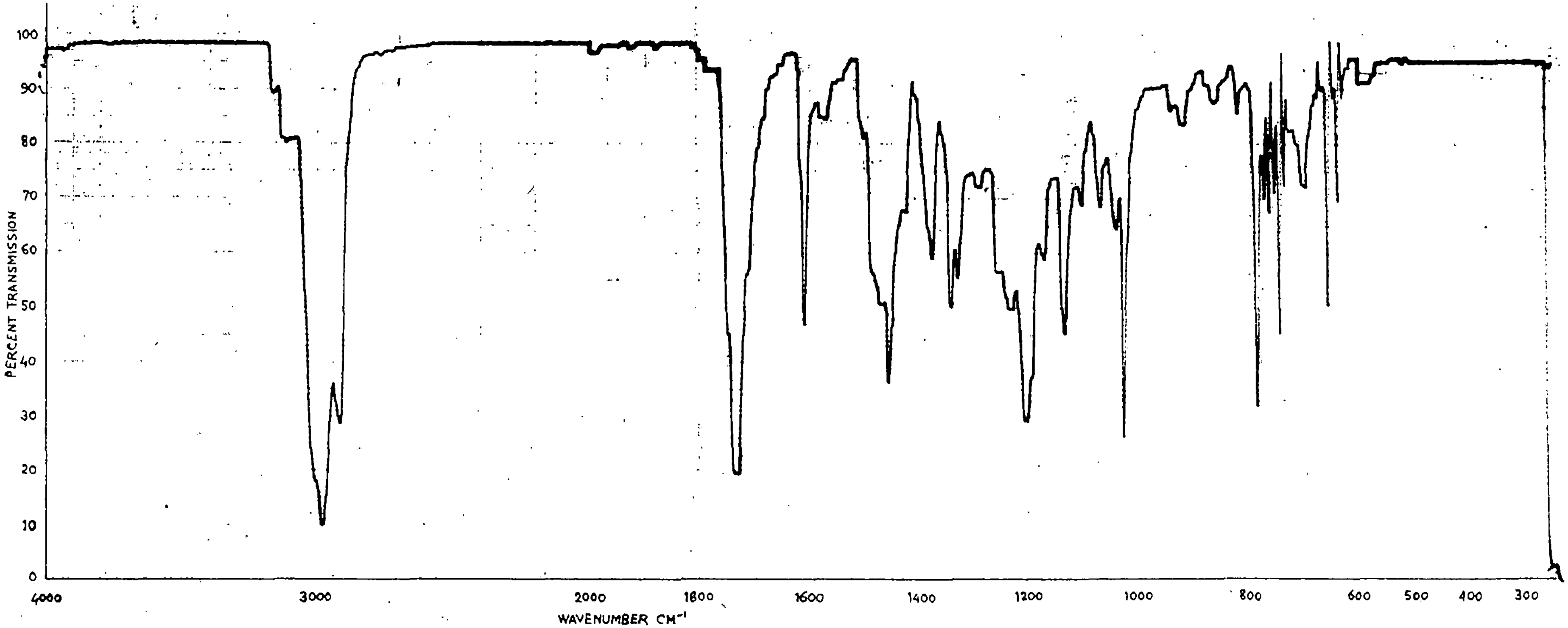


Fig. 27 IR spectrum of 2,2'-bipyridyl chelate of β-carboethoxyethyltin trichloride

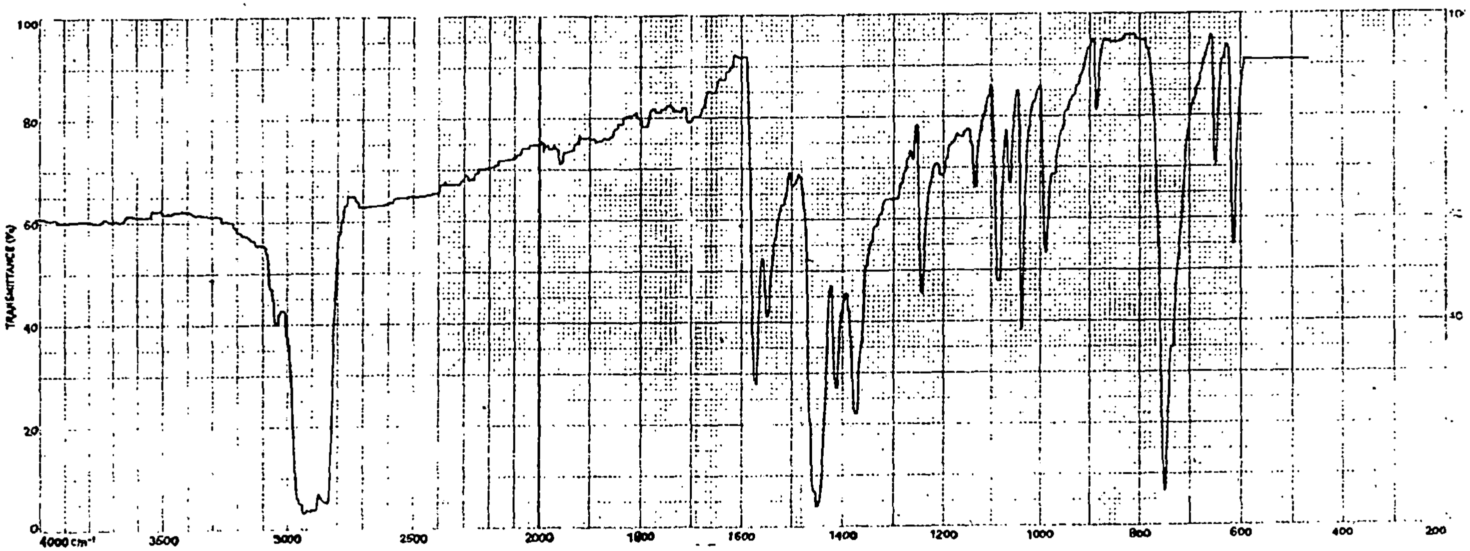


Fig. 27a IR spectrum of 2,2'-bipyridyl

% Analysis for $C_5H_9O_2SnCl_3.C_{10}H_8N_2$

Found	C 36.98	H 3.67	N 6.02
	Sn 24.93		
Calculated	C 37.31	H 3.52	N 5.80
	Sn 24.66		

Infrared spectral data (cm^{-1}) (Fig. 27)

2910-3010 vs(b), 1730 vs, 1605 s, 1580 w, 1465 sh, 1455 vs, 1420 sh, 1375 m, 1340 s, 1330 m, 1290 w, 1260 sh, 1230 m, 1205 vs, 1170 m, 1135 s, 1105 w, 1070 w, 1045 w, 1030 vs, 945 w, 920 w, 870 w, 820 w, 785 s, 775 w, 765 w, 755 w, 745 m, 735 w, 700 m, 720 sh, 655 m, 640 m.

(i) With propylene diamine (1,3-diamino propane)

The compound β-carboethoxyethyltin trichloride (980 mg) was dissolved in chloroform and then a pure sample of propylene diamine (441 mg) mixed with little chloroform was added to the solution of the estertin compound drop-wise with constant shaking (The molar proportion of the reactants was 1:1). The mixed solution was then concentrated to some extent on a steam bath. It was then cooled to room temperature. The white crystalline solid deposited was washed with chloroform four times. The residual solid, having a melting point 246°C was confirmed as stannous chloride (by qualitative analysis). In each time the washing was collected. All these washings were mixed, which

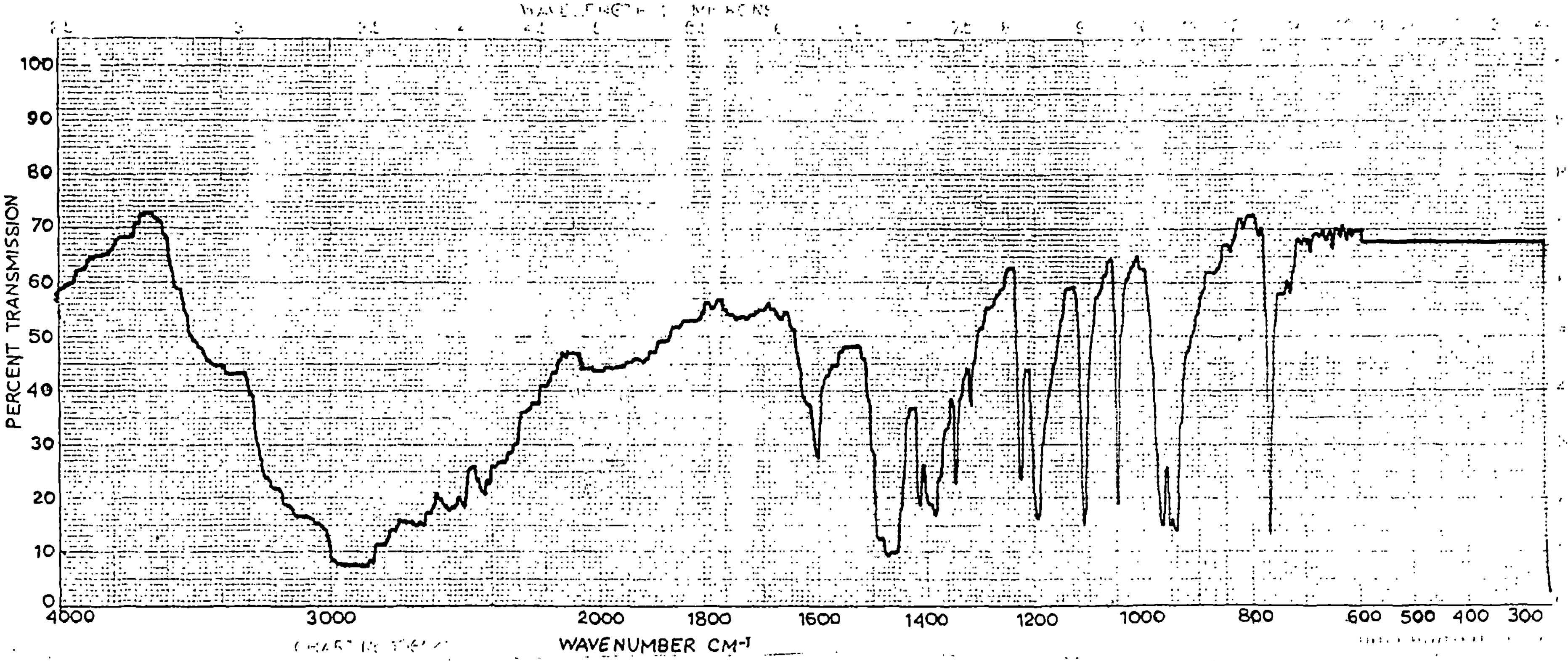


Fig. 28a Propylenediamine dihydrochloride (1,3-diaminopropane dihydrochloride)

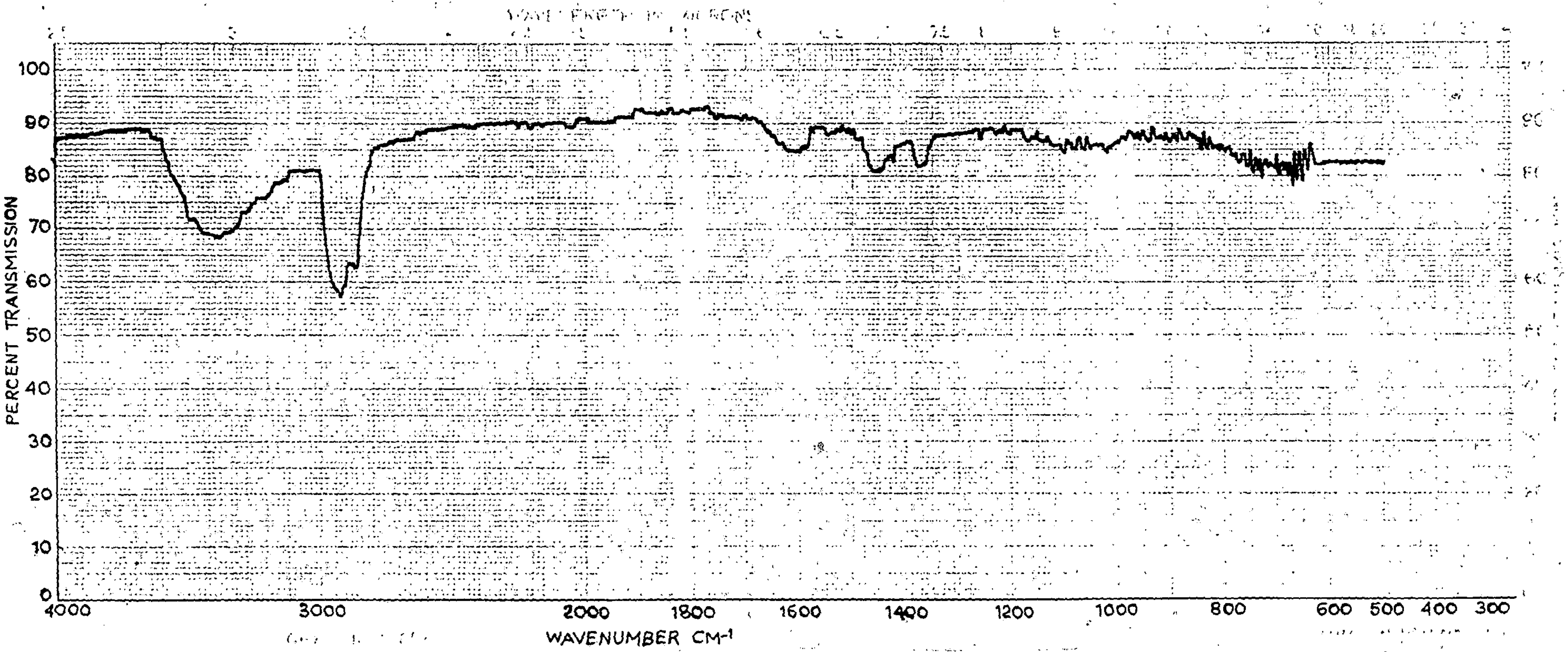


Fig.28b IR spectrum of stannous chloride

furnished white crystals on evaporating the solvent. The solid was recrystallized from chloroform. The melting point of the final crystals was 244°C.

% Analysis for $C_3H_{12}N_2Cl_2$

Found	C	24.49	H	8.16	N	19.05
Calculated	C	25.01	H	7.98	N	18.76

Infrared spectrum (Fig. 28)

A complete removal of stannous chloride from the obtained propylene diamine dihydrochloride was not possible and hence a trace amount of tin (0.63%) was found during the elemental analysis of it for tin.

The fraction containing ethyl acrylate could not be properly characterised.

(j) Reaction with 1,5-diphenyl carbazone

Reaction of β-carboethoxyethyltin trichloride with 1,5-diphenylcarbazone was attempted. Method used was same as that of used during the reaction of β-carboethoxyethyltin trichloride with 1,5-diphenylthiocarbazone, but unfortunately no pure solid could be isolated though a sharp colour change from orange to deep violet took place immediately after the neutralisation of the liberated hydrogen chloride with drops of ammonia. Formation of such deep violet colouration indicates the complexation of the diphenyl carbazone molecule at the tin centre.

However, the compound could not be isolated in pure state so far. Further work is in progress.

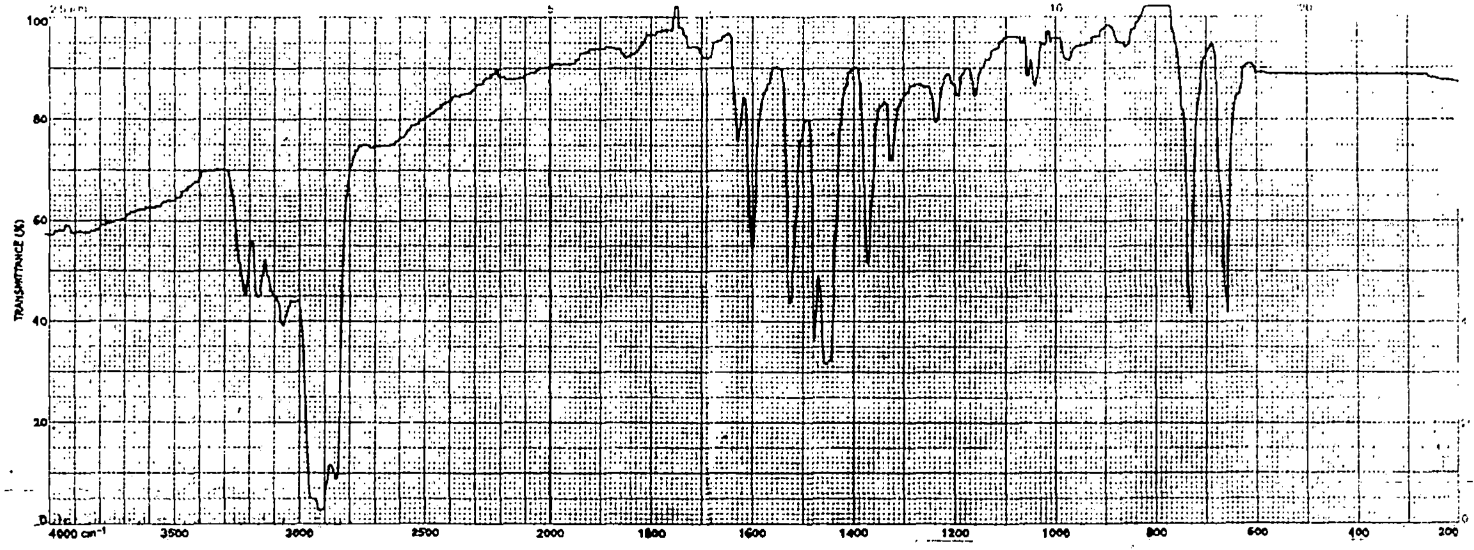


Fig. 29a IR spectrum of pyridine hydrochloride

1. Reactions of β-benzoyl-α-phenylethyltin trichloride

(a) With pyridine

The compound β-benzoyl-α-phenylethyltin trichloride (1.3 gm) was dissolved in minimum quantity of chloroform. Then pyridine (0.25 ml) mixed with little chloroform was added to the solution of the said tin compound with constant stirring the reaction mixture (molar proportion of the reactants was 1:1). The mixed solution was concentrated to one fifth of the original volume on a steam bath and then cooled to room temperature and kept undisturbed for about one hour. White crystalline solid was separated out. The crude solid melted at 138-139°C (a part of it remained unmelted upto 200°C). The crude solid contained stannous chloride, which was tested by mercuric chloride. After crystallising several times from chloroform, the white crystals were freed from stannous chloride which showed a melting point 140-141°C. The mixed melting point of the solid with β-benzoyl-α-phenylethyltin trichloride (m.p. 140°C) was found 130°C.

% Analysis for $C_5H_5N.HCl$

Found	C	51.53	H	5.25	N	11.76
Calculated	C	51.95	H	5.19	N	12.12

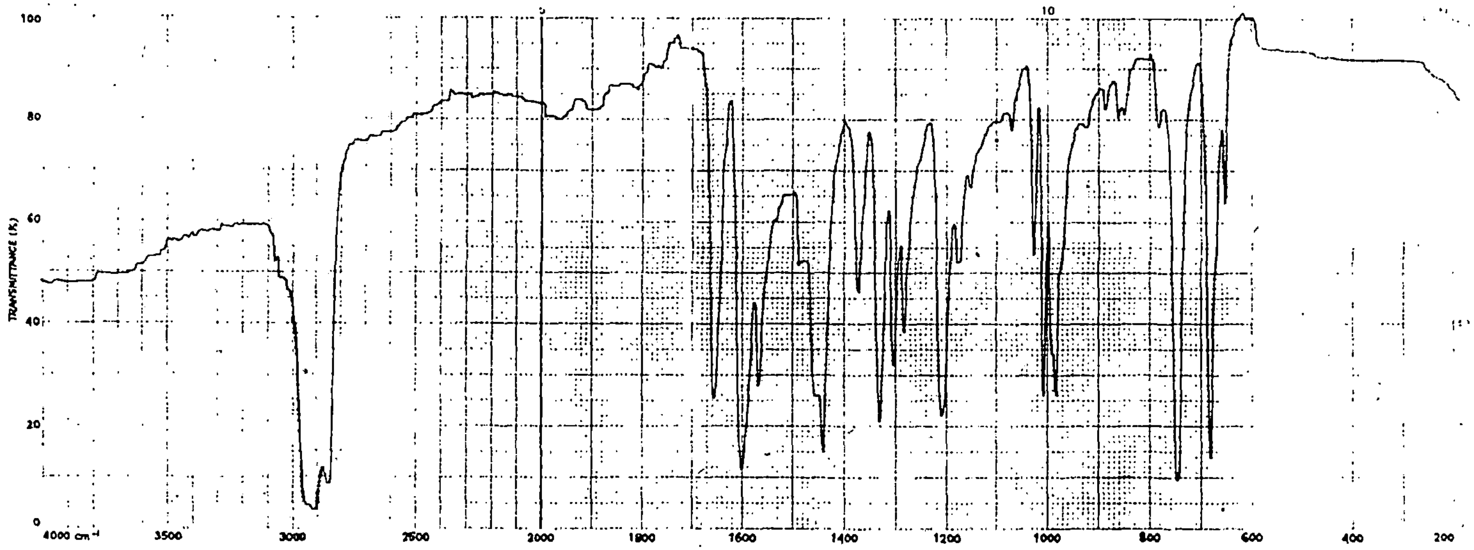


Fig. 29b IR spectrum of benzylideneacetophenone (chalcone)

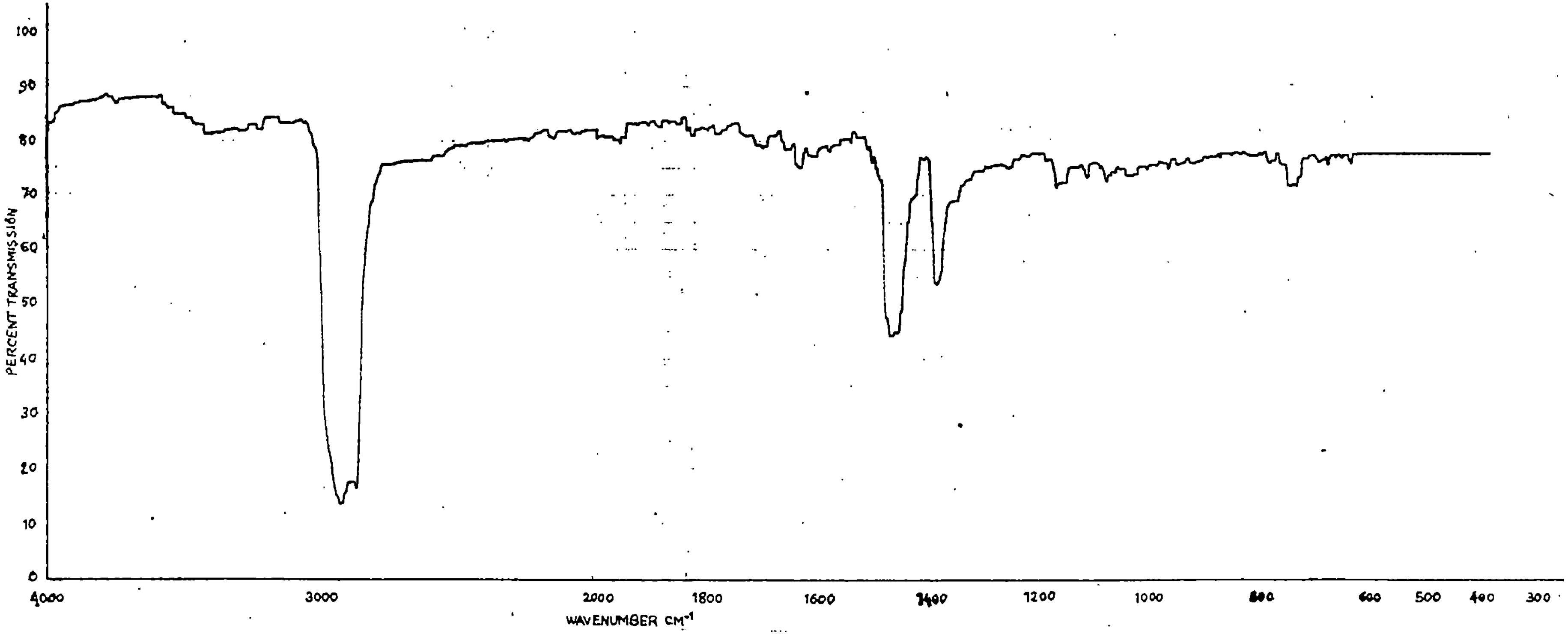


Fig. 29c IR spectrum of stannous chloride

The pyridine hydrochloride was further characterised by IR spectrum. (Fig 29 a)

The filtrate of this reaction after the separation of the crude solid (m.p. 138-139°C) was concentrated to a small volume to yield a solid (m.p. 53-55°C). On further crystallisation from rectified spirit, it melted at 56°C and was found to be chalcone. The elemental analyses and IR spectrum also gave further support.

% Analysis for $C_{15}H_{12}O$

Found	C	86.21	H	5.45
Calculated	C	86.54	H	5.77

IR spectrum (Fig. 29 b)

On changing the reaction conditions and reactant proportion, no change in reaction products could be observed.

(b) <u>With picolines</u>

To the solution of β-benzoyl-α-phenylethyltin trichloride (1.3 gm) in chloroform, a mixture of 0.3 ml picoline (β-picoline or γ-picoline) in minimum quantity of chloroform was added with stirring the reaction mixture. The molar proportion of the reactants was 1:1 . The mixed solution was concentrated on a steam bath and kept undisturbed for two hours. The solid separated was a mixture of picoline hydrochloride (characterised by

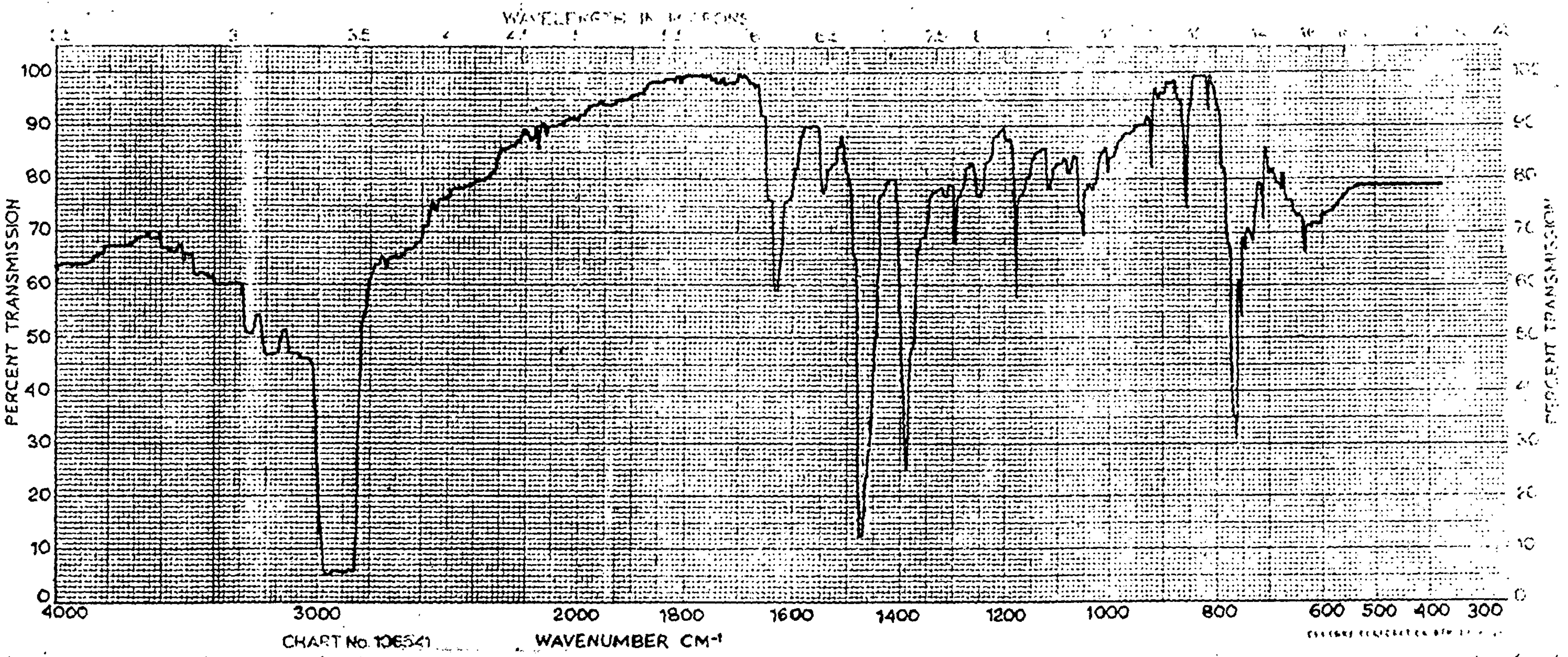


Fig. 30a IR spectrum of β-picoline hydrochloride

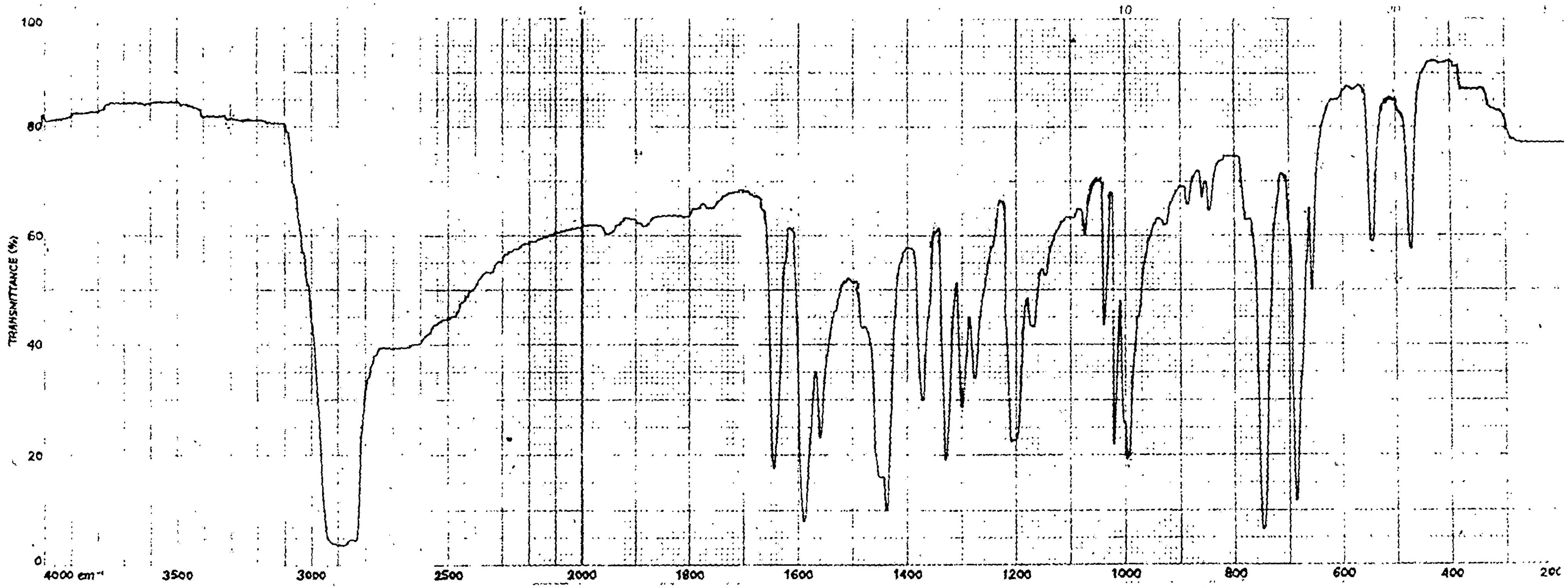


Fig. 30b IR spectrum of benzylideneacetophenone (chalcone)

different analytical data) and stannous chloride (tested by mercuric chloride). Picoline hydrochloride was freed from stannous chloride by recrystallising several times from chloroform.

% Analysis for $C_6H_7N.HCl$ (from β -picoline)

Found	C	55.14	H	5.81	N	11.21
Calculated	C	55.60	H	6.18	N	10.81

Melting point 160°C

IR spectrum (Fig. 30a)

% Analysis for $C_6H_7N.HCl$ (from γ -picoline)

Found	C	55.08	H	6.01	N	10.27
Calculated	C	55.60	H	6.18	N	10.81

Melting point 163°C

IR spectrum (Fig. 30c)

The filtrate of this reaction after the separation of crude solid (mixture of picoline hydrochloride and stannous chloride) was concentrated to produce a solid of melting point 57°C which was characterised as chalcone.

% Analysis for $C_{15}H_{12}O$

	From the reaction with β -picoline				From the reaction with γ-picoline			
Found	C	85.86	H	5.49	C	85.79	H	5.35
Calculated	C	86.54	H	5.77				

IR spectrum (Fig. 30b) ~~(Fig. 30b)~~

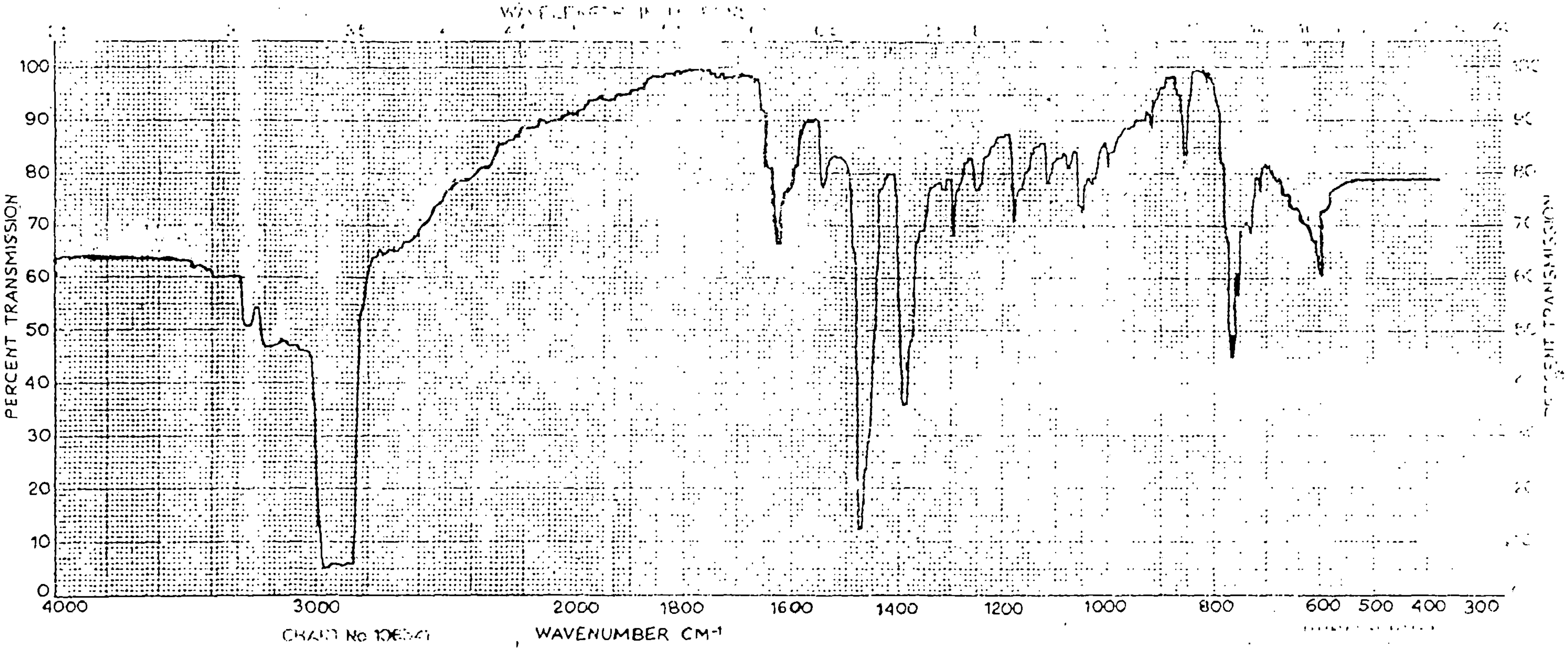


Fig.30c IR spectrum of γ-picoline hydrochloride

Varying the proportion of the reactants, no change of reaction products was observed.

(c) <u>With triethylamine</u>

To the solution of β-benzoyl-α-phenylethyltin trichloride (1.3 gm) in chloroform, a mixture of triethylamine (0.3 gm) in chloroform (molar proportion of the reactants 1:1) was added with stirring. The mixed solution was heated and kept for an hour at room temperature. The white solid formed was freed from stannous chloride by recrystallisation from requisite quantity of chlorform.

Melting point 259°C

% Analysis for $C_6H_{15}N.HCl$

Found	C	51.87	H	10.98	N	10.50
Calculated	C	52.36	H	11.64	N	10.18

IR spectrum (Fig. 31)

The filtrate part of this reaction after the separation of crude solid was concentrated to separate solid substance which was then confirmed as chalcone.

Melting point 56°C

% Analysis for $C_{15}H_{12}O$

Found	C	85.69	H	5.22
Calculated	C	86.54	H	5.77

~~IR spectrum~~ (~~Fig. 31b~~)

No change in reaction products was found on changing the reaction parameters.

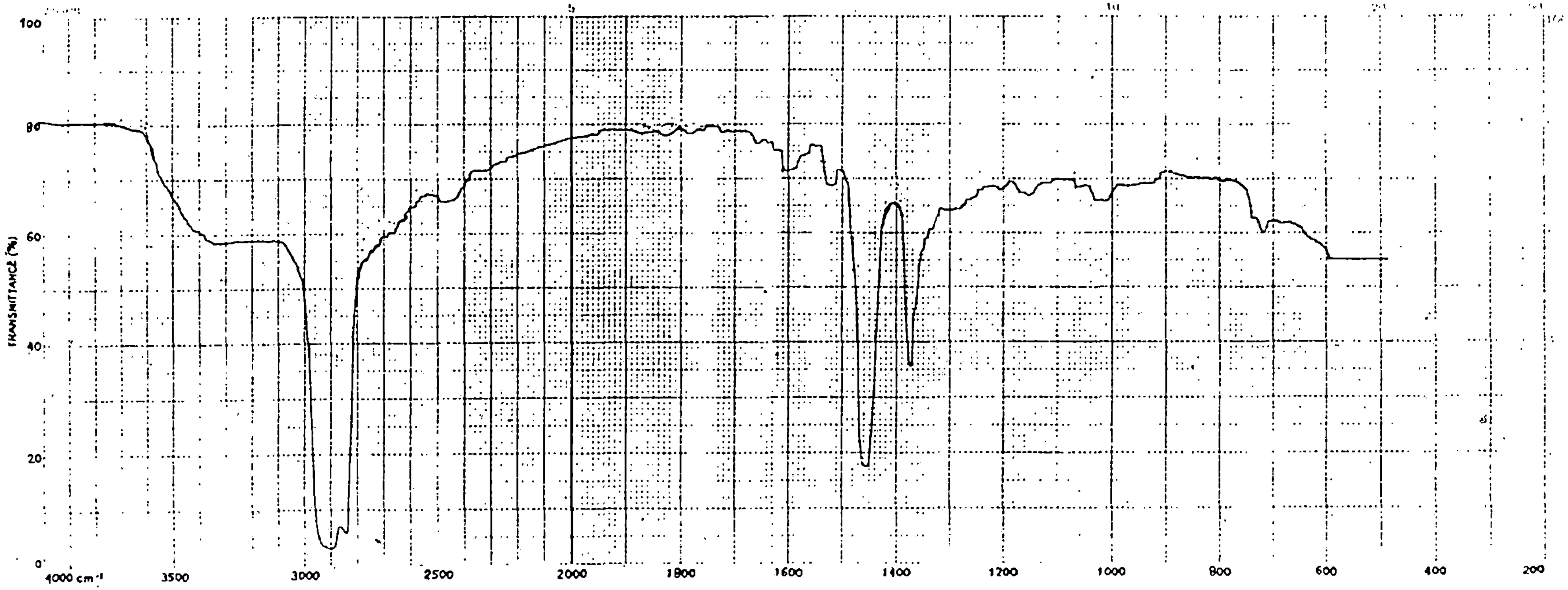


Fig. 31 IR spectrum of Triethylamine hydrochloride

(d) With triethanolamine

To the cold solution of β-benzoyl-α-phenylethyltin trichloride (1.3 gm) in chloroform, a mixture of triethanolamine (0.5 gm) in chloroform (molar proportion of the reactants 1:1) was added with stirring. The mixed solution was heated and kept for an hour at room temperature. The white solid separated was purified to yield triethanolamine hydrochloride and stannous chloride by the method described earlier. Triethanolamine hydrochloride was characterised as follows:

Melting point 176-177°C

% Analysis for $C_6H_{15}O_3N.HCl$

Found	C	38.32	H	8.44	N	7.85
Calculated	C	38.81	H	8.63	N	7.55

IR spectrum (Fig. 32)

The filtrate of this reaction after the separation of crude solid was concentrated to form a solid which was then characterised as chalcone (m.p. 56°C).

% Analysis for $C_{15}H_{12}O$

Found	C	86.01	H	5.43
Calculated	C	86.54	H	5.77

~~IR spectrum~~ (~~Fig. 32 b~~)

No change in reaction products was found on changing the reaction parameters.

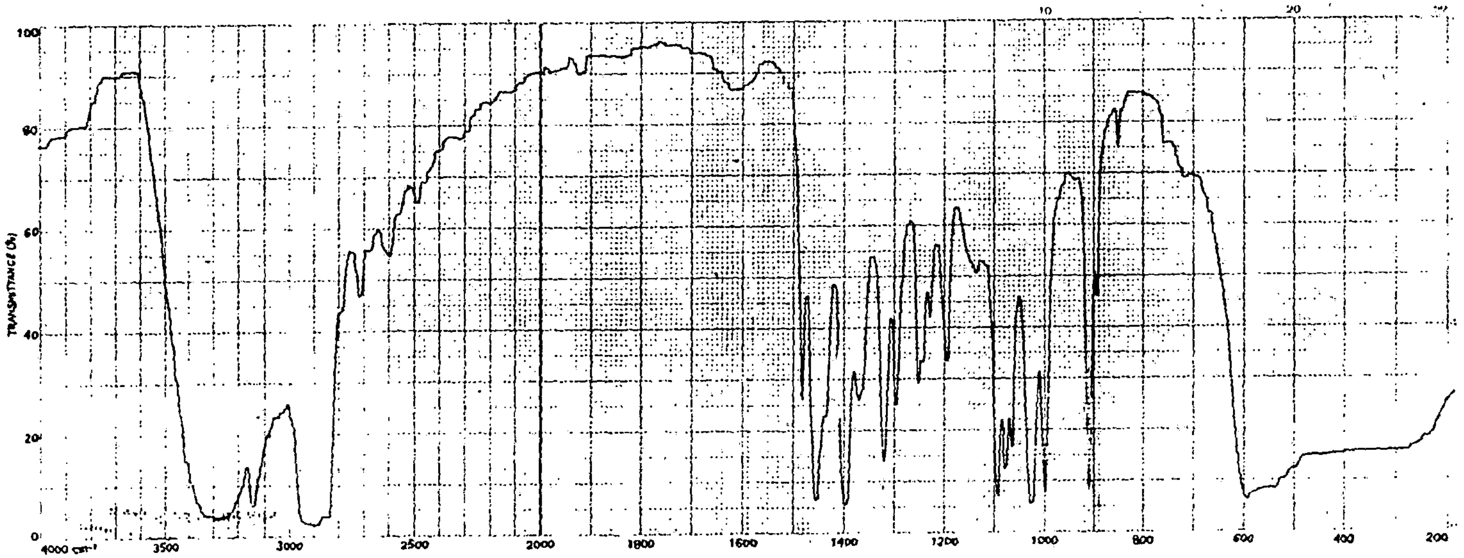


Fig. 32 IR spectrum of Triethanolamine hydrochloride

(e) With 2,2'-bipyridyl

To a solution of β-benzoyl-α-phenylethyltin trichloride (1.3 gm) in chloroform, a chloroform solution of 0.47 gm of 2,2'-bipyridyl was added with constant stirring at room temperature. (The molar proportion of the reactants was 1:1). The mixture was heated on a steam bath and then allowed to stand at room temperature for an hour. The solid substance obtained was a mixture of which one substance was stannous chloride. The stannous chloride was removed by repeated crystallisation from chloroform. The pure product obtained after the separation of stannous chloride melted at 171°C. It was found to be bipyridyl dihydrochloride by elemental analyses and IR spectrum.

% Analysis for $C_{10}H_8N_2.2HCl$

Found	C	52.00	H	4.15	N	12.49
Calculated	C	52.40	H	4.37	N	12.23
IR spectrum						(Fig. 33 a)

The filtrate after the separation of crude product was concentrated to a small volume over steam bath. On cooling it yielded a solid, which after recrystallisation from rectified spirit was confirmed as chalcone (m.p. 56°C) by mixed melting point determination with an authentic sample of chalcone, from elemental analyses and also by IR spectrum.

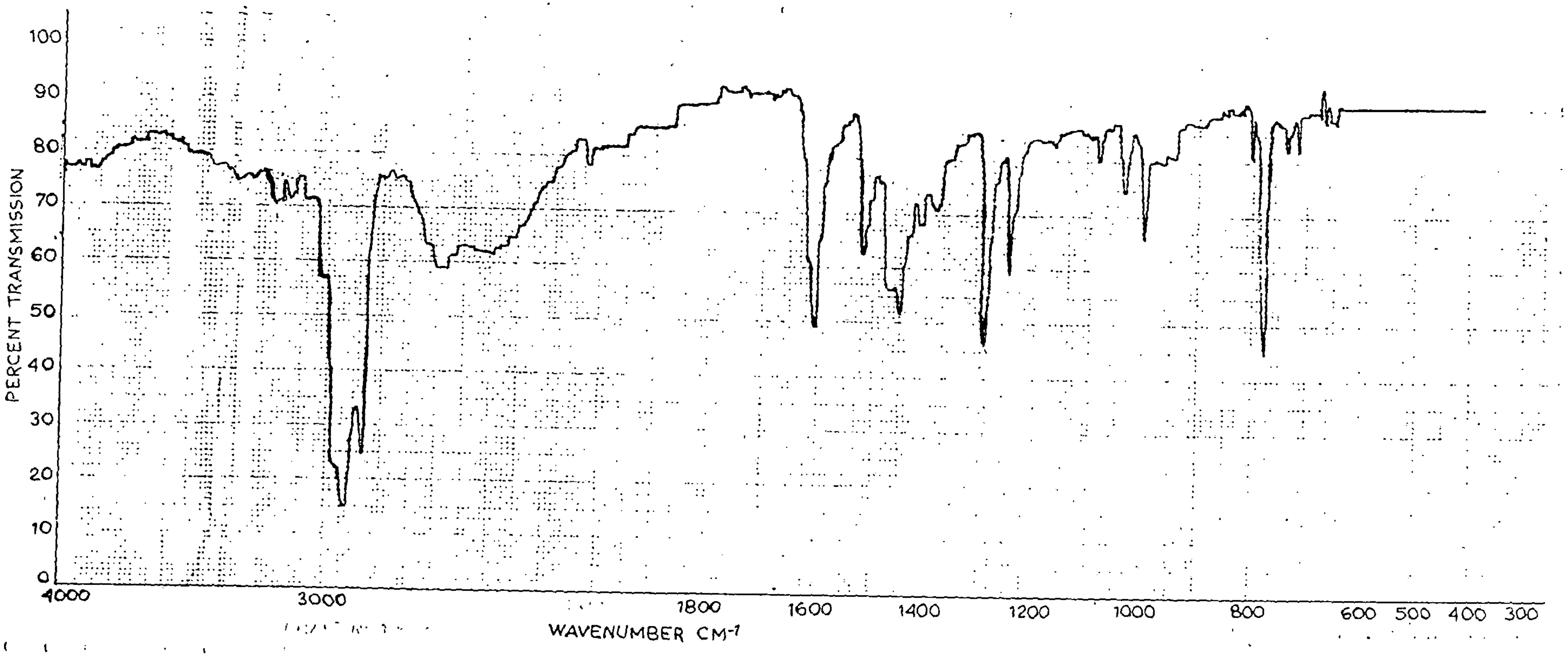


Fig. 33a IR spectrum of 2,2'-bipyridyl dihydrochloride

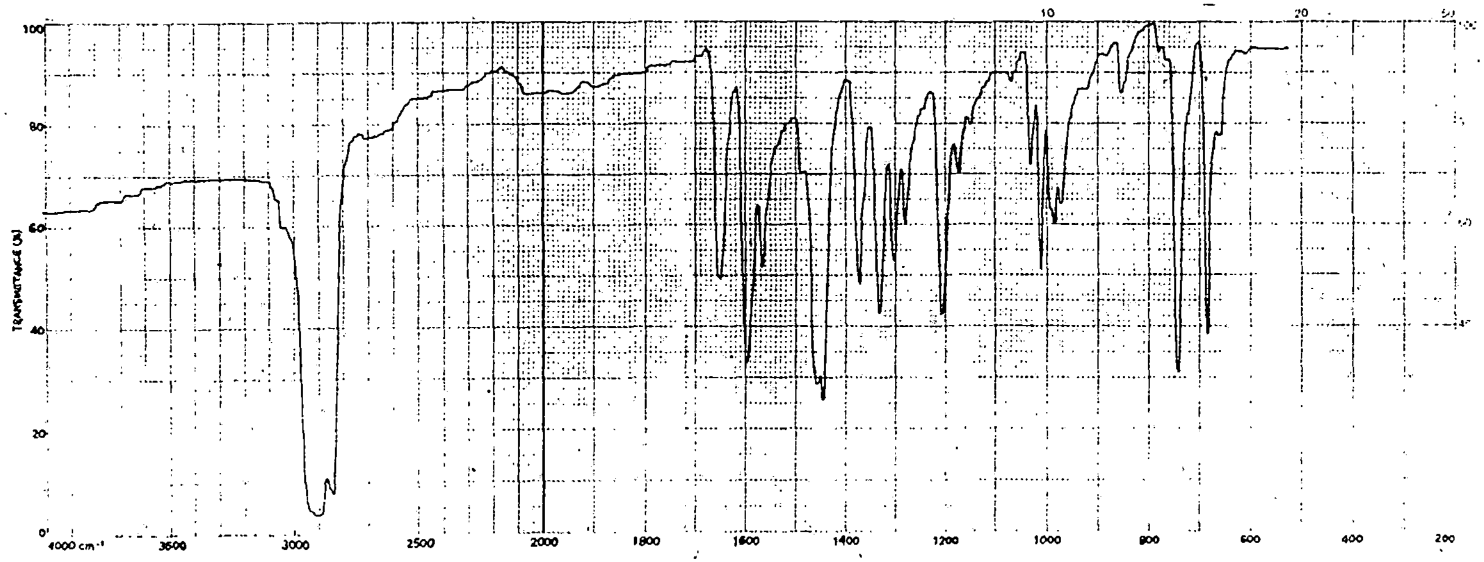


Fig. 33 b IR spectrum of benzylideneacetophenone (chalcone)

% Analysis for $C_{15}H_{12}O$

Found	C	86.86	H	5.33
Calculated	C	86.54	H	5.77

IR spectrum (Fig. 33b)

On changing the reaction conditions etc no change in the reaction products could be found.

(f) With 1,10-phenanthroline (monohydrate)

The compound β-benzoyl-α-phenylethyltin trichloride (1.3 gm) was dissolved in chloroform and a solution of 1,10-phenanthroline (monohydrate) (600 mg) in chloroform was added with stirring. The reactants was used in molar proportion 1:1 the mixed solution was then heated on a steam bath and then cooled to room temperature for about one hour. The solid appeared was found to melt partially at 210°C. This crude solid was freed from stannous chloride by repeated crystallisation from chloroform in the similar fashion as mentioned earlier. The melting point of the crystallised solid was 226°C.

% Analysis for $C_{12}H_8N_2.2HCl$

Found	C	56.08	H	4.23	N	10.54
Calculated	C	56.92	H	3.95	N	11.07

IR spectrum (Fig.34)

The filtrate after the separation of crude solid (m.p. 210°C) was concentrated to a small volume from which

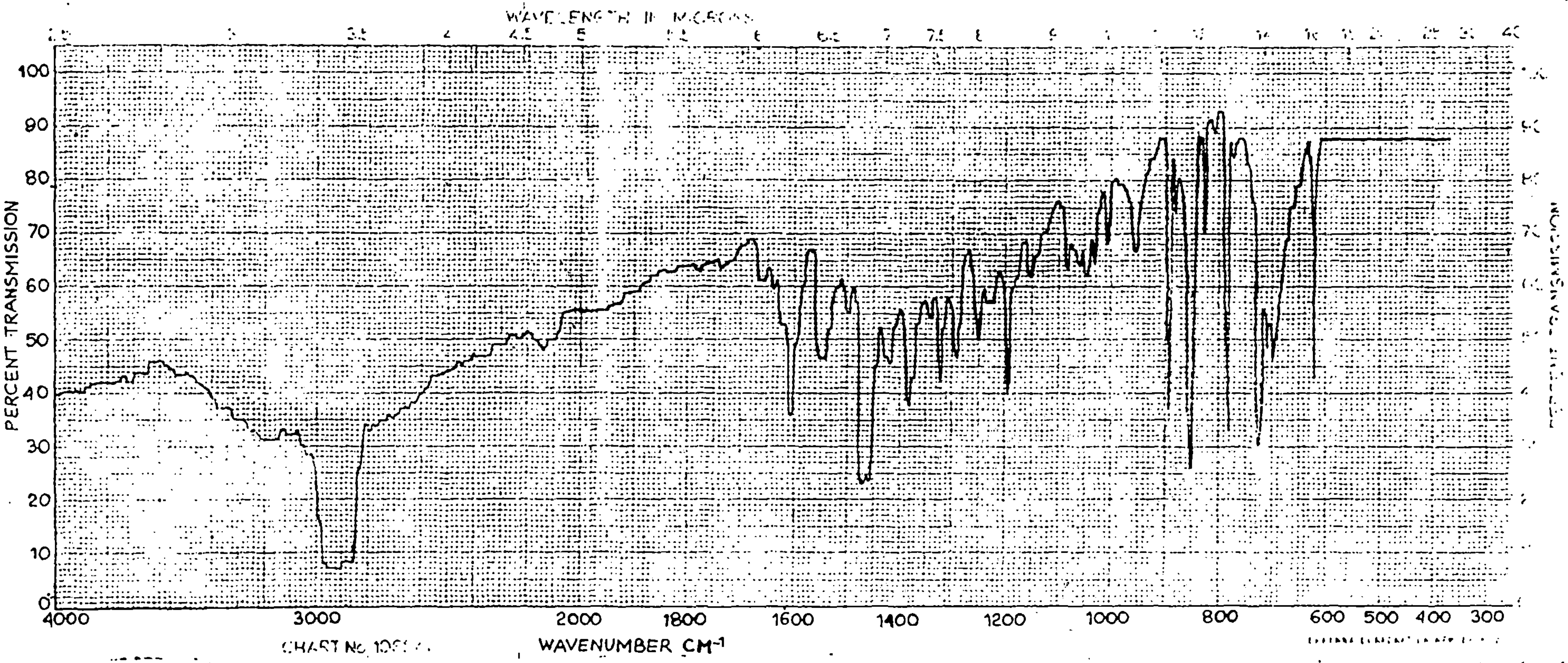


Fig. 34 IR spectrum of 1,10-phenanthroline dihydrochloride

chalcone (m.p. 56°C) was separated as confirmed by elemental analyses and IR spectrum.

% Analysis for $C_{15}H_{12}O$

Found	C	86.17	H	5.87
Calculated	C	86.54	H	5.77

~~IR spectrum~~ (~~Fig. 34b~~)

On changing reaction parameters no change in reaction products was observed.

(g) With 1,5-diphenylthiocarbazone (dithizone)

The compound β-benzoyl-α-phenylethyltin trichloride (0.868 gm) and dithizone (0.512 gm) were taken in 200 ml of chloroform and the mixture was heated over a steam bath for fifteen minutes, when the colour of the solution sharply changed to deep red. The few drops of ammonia solution were added. The colour of the solution changed to green. On concentrating the solution, a gummy product was obtained. The addition of base cleaved the tin-carbon bond, hence a pure product could not be obtained. Addition of pyridine or aniline in place of ammonia did not give any better result. Change of solvents or molar proportion of the reactants did not improve the situation in any way.

β-benzoyl-α-phenylethyltin trichloride and dithizone in chloroform solution in absence of any base gave a deep red coloured solution, from which a crystalline red compound with greenish fluorescence was separated.

The reaction was found to be effected by reactant proportion as evident from the table (Table 1).

Table 1

β-benzoyl-α-phenyl-ethyltin trichloride	Dithizone	Molar ratio	Comment
a) 0.868 gm	0.512 gm	1:1	No crystalline product could be obtained from the gum.
b) 0.868 gm	1.024 gm	1:2	Some crystals could be separate from the gum.
c) 0.868 gm	1.536 gm	1:3	Mainly crystallin Product.

The details of the reaction (c) may be described as follows.

The mixture of β-benzoyl-α-phenylethyltin trichloride (0.868 gm) and dithizone (1.536 gm) in chlorofrom was refluxed in a round bottomed flask for about two hours. It was then cooled and filtered. The very little solid residue obtained was not worked up. The filtrate was concentrated to about one-tenth of its original volume. The solid appeared on cooling was filtered off (unreacted dithizone). The filtrate was again concentrated to a small volume and few drops of methanol were added and kept undisturbed in a corked

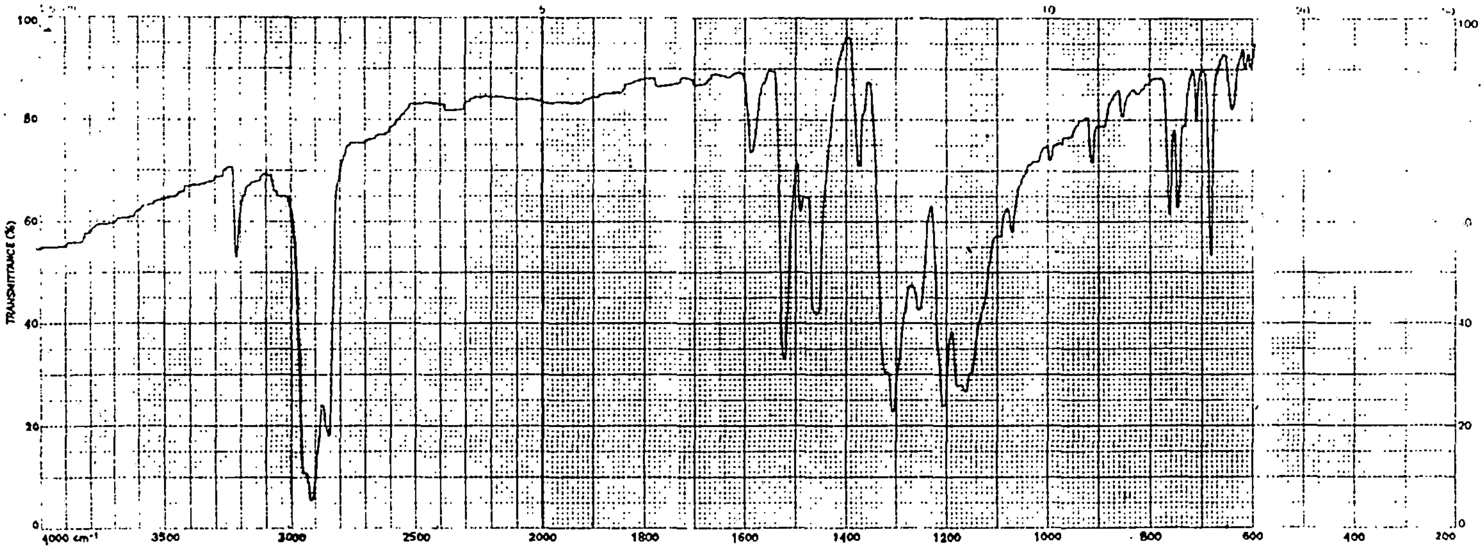


Fig. 35 IR spectrum of 1,5-diphenylthiocarbazone derivative of β-benzoyl-α-phenylethyltin trichloride

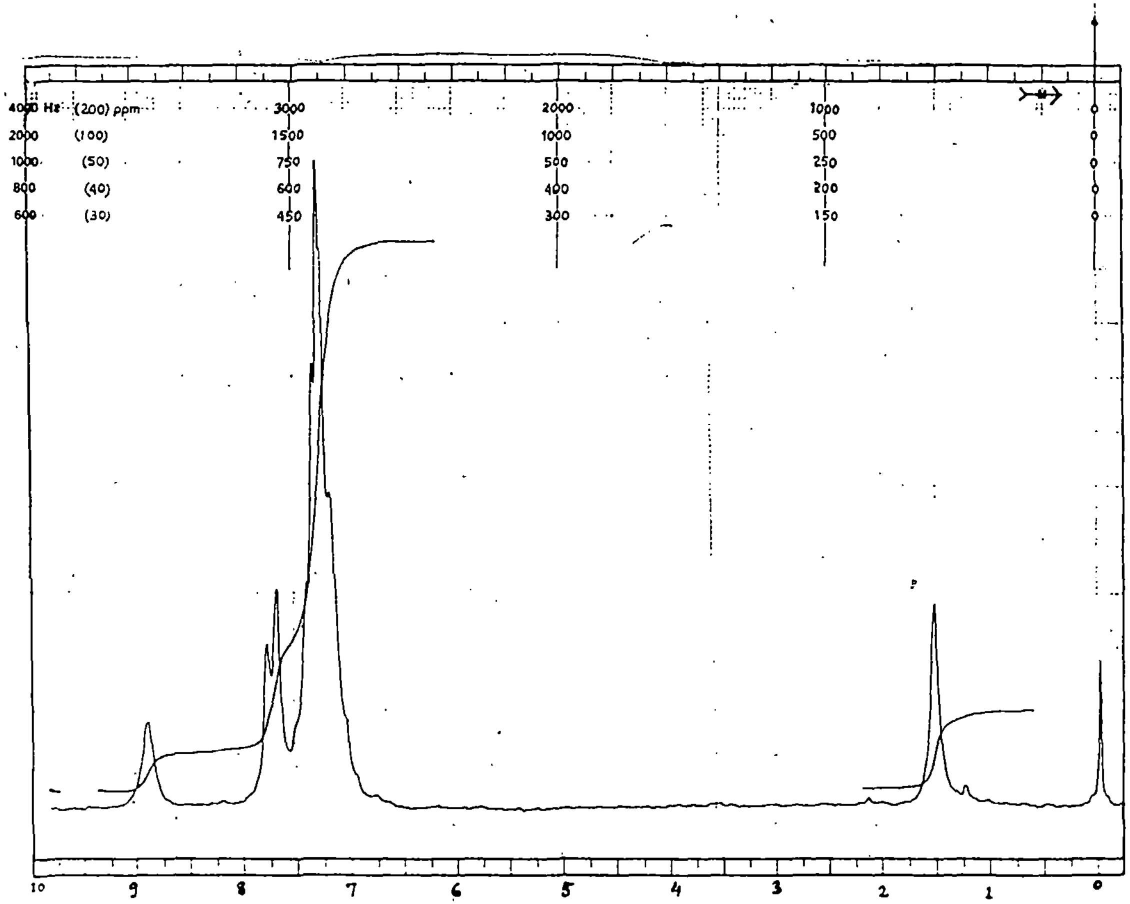


Fig. 36 ^{1}H NMR spectrum of 1,5-diphenylthiocarbazone derivative of β-benzoyl-α-phenylethyltin trichloride.

conical flask for two days. Fine red crystals with greenish fluorescent appeared. It was purified by repeated crystallisations in the same fashion. The pure solid showed a melting point 185°C.

% Analysis for $C_{34}H_{31}N_8ClSSn$

Found	C	52.65	H	3.99	N	13.63	Sn	13.88
Calculated	C	53.02	H	4.02	N	14.55	Sn	15.46

IR spectral data (cm^{-1}) (Fig. 35)

3205 w, 2850-2950 vs(b), 1590 w, 1520s, 1490 w, 1455 s, 1375 m, 1325 sh, 1305 s, 1260 m, 1205 s, 1150-1180 s(b), 1065 w, 915 w, 815 sh, 855 w, 765 m, 745 m, 710 w, 680 s, 635 m, 615 w, 600 w.

^{1}H NMR spectral data (chemical shift δ) (Fig. 36)

Methine, methyl, phenyl and =NH protons appear at 1.25, 1.5, 7.0-8.0 and 8.9 respectively.

The compound was found soluble in chloroform, benzene, diethylether etc.

(h) With 1,5-diphenylcarbazone

The reaction of β-benzoyl-α-phenylethyltin trichloride with diphenylcarbazone was carried out with the molar proportion of the reactants 1:3 . Thus 0.87 gm of β-benzoyl-α-phenylethyltin trichloride and 1.53 gm of diphenylcarbazone were taken in 200 ml chloroform and refluxed for about one and half hour. It was then cooled and filtered. The residue being very small was rejected.

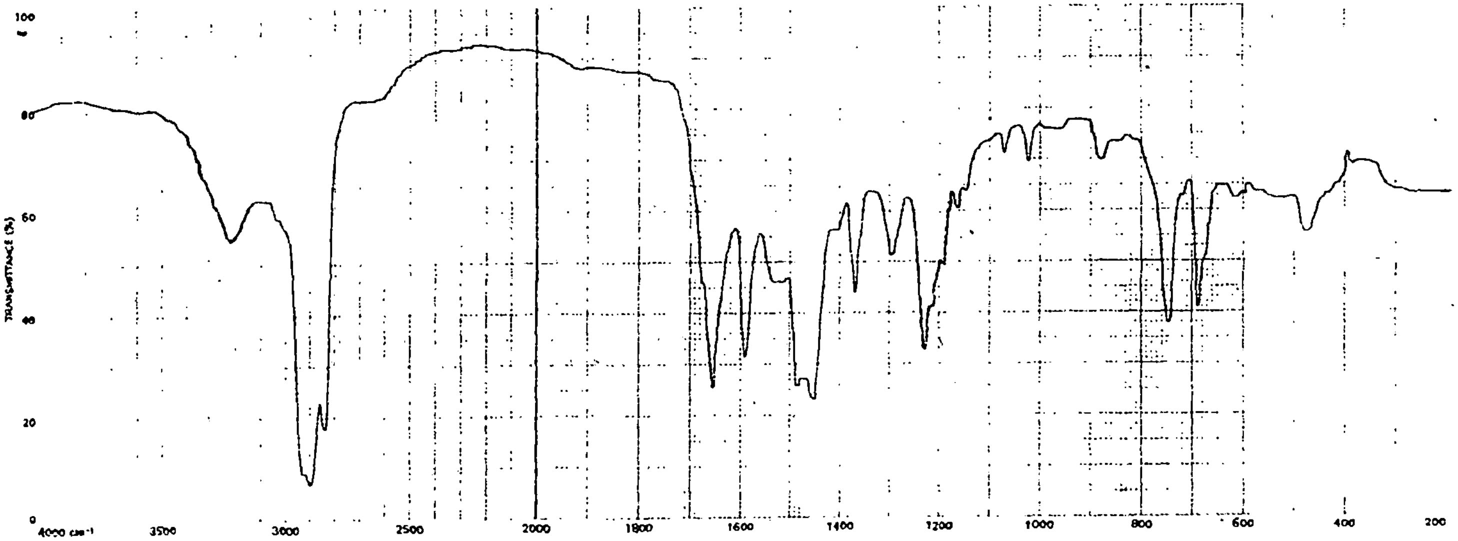


Fig. 37 IR spectrum of 1,5-diphenylcarbazone derivative of β-benzoyl-α-phenylethyltin trichloride

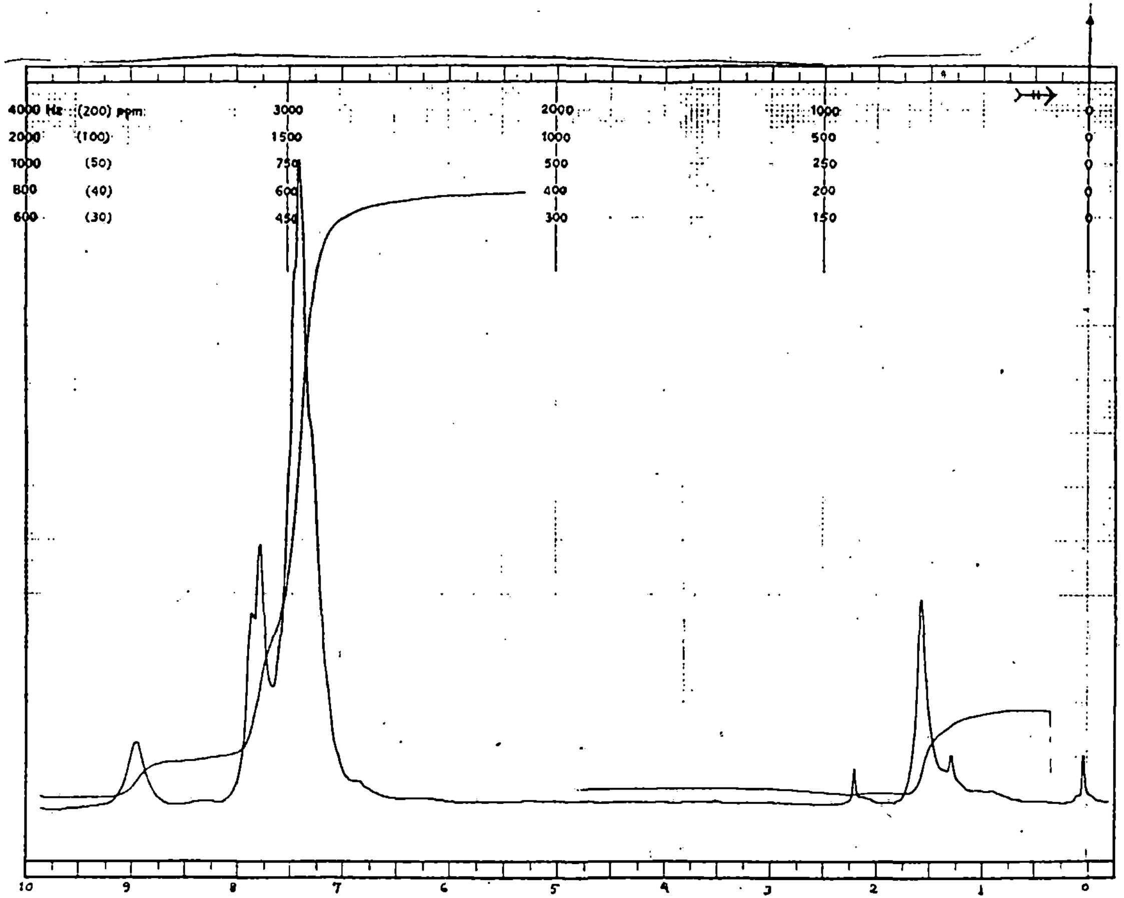


Fig. 37a ^{1}H NMR spectrum of 1,5-diphenylcarbazone derivative of β-benzoyl-α-phenylethyltin trichloride

The filtrate was concentrated from which unreacted diphenylcarbazone was separated which was then filtered off. This filtrate was concentrated to a very small volume from which a gummy solid was separated. The deep violet crude solid could not be freed completely from gummy matter. The melting point of this solid was found 175°C.

% Analysis for $C_{34}H_{31}N_8OClSn$

Found	C	54.95	H	4.69	N	14.28	Sn	15.37
Calculated	C	55.32	H	4.20	N	15.18	Sn	16.13

IR spectral data (cm^{-1}) (Fig. 37)

3300 m(b), 2840-2940 vs (b), 1655 s(b), 1590 s, 1540 sh, 1485 s, 1455 vs, 1370 m, 1295 m, 1240 m, 1210 s(b), 1165 w, 1170 w, 1120 w, 880 w, 745 s, 685 s, 620 w, 475 m.

The compound was found to dissolve fairly in chloroform, benzene, diethylether etc.

2. Reactions of β-acetyl-α-phenylethyltin trichloride

(a) With pyridine

Pyridine (0.25 ml) mixed with small amount of chloroform was added to a chloroform solution of β-acetyl-α-phenylethyltin trichloride (1.1 gm) with constant stirring at room temperature. The reactants used in the molar proportion 1:1. The reaction mixture was then worked up as described in the previous similar experiment.

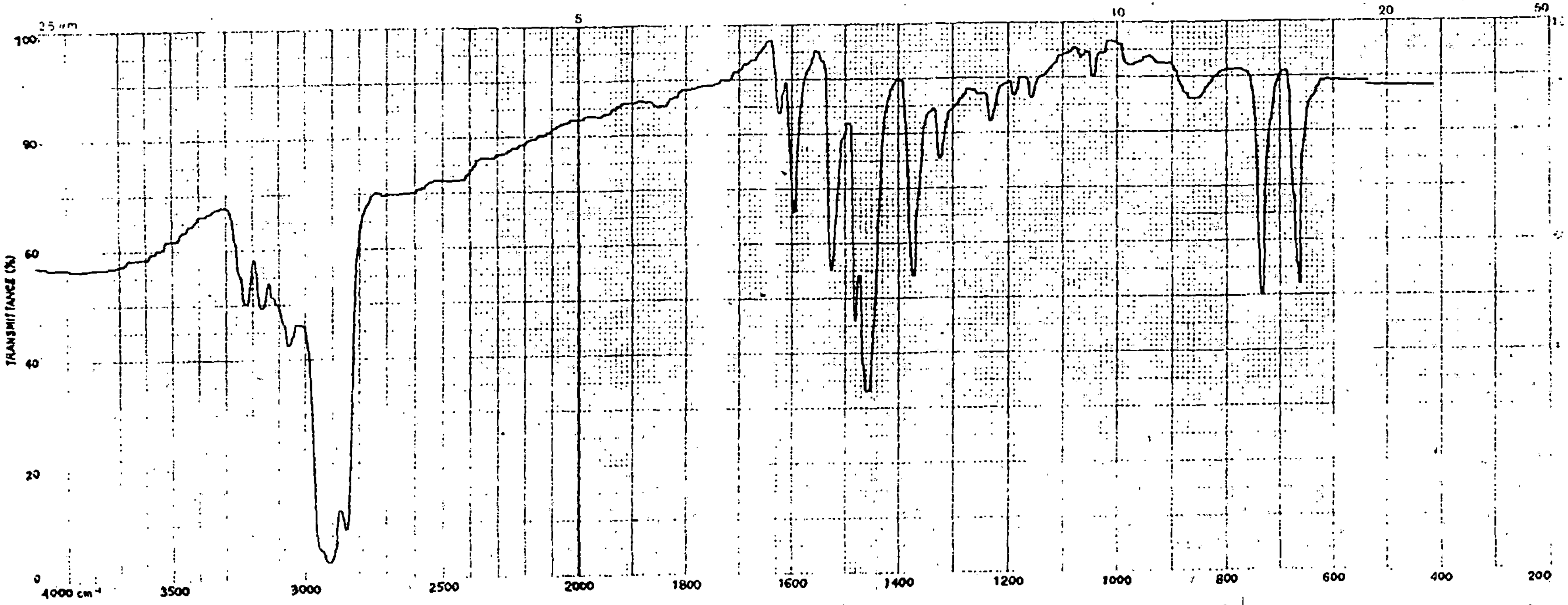


Fig. 38a IR spectrum of pyridine hydrochloride

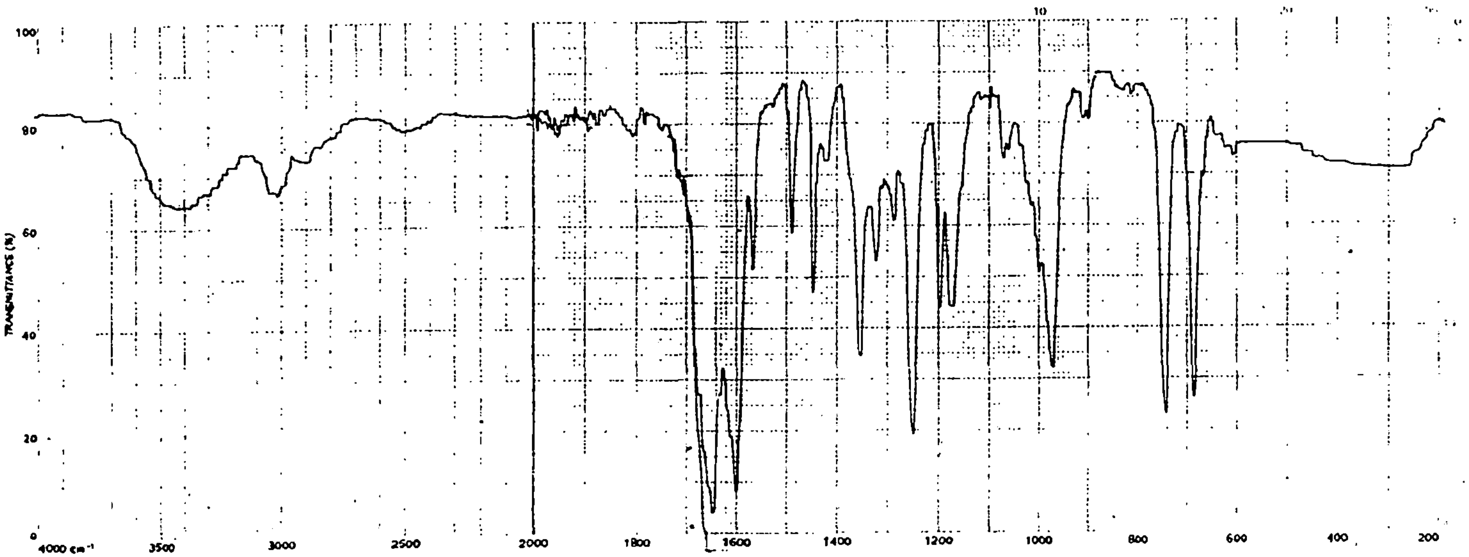


Fig. 38b IR spectrum of Benzylideneacetone (neat).

From the reaction product pyridine hydrochloride (m.p. 141°C) and stannous chloride were recovered.

% Analysis for $C_5H_5N.HCl$

Found	C	51.61	H	5.37	N	12.39
Calculated	C	51.95	H	5.19	N	12.12

IR spectrum (Fig. 38a)

The filtrate of this reaction after the separation of crude pyridine hydrochloride and stannous chloride was concentrated to a small volume. Little amount of gummy solid was obtained which could not be purified further, but an infrared spectrum (neat, Fig. 38b) of the gummy substance was taken and was found very much similar to that of pure benzilideneacetone.

No change of reaction products could be found on changing the reaction conditions including the molar proportion of the reactants.

(b) With picolines

To the solution of β-acetyl-α-phenylethyltin trichloride (1.1 gm) in chloroform, a mixture of 0.3 ml picoline (β-picoline or γ-picoline) in little amount of chloroform was added with stirring the reaction mixture. The molar proportion of the reactants was 1:1. The reaction mixture was then worked up in the same fashion as done in

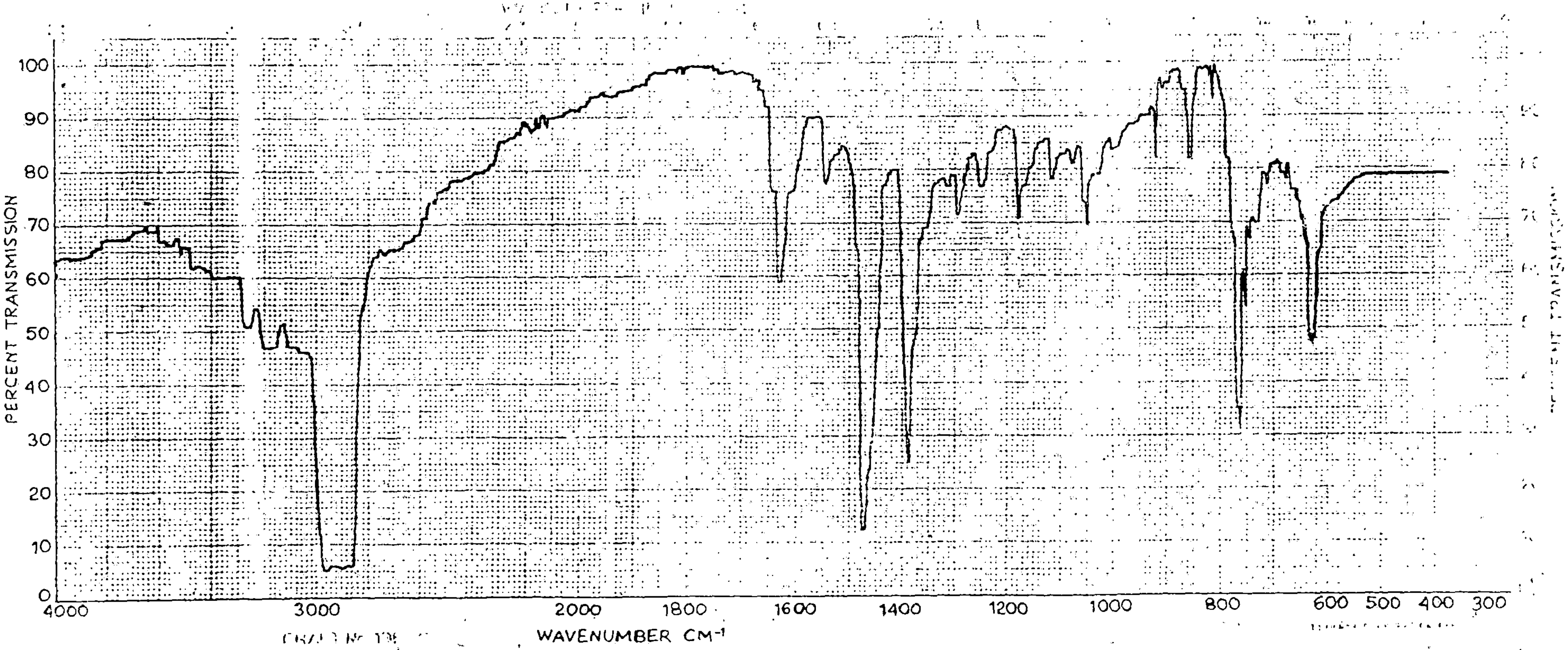


Fig. 39a IR spectrum of β -picoline hydrochloride

case of similar reaction with β-benzoyl-α-phenylethyltin trichloride.

% Analysis for $C_6H_7N.HCl$ (from β-picoline)

Found	C	54.84	H	5.84	N	11.31
Calculated	C	55.60	H	6.18	N	10.81

Melting point 159-160°C

IR spectrum (Fig. 39a)

% Analyses for $C_6H_7N.HCl$ (from γ-picoline)

Found	C	56.23	H	6.21	N	10.27
Calculated	C	55.6	H	6.18	N	10.81

Melting point 163°C

IR spectrum (Fig. 39b)

The filtrate of this reaction (in each case) after the separation of picoline hydrochloride and stannous chloride produced gummy mass after concentration to a very small volume. The gummy mass could not be purified further.

The reaction was carried out by changing the molar proportion of the reactants and no change in product was found.

(c) <u>With triethylamine</u>

To the chloroform solution of β-acetyl-α-phenylethyltin trichloride (1.1 gm), a mixture of triethylamine (0.3 gm) in chloroform (molar proportion of the reactants

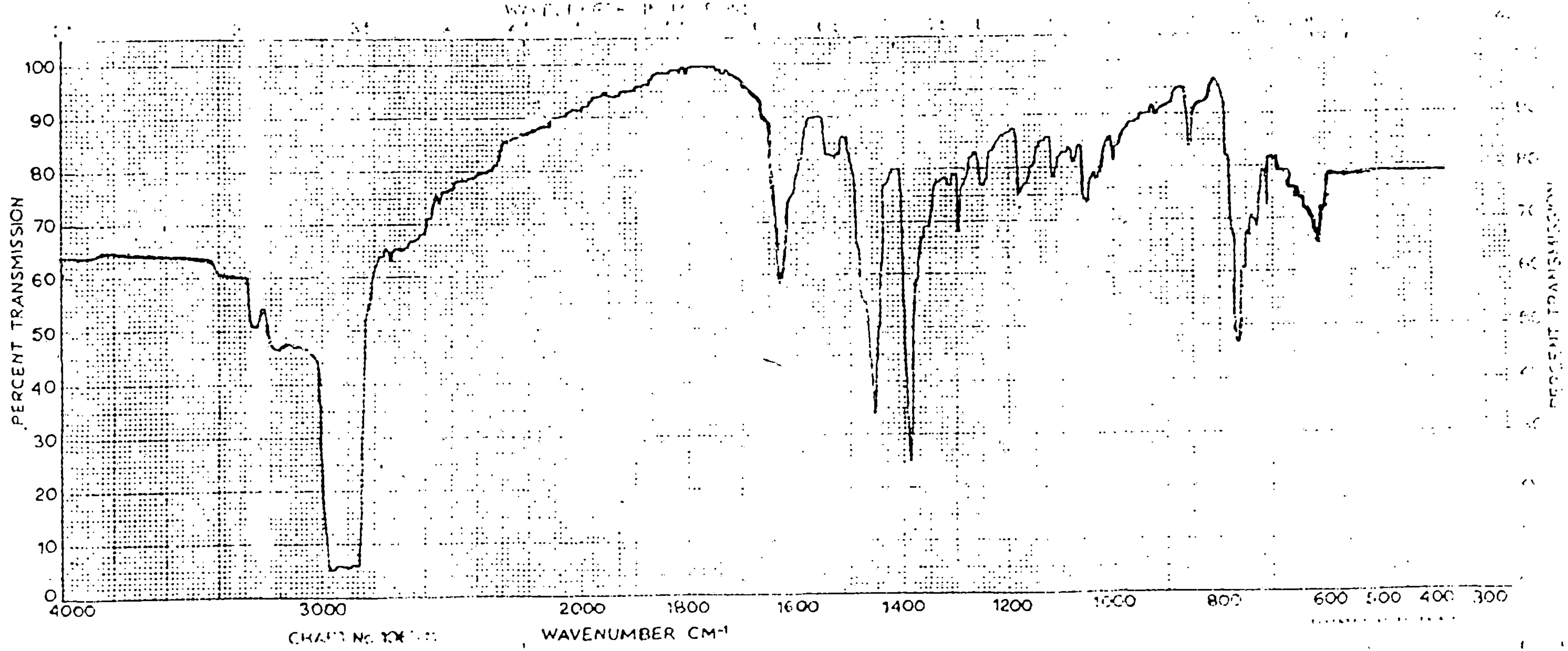


Fig. 39b IR spectrum of γ-picoline hydrochloride

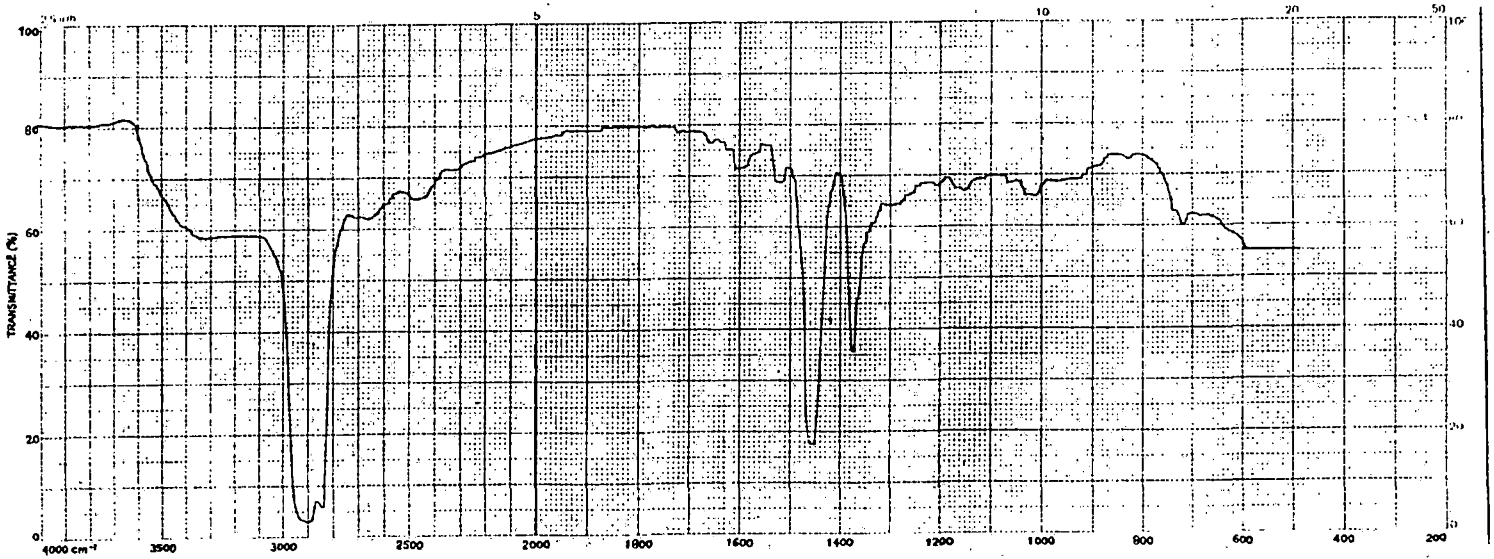


Fig. 40 IR spectrum of Triethylamine hydrochloride

1:1) was added with stirring and then the mixture was heated and kept at room temperature for about one hour. White solid separated was freed from stannous chloride by recrystallisation from requisite amount of chloroform.

Melting point (dec) 259°C

% Analysis for $C_6H_{16}O_3NCl$

Found	C	55.85	H	11.21	N	10.71
Calculated	C	52.36	H	11.64	N	10.18

IR spectrum (Fig. 40)

The presence of benzylideneacetone and stannous chloride was detected in the filtrate part of the reaction after the separation of crude solid.

No change of products was found on varying reaction parameters.

(d) With triethanolamine

To the chloroform solution of β-acetyl-α-phenylethyltin trichloride, (1.1 gm) a mixture of triethanolamine (0.5 gm) in chloroform (molar proportion of the reactants 1:1) was added with stirring and then the mixture was heated and kept undisturbed for about two hours. White solid separated was freed from stannous chloride by recrystallisation from requisite amount of chloroform.

Melting point 177°C

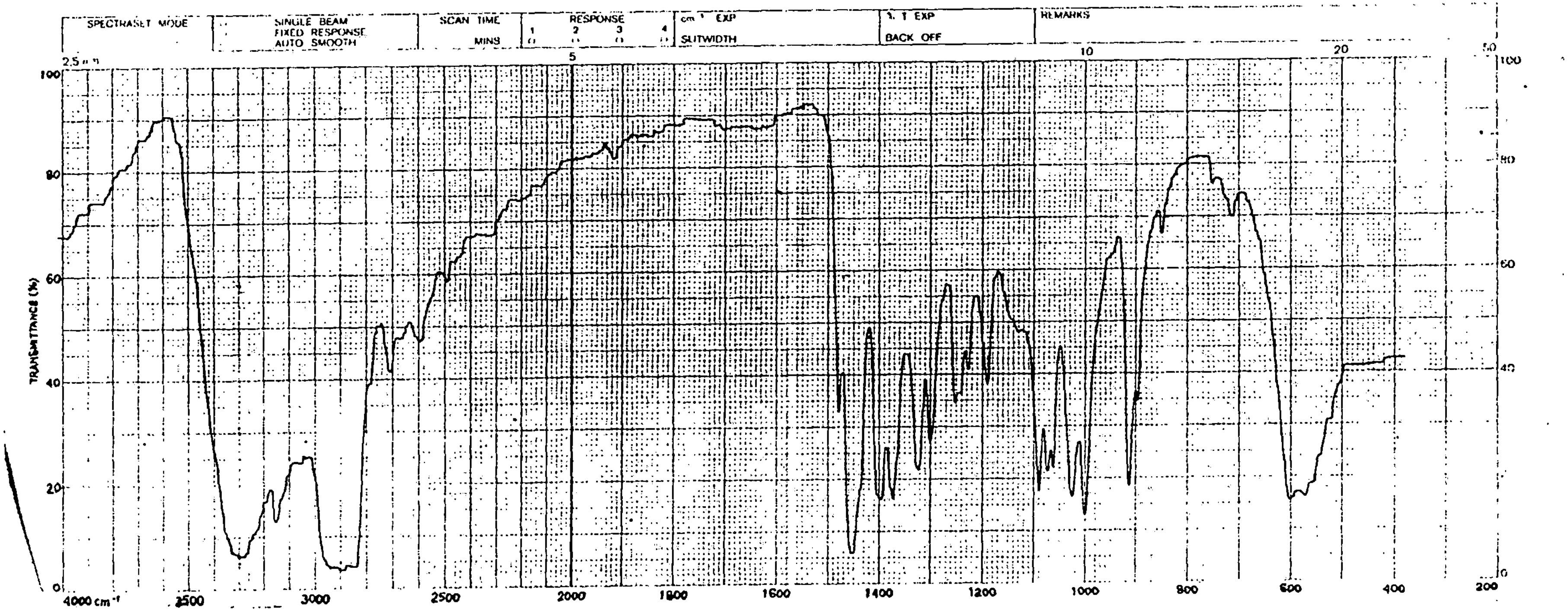


Fig. 41 IR spectrum of Triethanolamine hydrochloride

% Analysis for $C_6H_{16}O_3NCl$

Found	C	38.23	H	8.41	N	7.97
Calculated	C	38.81	H	8.63	N	7.55

IR spectrum (Fig. 41)

The filtrate of this reaction after the separation of crude solid was concentrated to a gummy solid which was confirmed to contain benzylideneacetone and stannous chloride.

No change of products was found on varying reaction parameters.

(e) With 2,2'-bipyridyl

To a chloroform solution of β-acetyl-α-phenylethyltin trichloride (1.1 gm) a chloroform solution of 2,2'-bipyridyl (470 mg) was added with stirring. The reactants used in the molar proportion 1:1. The mixed solution was then heated on a steam bath and then cooled to room temperature. On standing for about one hour, a solid was found to separate. The solid was crystallised several times from chloroform to separate stannous chloride from this. The melting point of the crystallised product was found 170°C.

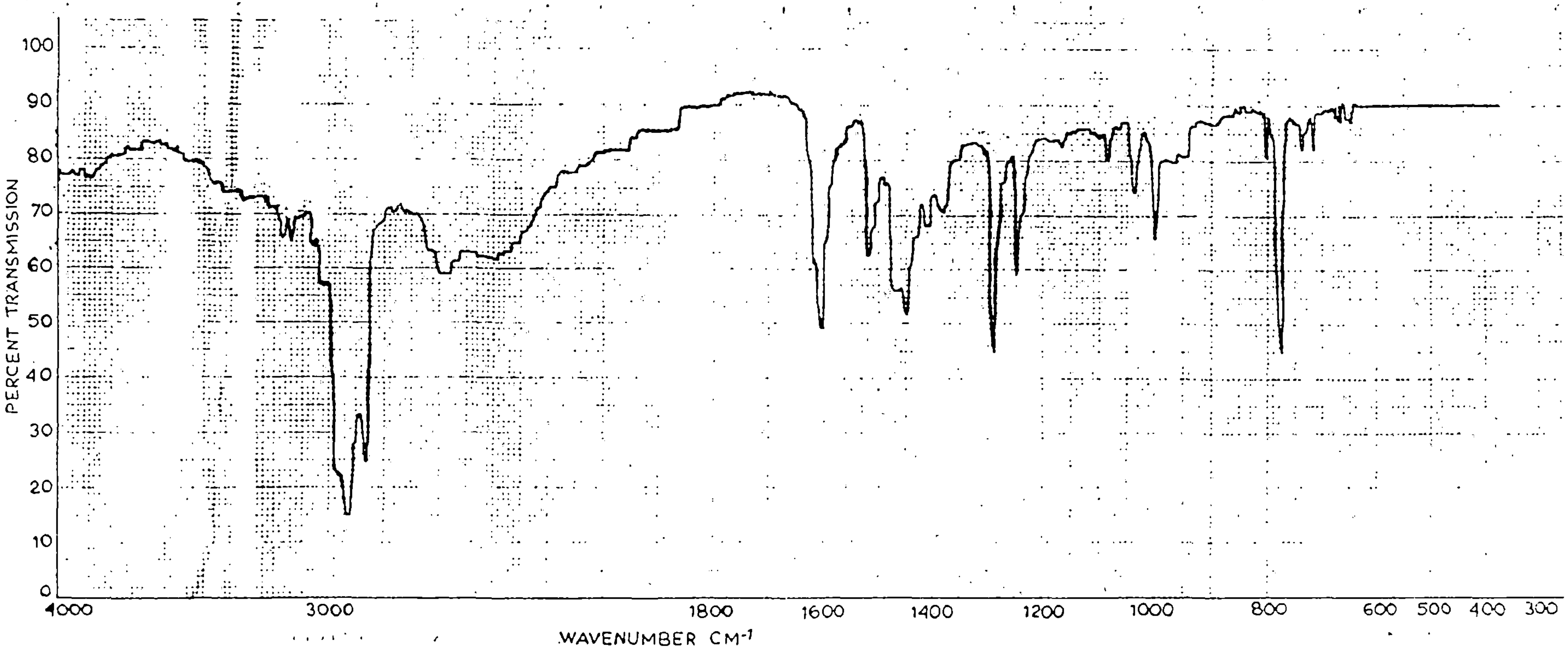


Fig. 42 IR spectrum of 2,2'-bipyridyl dihydrochloride

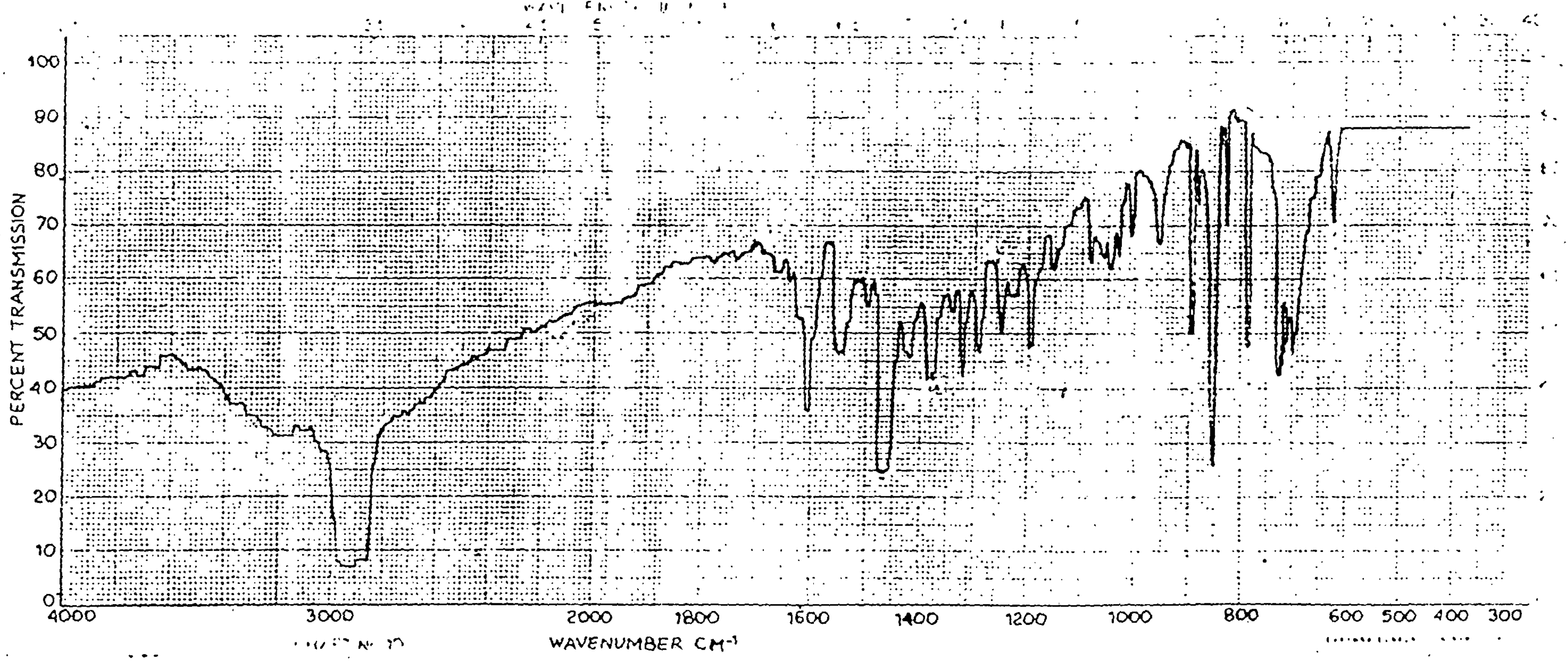


Fig. 43 IR spectrum of 1,10-phenanthroline dihydrochloride

% Analysis for $C_{10}H_8N_2 \cdot 2HCl$

Found	C	52.12	H	4.03	N	11.71
Calculated	C	52.40	H	4.37	N	12.23

IR spectrum (Fig. 42)

The filtrate after the separation of the crude solid furnished gummy solid on concentration. The gummy solid could not be properly characterised.

The reaction products remained unchanged even on changing the reaction parameters in any way.

(f) With 1,10-phenanthroline (monohydrate)

To a chloroform solution of β-acetyl-α-phenylethyltin trichloride (1.1 gm), a chloroform solution of phenanthroline (monohydrate) (600 mg) was added with stirring. The mixed solution was then heated on a steam bath and then kept at room temperature for one hour. The reactants was used in the molar proportion 1:1. On keeping to room temperature, a solid (m.p. 210°C along with little unmelted portion) appeared. The crude solid was freed from stannous chloride by repeated crystallisation from chloroform and the melting point of the pure solid was found 226°C.

% Analysis for $C_{12}H_8N_2 \cdot 2HCl$

Found	C	55.73	H	4.17	N	10.50
Calculated	C	56.92	H	3.95	N	11.07

IR spectrum (Fig. 43)

The filtrate of the crude solid (m.p. 210°C) could not be worked up to produce any gum free solid.

On changing the reaction parameters in any way, no change in reaction products could be observed.

(g) With 1,5-diphenylthiocarbazone (dithizone)

The compound β-acetyl-α-phenylethyltin trichloride (1·25 gm) and dithizone (2.55 gm) were mixed and taken in chloroform medium (the molar proportion of the reactants was kept at~1:3) and was refluxed for about two hours. It was then cooled and filtered. The filtrate was concentrated to some extent (one-tenth of its original volume). Unreacted dithizone came out of the solution which was separated by filtration. The filtrate was concentrated to a very small amount and to this few drops of ammonia solution was added and kept for two days. Fine greenish fluorescent red crystals separated out. The crystals were purified by repeated crystallisation and the melting point of the purified compound was found 190°C.

% Analysis for $C_{34}H_{31}N_8ClSSn$

Found	C	47.12	H	3.44	N	13.65	Sn	14.42
Calculated	C	55.32	H	4.02	N	14.55	Sn	15.46

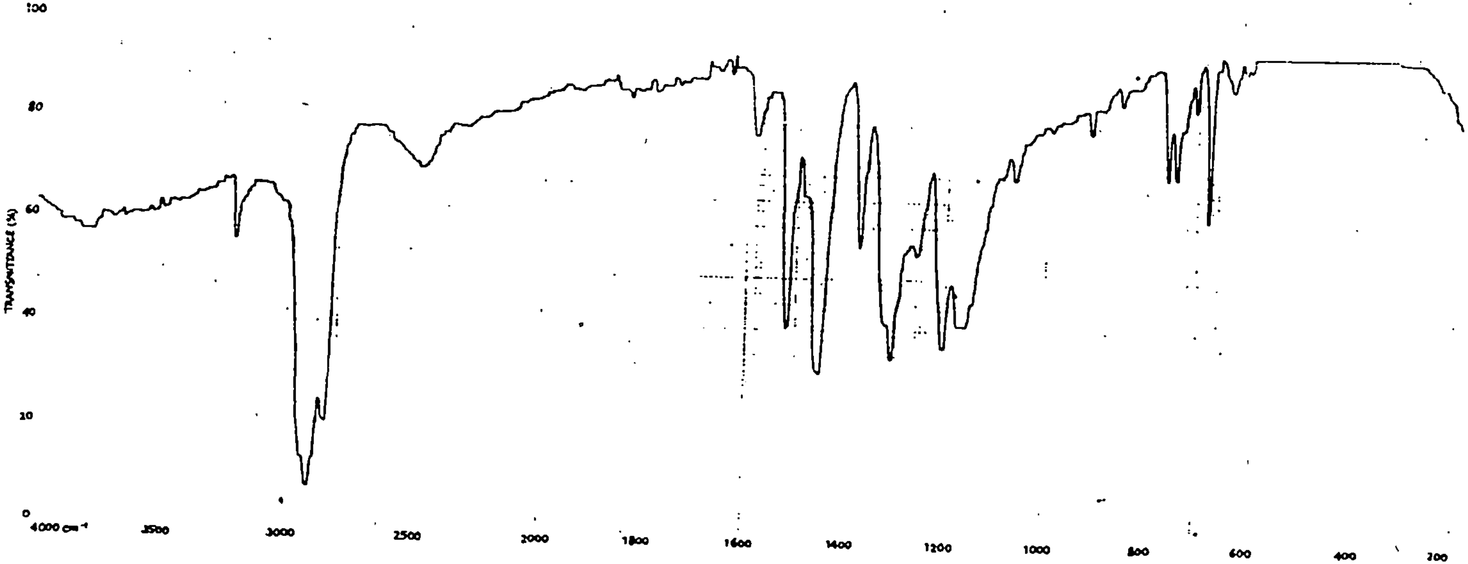


Fig. 44 IR spectrum of 1,5-diphenylthiocarbazone derivative of β-acetyl-α-phenylethyltin trichloride

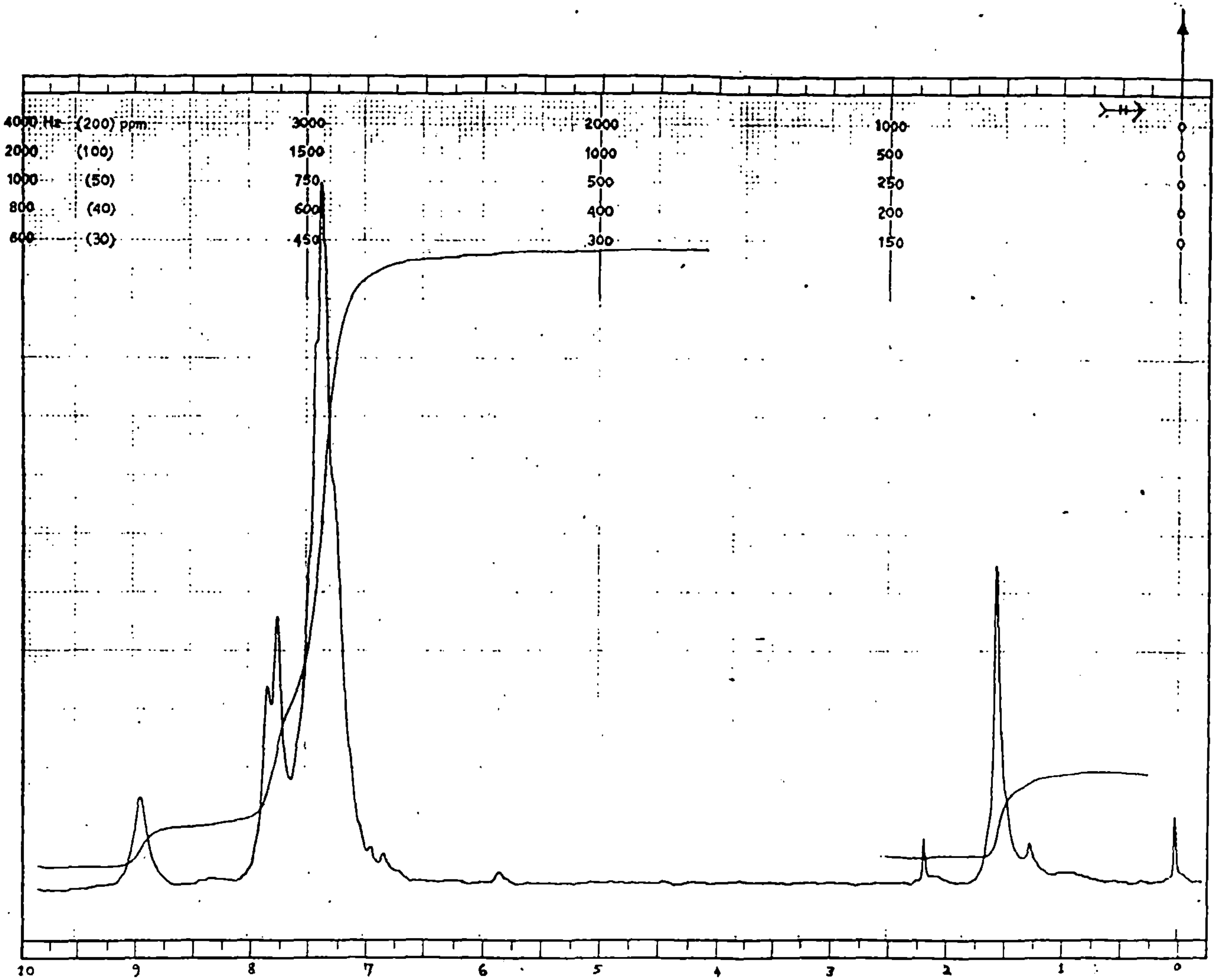


Fig. 45 ^{1}H NMR spectrum of 1,5-diphenylthiocarbazone derivative of β-acetyl-α-phenylethyltin trichloride

IR spectral data (cm^{-1}) (Fig. 44)

3205 w, 2840-2940 vs (b), 1585 w, 1520 vs, 1490 sh, 1455 vs, 1375 s, 1325 sh, 1305 vs, 1260 m, 1210 vs, 1140-1180 s(b), 1065 w, 915 w, 855 w, 760 m, 740 m, 705 w, 680 s, 635 w.

^{1}H NMR spectral data (chemical shift δ) (Fig. 45)

Methine, methyl, phenyl and =NH protons appear at 1.25, 1.5, 7.0-8.0 and 8.9 respectively.

The compound was found soluble in chloroform, benzene, diethylether etc.

(h) <u>With 1,5-diphenylcarbazone</u>

The reaction of β-acetyl-α-phenylethyltin trichloride and diphenylcarbazone was carried out similarly by using the molar proportion of the reactants as 1:3. Thus 1·25 gm of β-acetyl-α-phenylethyltin trichloride and 2.40 gm of diphenyl carbazone were taken in chloroform medium and refluxed for about one and half hour. It was then cooled and filtered. The filtrate was concentrated to small volume from which unreacted diphenylcarbazone was separated out. The filtrate was concentrated to get a gummy solid (deep violet) which could not be further purified. The melting point of the crude solid was found 175°C.

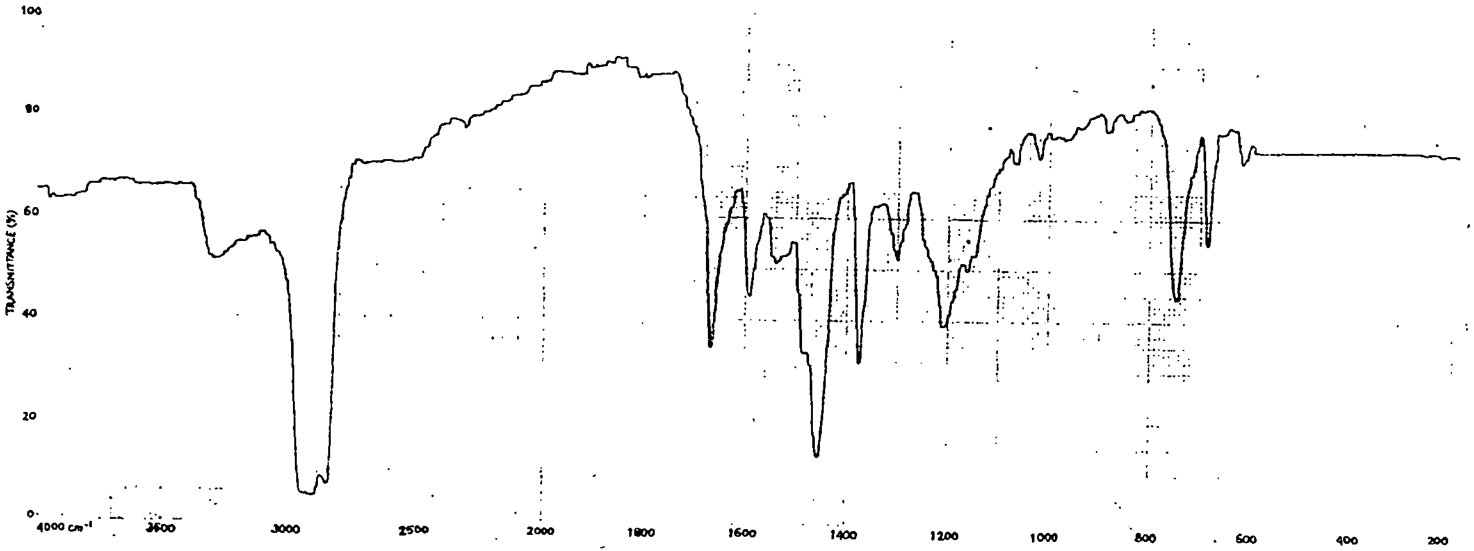


Fig. 46 IR spectrum of 1,5-diphenylcarbazone derivative from the reaction of β-acetyl-α-phenylethyltin trichloride

% Analysis for $C_{34}H_{31}N_8OClSn$

Found	C	53.82	H	4.57	N	15.79	Sn	15.26
Calculated	C	55.32	H	4.20	N	15.18	Sn	16.13

IR spectral data (cm^{-1}) (Fig. 46)

3300 m(b), 2840-2960 vs(b), 1660 m(b), 1590 m, 1540 m(b), 1490 sh, 1455 vs, 1375 s, 1300 m, 1255 sh, 1210 s(b), 1120 w, 745 s, 685 s, 620 w.

The compound was fairly soluble in chloroform, benzene, diethyl ether etc.

The reaction of β-benzoyl-α-phenylethyltin trichloride and β-acetyl-α-phenylethyltin trichloride separately with various bases like aniline, trimethylamine and -picoline were studied and in each dase base hydrochloride could be obtained. Though these reactions were not investigated in detail, the melting points of these base hydrochlorides were determined in each case and found as follows:

Aniline hydrochloride	195°C
Trimethylamine hydrochloride	282-284°C
α-picoline hydrochloride	152°C.

The reactions of β-benzoyl-α-phenylethyltin trichloride with thiourea, glycine were attempted separately. In each case no reaction took place and the original reactants could be recovered unchanged.

DISCUSSIONS

The IR spectra of estertin adducts and chelates revealed some interesting features. Maughan, Wardell and Burley (88) studied the IR spectra of the adducts of $Cl_3SnCH_2CH_2COOR$ (R = CH_3, iso-C_3H_7, C_6H_5, H) and $Cl_2Sn(CH_2CH_2COOR)_2$ [where R = CH_3 and iso-C_3H_7]. They reported that ν(C = O) stretching frequency of $Cl_3SnCH_2CH_2COOCH_3$ appeared at 1660 cm^{-1} compared to simple esters appearing at 1740 cm^{-1} due to internal coordination of carbonyl to tin atom. Adduct or complex formation may influence the ν(C = O) frequency. Complexation of $Cl_3SnCH_2CH_2COOCH_3$ with chelating ligands like bipyridyl or phenanthroline shifts the ν(C = O) frequency to $\sim$ 1730 cm^{-1} from 1660 cm^{-1}. Similar observations have also been reported by other workers (101,102,103 but with mono dentate ligands like pyridine, quinoline, etc. the ν(C = O) frequency was not effected appreciably. The 1:1 complexation by monodentate ligands brought about only slight shifts (sometimes no change) in the carbonyl absorption values. For example, in pyridine adduct ν(C=O) appeared at 1648 cm^{-1} and in quinoline adduct it appeared at 1665 cm^{-1}. The small shifts in ν(C = O) frequency was attributed for little change in the character of the C = O bond in presence of additional ligand molecule attaching to tin atom. In going from the penta coordinated tin (in $Cl_3SnCH_2CH_2COOCH_3$) to hexa coordinated tin in the corresponding adduct one might assume in the absence of other effects, the ν(C = C) values should increase, since the $>C = O \longrightarrow Sn$ interaction should be reduced and as a consequence greater double bond character of the carbonyl bond would result. However, there was no such observation indicating the presence of some other compensating effect.

This compensating effect could be back bonding from tin to oxygen (using the carbonyl antibonding orbital) as the additional ligand complexes. Another cause may be structural change from trigonal bipyramidal (before complexation) to octahedral (after complexation).

The observation made by Maughan and Wardell with the compound β-carbomethoxyethyltin trichloride is shown below (Table 2).

Table 2 The carbonyl frequencies for mixtures of β-carbomethoxyethyltin trichloride(A) and donors (D) in methylene chloride solution at 25 ± 1°C are shown.

Donor	[A]/[D]	$(C=O)(cm^{-1})$	Comments
	1/0	1668	-
Triphenylphosphine	1/1	1667	No interaction
Trimethoxyphosphine	1/1.5	1668	1/1 complexation carbonyl group still coordinated
Pyridine	1/1	1648	1/1 complex
	1/14	1730	1/2 complex
Quinoline	1/1	1665	1/1 complex
Bipyridyl	1/1	1730	Chelate complex
Phenanthroline	1/1	1733	Chelate complex

During the present investigation, the following data were obtained (Table 3).

Table 3

Compound	Melting point in ^{o}C	$\nu(C=O)$ in cm^{-1}
$Cl_3SnCH_2CH_2COOC_2H_5$	68	1665
$Cl_3SnCH_2CH_2COOC_2H_5$.pyridine (adduct)	91	1665
$Cl_3SnCH_2CH_2COOC_2H_5$. β-picoline (adduct)	81	1670
$Cl_3SnCH_2CH_2COOC_2H_5$. γ-picoline (adduct)	85	1670
$Cl_3SnCH_2CH_2COOC_2H_5$. iso quinoline (adduct)	87	1660
$Cl_3SnCH_2CH_2COOC_2H_5$.tripenyl phosphine (adduct)	60	1660
$Cl_3SnCH_2CH_2COOC_2H_5$.2,2'-bipyridyl (chelate complex)	88	1730
$Cl_3SnCH_2CH_2COOC_2H_5$.1,10-phenanthroline (chelate complex)	97	1735
$ClSn(Ox)_2CH_2CH_2COOC_2H_5$ (Bis-oxinate chelate complex)	181	1735
$ClSn(HDz)_2CH_2CH_2COOC_2H_5$ (Bis-dithizonate chelate complex)	161	1700

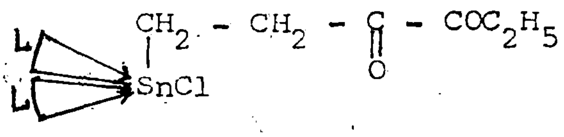
[HOx = 8-hydroxy quinoline (oxine) and H_2Dz = 1,5 diphenylthiocarbazone (dithizone)]

In case 1:1 complexation (adduct formation) with monodentate ligand pyridine, there is no change in $\nu(C = O)$ absorption value from that of uncomplexed molecule. In the cases of 1:1 adduct with β-picoline and γ-picoline there are little increase in $\nu(C = O)$ absorption values and the 1:1 adducts with isoquinoline and triphenyl phosphine show little decrease in $\nu(C = O)$ absorption values in their infrared spectra. All these are in good agreement with Wardell's observation for similar type of compounds.

It is suggested that with adduct formation the penta coordinated tin is converted to a octahedral hexa coordinated tin atom.

But with the bidentate ligands like bipyridyl or phenanthroline which form chelate complex with $Cl_3SnCH_2CH_2CO_2C_2H_5$ there are sharp changes in $\nu(C = O)$ frequency from 1665 cm^{-1} (before complexation) to range of 1730-1735 cm^{-1} indicating a clear change in intramolecular carbonyl coordination to tin centre. It is also reasonable that such accommodation of a bidentate ligand to a penta coordinated tin centre may initiate the fission of the internal carbonyl coordination which resulted a hexa coordinated structure as hepta coordinated tin may not be stable. To make tin hexa coordinating by such bidentate ligand molecules, the intramolecular carbonyl coordination should be cleave. The spectral evidences support such contention.

In the present case two coordinated complex compound of p-carboethoxyethyltin trichloride viz.



$$\mathrm{L_2 \rightrightarrows \underset{SnCl}{\overset{CH_2}{|}}{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}COC_2H_5}$$

where L = C_9H_7NO,
$C_{13}H_{11}N_4S$

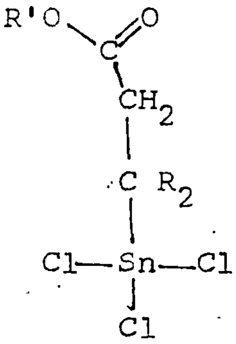
have been prepared.

In the infrated spectra of these two compounds (oxinate and dithizonate) the cleavage of intramolecular carbonyl coordination is indicated by the increase in carbonyl stretching absorption frequency from $\nu(C = O)$ value 1665 cm^{-1} (for parent estertin chloride) to $\nu(C = O)$ value 1735 cm^{-1} (for derived chelate). For bis-oxinate derivative of β-carboethoxyethyltin trichloride $\nu(C = O)$ absorption value is seen at 1735 cm^{-1} and for bis - dithizonate derivative $\nu(C = O)$ absorption value is seen at 1740 cm^{-1}. Except the study of carbonyl absorption frequency of these compounds, still another absorption frequency is very important which is $\nu(Sn \leftarrow N)$ stretching frequency since this mode is absent in both the starting compounds, the estertin chloride and the ligands. But this $\nu(Sn \leftarrow N)$ absorbs in the region below 400 cm^{-1} in the infrared spectrum. Unfortunately no assignment could be made for this stretching mode in the prepared adduct and chelate derivatives of β-carboethoxyethyltin trichloride because of the lack of experimental facilities.

Hence beside the study of such $\nu(C = O)$ stretching absorption in the infrared spectra of such complex compounds (adducts, adduct type chelates and chelates) of β-carboethoxyethyltin trichloride there are ~~no other~~ hardly any remarkably distinct~~ive~~ absorption peaks.

During the reaction of β-carboethoxyethyltin trichloride with 1,3 diaminopropane, Sn-C bond fission ~~was~~ took place ~~happended~~ giving rise to two solid reaction products both were of high melting points ∼ 244°C but one of them did not contain tin which was confirmed by elemental analyses as 1,3 diaminopropane dihydrochloride and the other was confirmed as stannous chloride. Their infrared spectra were also in accordance with their ~~interpreted~~ molecular composition.

Organotin alkyl and aryl compounds show strong Lewis acid character in the formation of large number of adducts or chelate compounds with various types of Lewis bases. The Lewis acid character of estertin type (I)

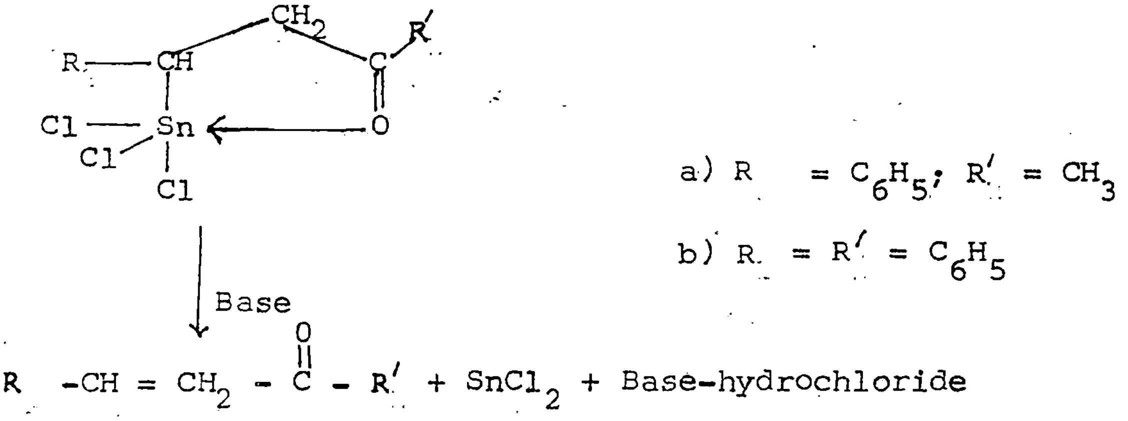


I

R' = alkyl

R = H, alkyl

has been established by the formation of a number adducts or chelates with different Lewis bases. However, from the investigations carried out so far, it was found that β-benzoyl -α- phenyl ethyl tin trichloride and β-acetyl-α -phenyl ethyl tin trichloride on reaction with a number of Lewis bases did not yield any adduct or chelate compounds.



a) R = C_6H_5; R′ = CH_3

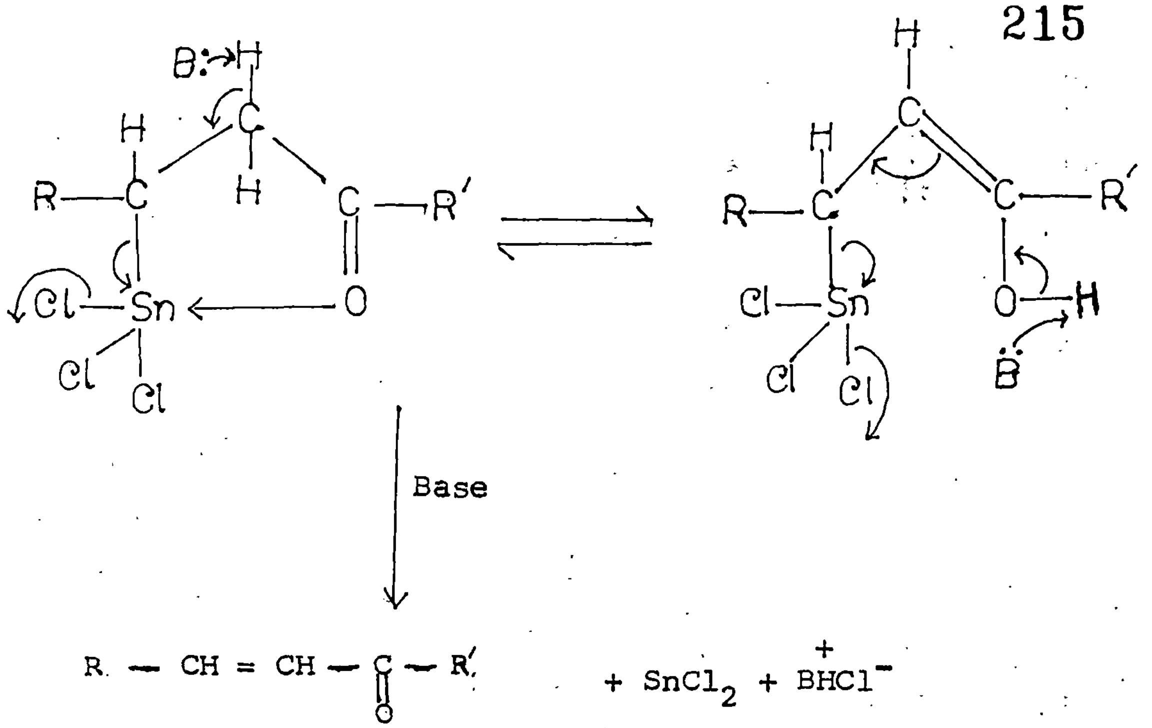
b) R = R′ = C_6H_5

$$R-CH=CH_2-\overset{O}{\overset{\|}{C}}-R' + SnCl_2 + \text{Base-hydrochloride}$$

Scheme I

except with Dithizone and Diphenyl carbazone which have already been discussed.

In β-benzoyl-α-phenyl ethyl tin trichloride, tin is assumed to be penta coordinated (discussed in previous chapter) through the coordination of carbonyl function. The coordination of carbonyl ~~withdraws~~ shifts the non bonding electrons towards tin thereby making the carbonyl carbon more electro positive. However, in compound $C_2H_5O.CO.CH_2CH_2SnCl_3$ the ester $-OC_2H_5$ group could reduce the electropositivity of carbonyl carbon relative to the purely ketonic compoud like (a) and (b). Obviously the proton abstraction followed by Sn-C bond cleavage to yield the precursor along with stannous chloride and base hydrochloride will be determined by acid-base strength.



Scheme II

The stronger the acids, the weaker the bases will be able to perform the above type of fission reactions. (scheme II)

The investigations carried out with a number of bases (though these were not exhaustive) having the pKa values ranging from about 4.5 - 10.7 (Table 4). On a broad analysis, it was found the bases having pKa ranging 4.5 - 10.7 could be effective to abstract the α -H from β-benzoyl-α -phenyl ethyltin trichloride and β-acetyl-α -phenyl ethyl tin trichloride. The resulting carbanion undergo elimination of stannous chloride with the eventual formation of chalcone or benzyldene acetone. On the other hand adduct formation has been noticed, when the same bases were treated with $C_2H_5OCO.CH_2CH_2SnCl_3$. This was encountered as the lower acidity of β -H in the estertin compound and hence the bases used with pKa values 4.5 - 5.99 are not sufficiently basic to abstract the proton to generate the carbanion or the enolate. The formation of adduct of this type has been reported previously in earlier discussion.

But when bases like diaminopropane (pKa = 10.55) is allowed to react with $C_2H_5O.CO.CH_2CH_2SnCl_3$, it did not give any adduct, instead it led to tin-carbon bond fission resulting stannous chloride, base hydrochloride and ethyl acrylate.

Table 4

(A) Fission of tin-carbon bond observed in the reaction of organotin chloride and base

Organotin Compound	Base	pKa of base
(I) β-benzoyl-α-phenyl ethyltin trichloride	Bipyridyl	4.50
	Aniline	4.87
	Pyridine	5.23
	Phenanthroline	5.58
	β - picoline	5.70
	γ - picoline	5.99
	α - picoline	6.00
	Triethanolamine	7.76
	8-hydroxyquinoline	9.81
	Triethylamine	10.75
(II) β-acetyl-α-phenyl ethyltin trichloride	Same set of bases were used as in case of β-benzoyl-α-phenylethyltin trichloride	
(III) β-carboethoxy ethyltin trichloride	1,3-diamino propane	10.55

(B) Formation of adduct or chelate compound of organotin chloride with base

Organotin compoud	Base	pKa (Base)
β-carboethoxyethyltin trichloride	Bipyridyl	4.50
	Pyridine	5.23
	Isoquinoline	5.40
	Phenanthroline	5.58
	β-picoline	5.70
	γ-picoline	5.99
	Triphenyl phosphine	
	8-hydroxyquinoline	9.81

Thiourea and glycine did not react with β-benzoyl-α-phenyl ethyl tin trichloride. On the other hand Diphenyl thiocarbazone (Dithizone) Diphenyl carbazone on being added to β-benzoyl-α-phenylethyltin trichloride or β-acetyl-α-phenylethyltin gave intense colour change suggesting complex formation. Organotin halides usually form complex compounds when treated with Dithizone or diphenyl carbzonate in presence of bases like ammonia, pyridine etc to remove the hydrohalide liberated during the reaction. But in these cases, addition of base leads to tin carbon bond cleavage, hence could not be successfully utilised. However, with addition of 3 mole of dithizone/ D.P.C to the above mentioned chloride under refluxing condition, reaction occurred and solid complexes were isolated. The IR and ^{1}H NMR spectra of these derivatives indicate the elimination of benzoyl or acetyl group from the organotin chloride with resultant formation of an organotin chelate compound. Such reactions are somewhat unusual for organotin chelate compound formation. Detailed mechanisms of such reactions have not studied so far.

The IR spectra (Fig. 35 and 44) of the 1,5-diphenylthiocarbazone (dithizone) complexes derived from β-benzoyl-α-phenylethyltin trichloride and β-acetyl-α-phenylethyltin trichloride are identical in character. In both these spectra there is a weak but sharp band at 3205 cm^{-1} which is assigned to ν(N-H) stretching frequency. The ν(N-H) bending vibration absorbs ~1520 cm^{-1}. The medium to strong bands at 1260-1375 cm^{-1} are possibly due to absorption by ν(N-phenyl) vibrations.

All the β-carboalkoxyethyltin dithizonates (101) show absorption bands between ~1110-1200 cm^{-1} due to presence of N-C-S group. With the present compound a number of bands found in the region 1150-1205 cm^{-1} may be atrributed to ν(N-C-S) coupled vibrations.

The ligand dithizone has a large number of absorption bands particularly in the region of 490-800 cm^{-1}.

The presence of so many bands in this region has made the assignment for ν(Sn-C) and ν(Sn-O) absorptions rather difficult in these dithizonates. The far infrared measurement could provide a better picture for several assignments but the lack of proper facilities have restricted us to investigate further in this area for the time being and consequently no assignment of ν(Sn-Cl) absorption is possible.

The appearance of strong absorption bands at $\sim$680 cm^{-1}, $\sim$740 cm^{-1} and $\sim$760 cm^{-1} are characteristic of monosubstituted phenyl ring deformation modes, of course in the present case its assignment is of little value. Since the spectrum was recorded in nujol mull, no assignment can be made on ν(C-H) absorption bands.

The IR spectrum (Fig. 37 and 46) of bis diphenylcarbazonate derivatives of β-benzoyl-α-phenylethyltin trichloride and β-acetyl-α-phenylethyltin trichloride are almost identical, indicating the same molecular pattern in both the cases.

In both these spectra, there is a medium band $\sim$3300 cm^{-1} which is due to ν(N-H) stretching absorption. A strong but broad absorption band in the vicinity of 1655 cm^{-1} which is absent in the corresponding dithizonates may be attributed to ν (C = O) absorptions of the 1,5-diphenylcarbazone molecule. The ν(N-H) bending absorption possibly occurs $\sim$1540 cm^{-1}.

The spectrum also shows a very characteristic nature in the region 1100-1240 cm^{-1}. The broad band and a number of weak bands in this region is possibly due to coupled N-C-O vibrations.

The strong band at 685 cm^{-1} and 745 cm^{-1} and the characteristic for monosubstituted phenyl ring deformation modes.

Due to presence of ligand bands assignment for ν(Sn-O) stretching absorption is not possible with certainity. Due to experimental inadequacy, the assignments for ν(Sn-N), ν(Sn-Cl) and ν(Sn-C) are not possible for the present case so far. Since the spectrum was recorded in nujol mull, no assignment for ν(C-H) absorption can be made.

From the spectrum of the bis dithizonate of β-benzoyl-α-phenylethyltin trichloride or β-acetyl-α-phenylethyltin trichloride one this is apparent that there is no indication of ν(C = O) absorption in the spectrum which may reasonably claim the removal of carbonyl group during complexation. Moreover in the corresponding diphenylcarbazonate complex appearance of absorption band 1655 cm^{-1} may reasonably be attributed to ν(C = O) absorption of 1,5-diphenylcarbazone molecule since such a band is absent in the similar dithizonate complexes in the present case.

Thus the spectral evidence may support the removal of carbonyl group of the β-benzoyl-α-phenylethyltin trichloride and β-acetyl-α-phenylethyltin trichloride during such complexation with dithizone or diphenylcarbazone.

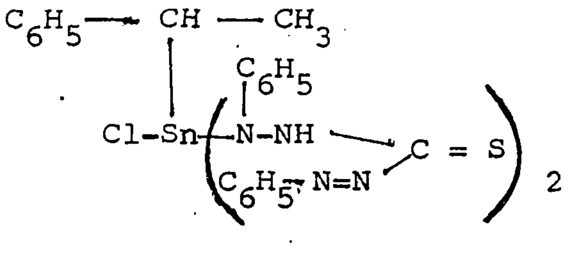
From the ^{1}H NMR spectrum (Fig. 36 and 45) at 90 MHz of dithizonate complex derived from β-benzoyl-α- phenylethyltin trichloride or β-acetyl-α-phenylethyltin trichloride (both being same) in $CDCl_3$ medium, the following observations are made.

The methine proton appears possibly at δ1.25. The methyl protons appear at δ1.5.

In this ^{1}H NMR spectrum, twenty five protons from five phenyl rings occupy the region δ7.0-8.0. The individual interpretation of these protons are not possible due to their appearance as an aggregate in the region.

The proton of the =NH group appears at δ 8.9.

The ratio of secondary amino proton (=NH proton): phenyl proton : methyl proton: methine proton is rather close to 2:25:3:1 which indicates a possible molecular formulation of the compound as follows. (II)



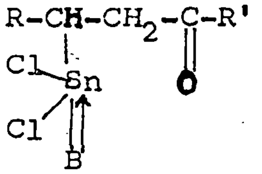
II

The corresponding diphenylcarbazonate complex derived from β-benzoyl-α-phenylethyltin trichloride and β-acetyl-α-phenyltin trichloride could not be purified to the desired level, yet with crude sample of diphenylcarbazonate derivative of β-benzoyl-α-phenylethyltin trichloride one ^{1}H NMR spectrum (Fig.37a) was taken, which is very similar to corresponding dithizonate derivative. ^{119}Sn NMR of these compounds could provide some better picture about the molecular formulation of these compounds yet due to lack of facilities in our laboratory, further investigation about structural aspects was not possible at present.

β-benzoyl-α-phenylethyltin trichloride and similar compounds react with many of the basic ligands but the course of reaction with bases may differ and probably it depends on the pK values of the bases.

The different probable reaction mechanisms can be put forward to explain the formation of different types of reaction products in the presence of different bases or compounds having at least an atom having a lone pair of electron within the molecule.

I. Mechanism to explain the formation of the compounds of the type



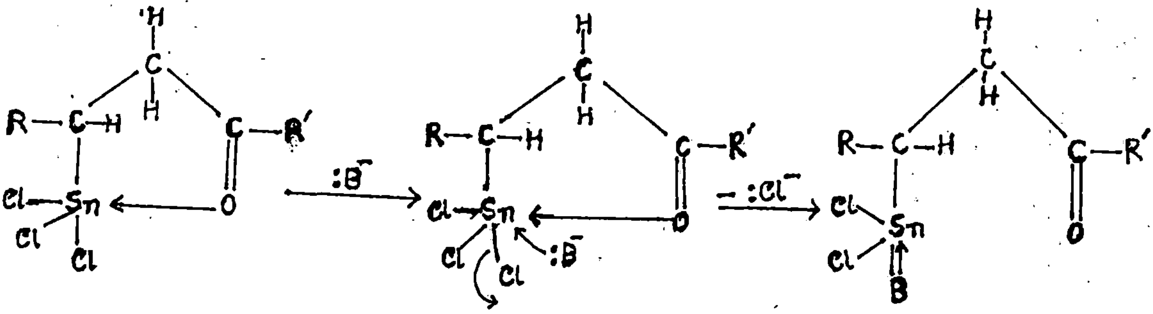
$$R-\underset{\underset{\underset{B}{\Uparrow}}{Cl_2Sn}}{\underset{|}{CH}}-CH_2-\underset{\underset{O}{\|}}{C}-R'$$

where R = hydrogen, alkyl or aryl group and R' = alkyl, alkoxyl or aryl group and the base is a bidentate ligand like diphenyl thiocarbazone, diphenyl carbazone etc. The formation of the said type of compounds can be justified firstly by the elemination of hydrogen chloride molecule. In many cases (specially where R = hydrogen or alkyl group and R' = alkyl or alkoxyl group) the elemination of hydrogen chloride was definitely established by forming ammonium chloride on adding ammonia to the reaction mixture. Secondly carbonyl stretching frequency of the substituted (by the reaction with the ligand) compound is found in the higher field tham that of the parent compound and this is probably due to non-coordinated C = O group in the substituted compound.

I(a) An ionic mechanism

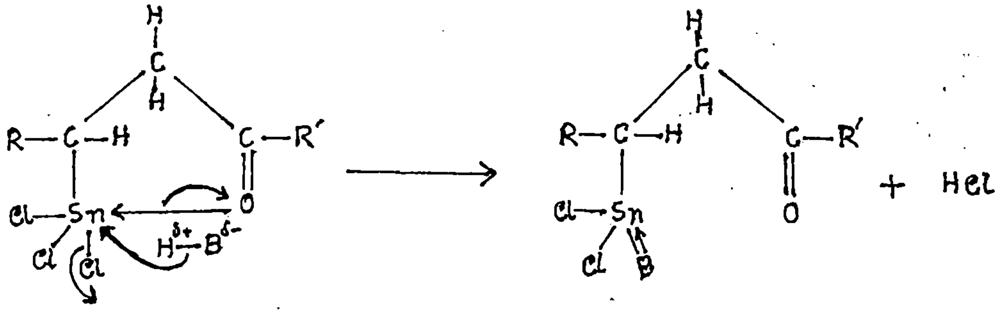
$$HB \rightleftharpoons H^+ + :\bar{B}$$

(Base)



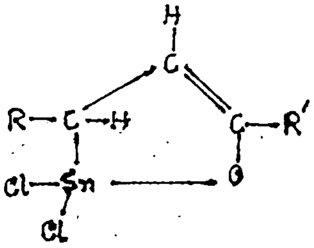
$$H^+ + :Cl^- \longrightarrow HCl$$ Scheme III

I(b) A concerted mechanism

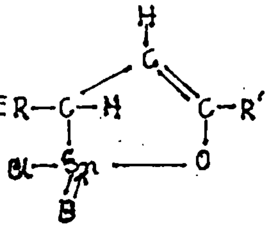


Scheme IV

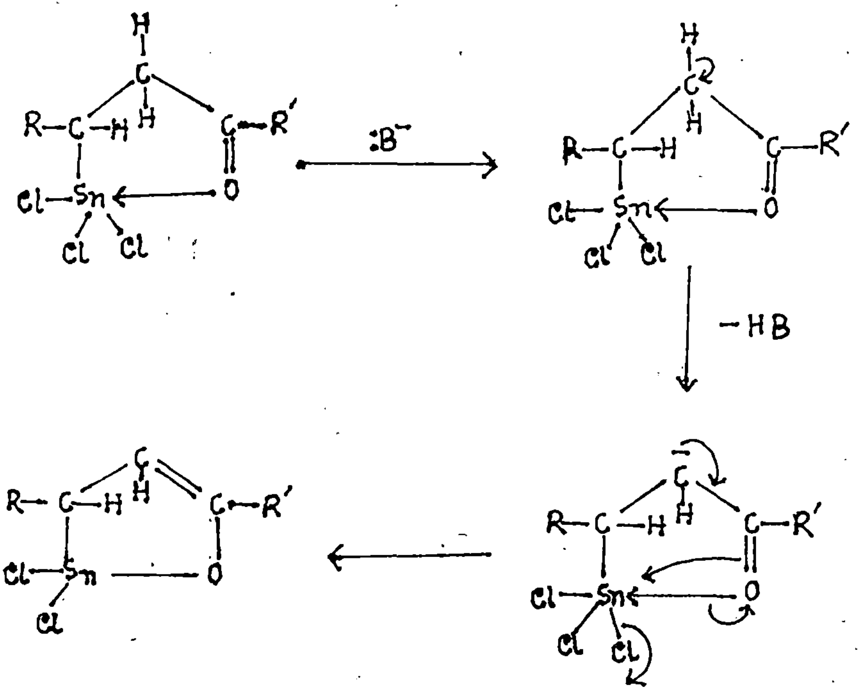
II Mechanism ~~(scheme)~~ to explain the formation of



and hence also of



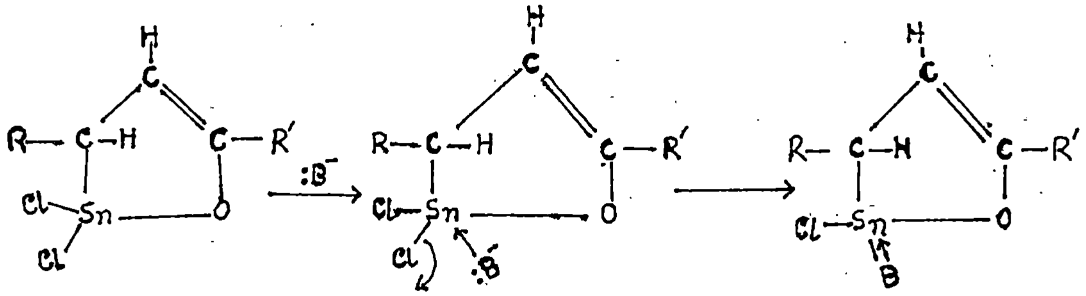
$$HB \rightleftharpoons H^+ + :B^-$$



Scheme V

The next step of the reaction may occur according to either of the following two mechanisms. (scheme VI or VII)

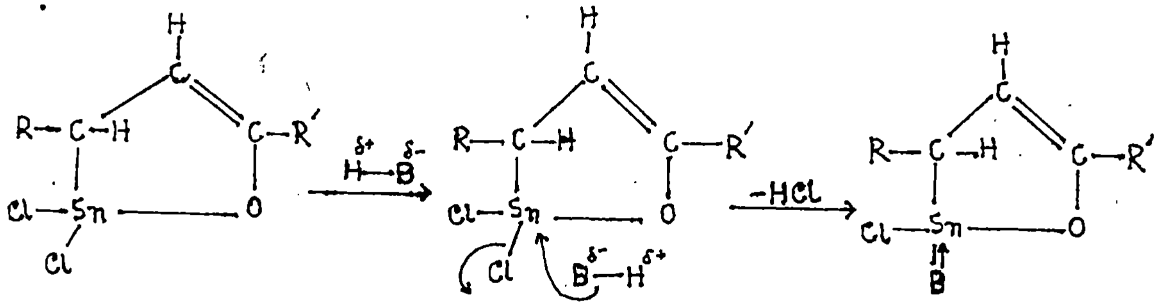
II(a) Ionic mechanism



(:B$^-$ is bidentate ligand)

Scheme VI

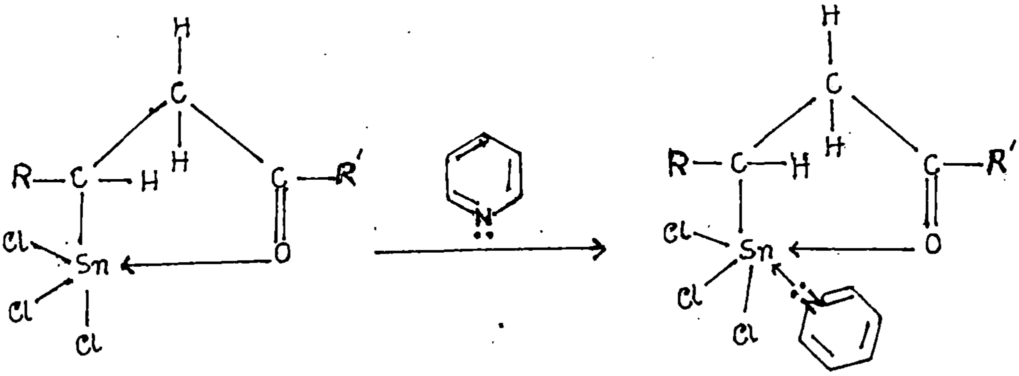
II(b) Concerted mechanism



Scheme VII

~~From the theoretical stand point~~ This type of mechanism (Scheme VI & VII) is favourable when R is electron withdrawing group.

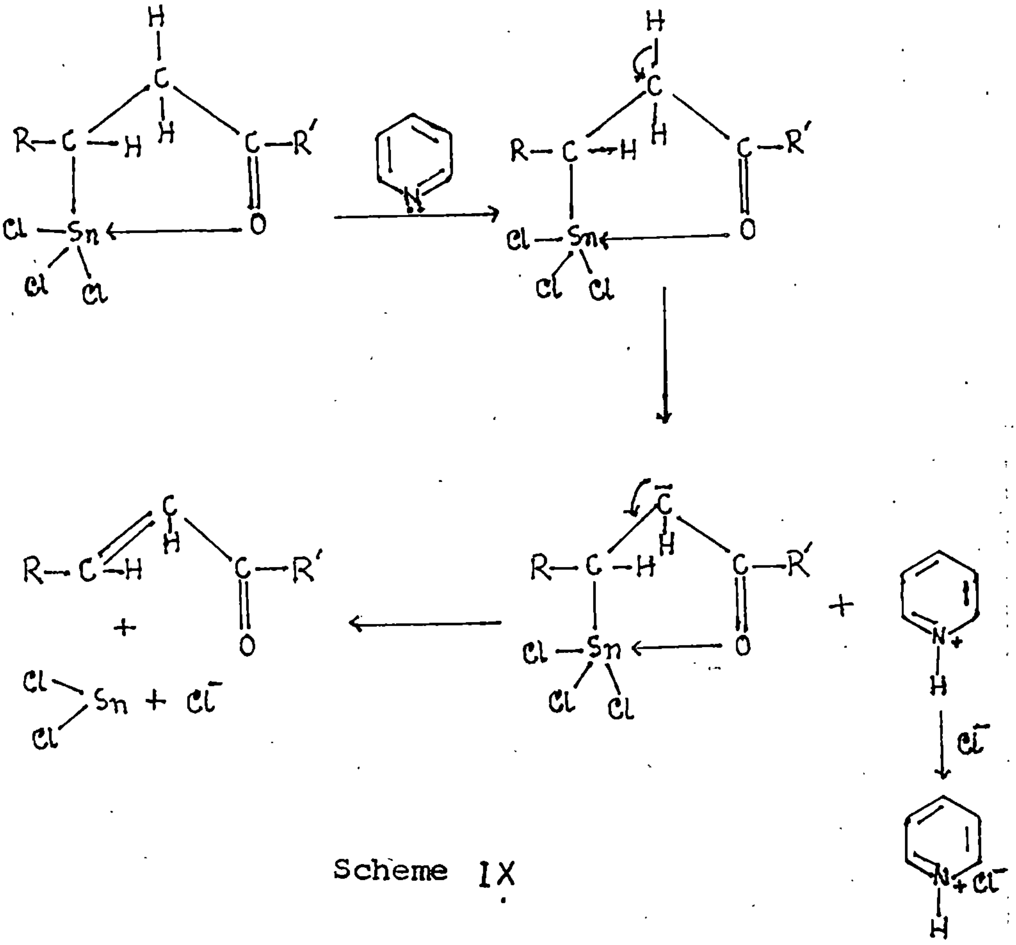
III Reaction mechanism (Scheme VIII) leading to adduct formation with the Lewis bases i.e. a neutral molecule having free electron pair in one of its atom e.g. the compound like pyridine.



Scheme VIII

IV Reaction mechanism leading to the decomposition product containing stannous chloride and R-CH = CH-C-R' also forming pyridine hydrochloride as the final reaction product (when pyridine is used as base).

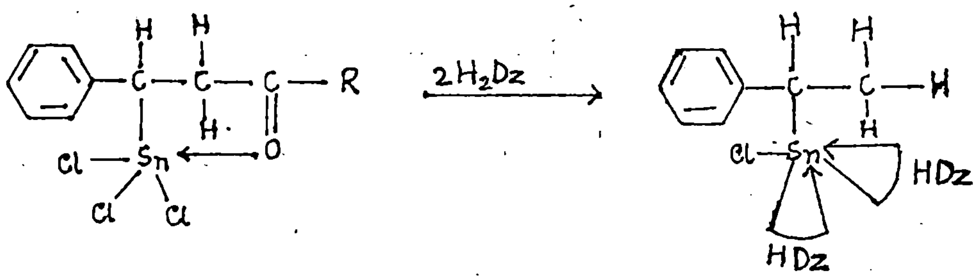
$$R\text{-}CH = CH\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}R'$$



Scheme IX

This type of reaction mechanism (Scheme IX) is in general will be favoured if R is electron withdrawing group and in fact during the reaction of β-phenyl carbonyl benzyltin trichloride with pyridine formation of Chalcone, stannous chloride and pyridine hydrochloride was found which can ~~only~~ be explained on the basis of such a mechanism. (scheme IX)

V. Reaction leading to elimination of benzoyl or acetyl group during the reaction of the compound where R = aryl group with 1,5-diphenylthiocarbazone or 1,5-diphenylcarbazone was observed. The mechanism of such reaction is not yet clear though the scheme of the reaction may be suggested as follows (Scheme X).



+ RCOCl

where R = CH_3 or C_6H_5 .

Scheme X

The β-benzoyl-α-phenylethyltin chloride exhibited strong acid character in chloroform and benzene solution. The pH of 10^{-2}M solution was found to be ∼ 1.5 . The compound is fairly soluble in chloroform, benzene diethyl ether, methanol, ethanol, acetone etc. The solubility in carbon tetrachloride was found remarkably less whereas it was more soluble in chloroform than in benzene.

The solubility of the compound in many solvents is not probably a physical change. For example, the original compound could not be recovered from an acetone solution but a yellow gummy product could only be obtained.

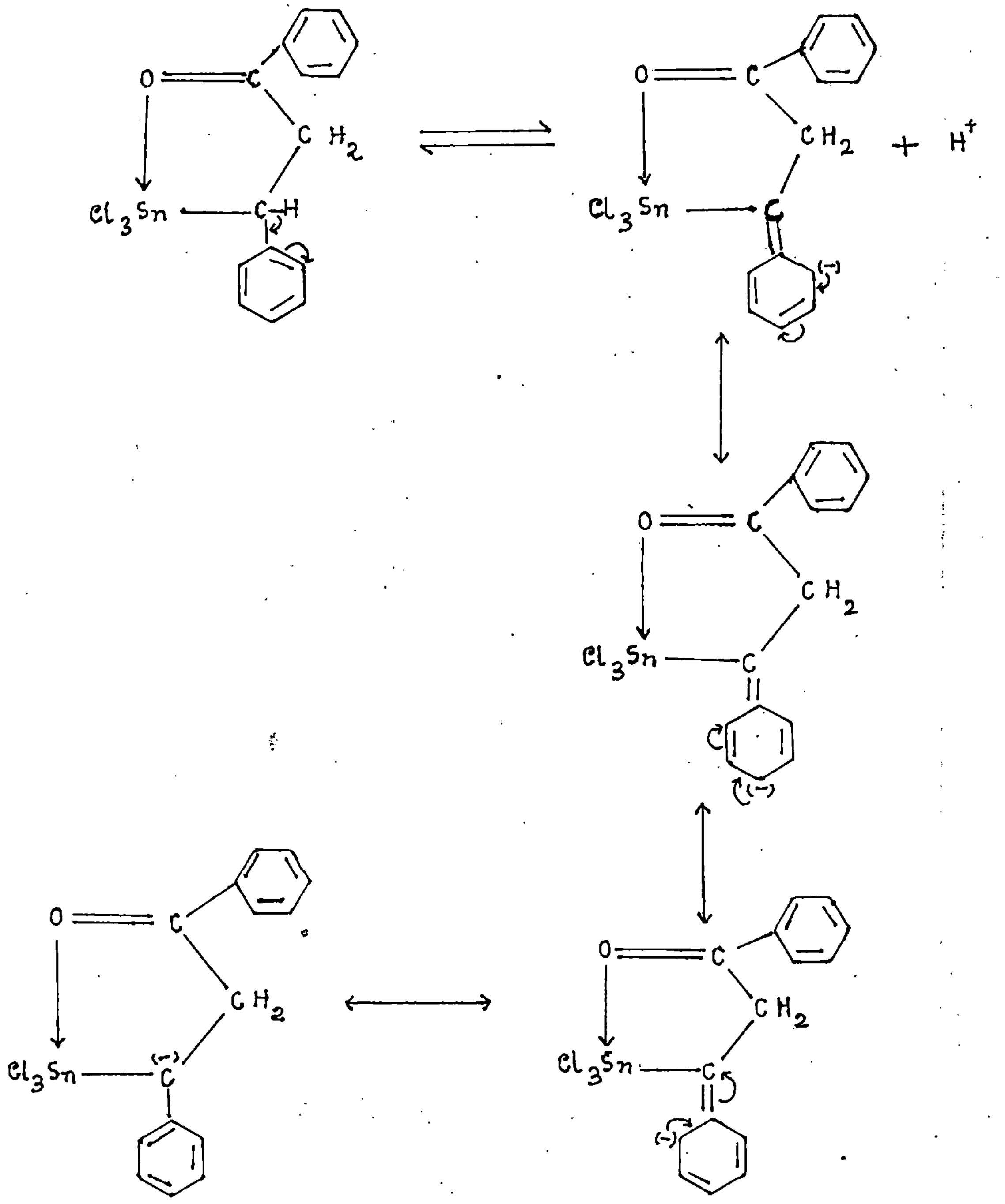
The above compound was very much sensitive to moisture and decomposed to yellow gummy product, which contained some amount of stannous chloride. It decomposed very quickly with ammonia.

The light yellow colour of the β-benzoyl-α-phenylethyltin trichloride changed into an intense yellow colour, when the compound was kept in a desiccator for some weeks. The presence of hydrogen chloride was also detected in the desiccator. On crystallisation of this intense yellow product from suitable solvents, the β-benzoyl-α-phenylethyltin trichloride could be obtained on a reduced amount.

The very light cream crystalline β-acetyl-α-phenylethyltin trichloride had similar type of acidic character in chloroform or benzene $[\mathrm{pH}\ (10^{-2}M) = \backsim 1.7]$. It had also a similar solubility in different organic solvents. In presence of moisture, the compound also decomposed to a brown gummy mass from which an uncharacterised deep brown solid (m.p. 110°C) could be recovered, which incidently did not contain any tin. The compound β-acetyl-α-phenylethyltin trichloride decomposed even inside a desiccator liberating hydrogen chloride and changed into dark brown product which could not be characterised so far.

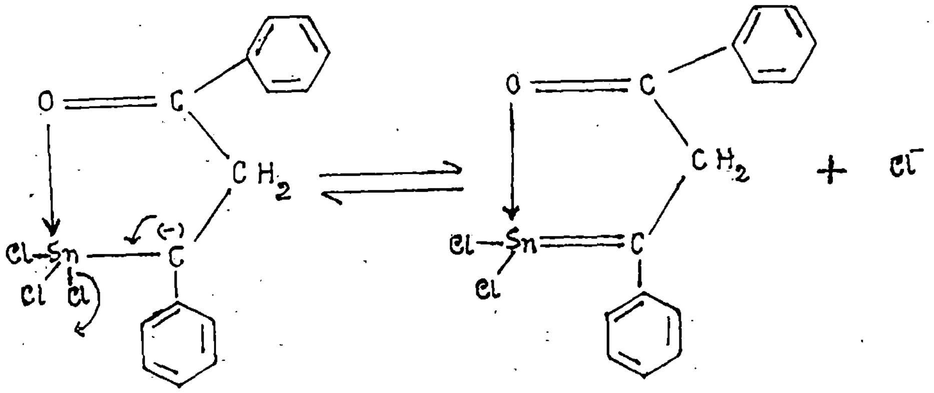
The β-styrylcarbonyl-α- phenylethyltin trichloride also exhibited more or less similar properties.

The acidic character of these compounds could be due to the presence of a phenyl group to the carbon atom containing $-SnCl_3$ group as indicated below e.g. β-benzoyl-α-phenylethyltin trichloride,



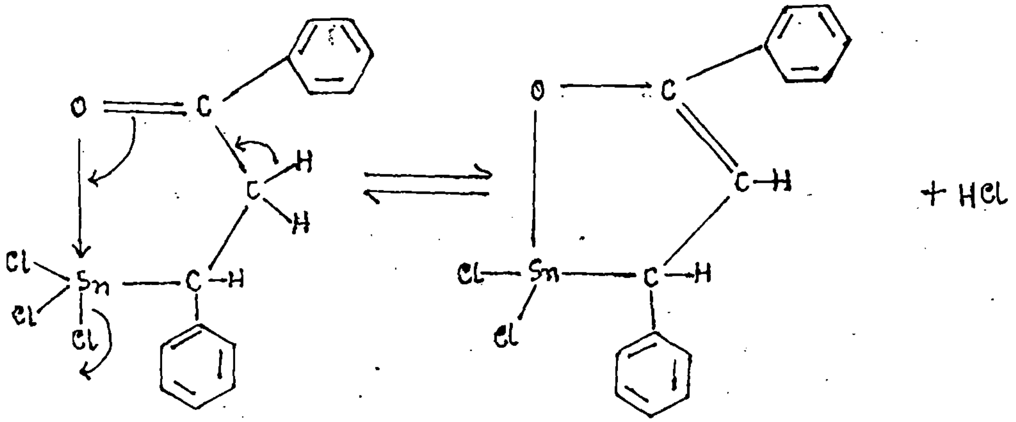
Scheme XLa

The stabilisation of the anion formed as existing in the form of resonance hybrid may explain the acidic character of the compounds. The compound even after repeated crystallisation and careful drying liberates hydrogen chloride even in a vacuum desiccator which may be due to presence of following equilibrium. (Scheme XIb)



Scheme XI b

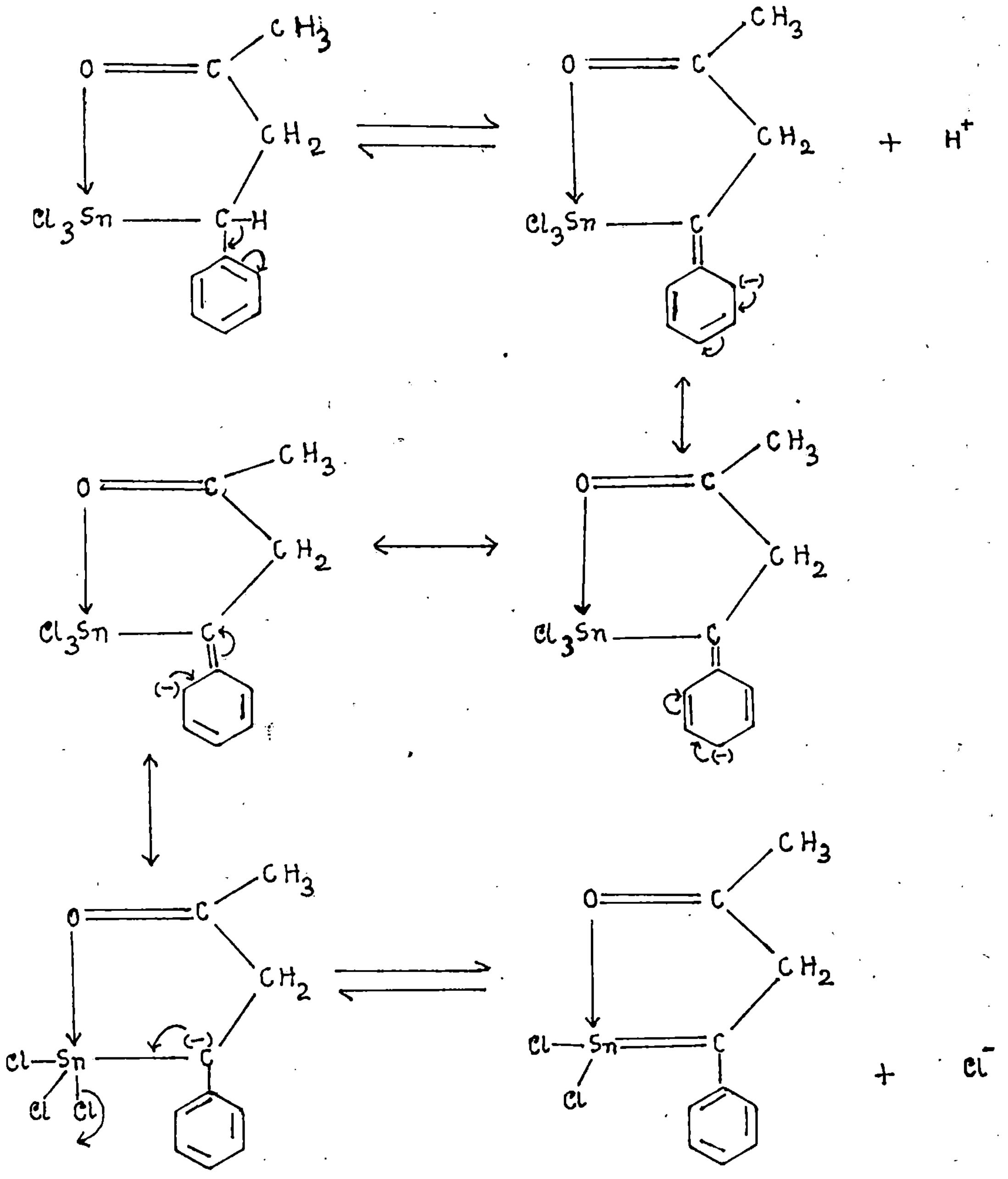
Alternatively the elimination of hydrogen chloride may also be suggested as follows. (Scheme XII)



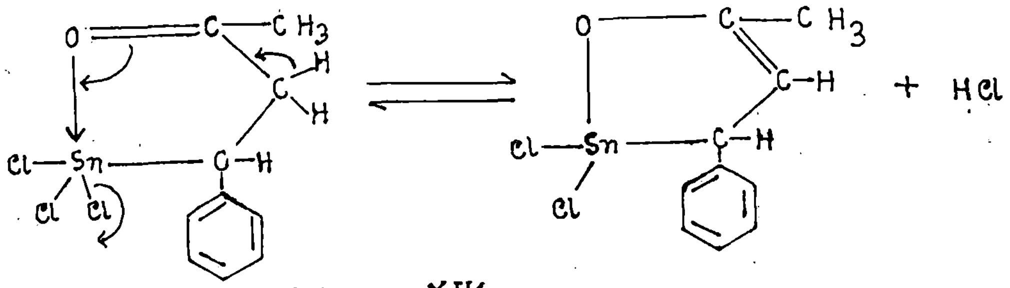
Scheme XII

In presence of moisture, the forward reaction is accelerated, resulting in some uncharacterised gummy product containing either no or very little amount of β-benzoyl-α-phenyl ethyltin trichloride.

The elimination of hydrogen chloride may similarly be suggested in case of β-acetyl-α- phenylethyltin trichloride. (Scheme XIII, XIV)



Scheme XIII



Scheme XIV

The darkening of the colour from very light yellow to intense yellow in case of β-benzoyl-α-phenylethyltin trichloride and from light cream to deep brown in case of β-acetyl-α-phenylethyltin trichloride takes place even on keeping the compound in purified and dried condition. The phenomenon is very much similar to the case of phenol and phenoxide ion. The increase of λ_{max} in case of phenoxide ion than that of phenol has been explained as follows (208).

The larger the amount of conjugation and the larger the number of charged resonating structures (with fairly close energy content), the greater is the resonance energy and so lower is the energy content of the resonance hybrid. Also, the smaller the difference in energy levels between the ground state and the first excited state, the larger is the wave length of absorption. This is because charged structures contribute more to excited state than to ground state. Again if all the contributing resonating structures are charged, and only of one kind as in the case of phenoxide ion (only a negative charge), the charge delocalisation in this case increases the stability of the resonance hybrid still further. Hence there is the increase in the wave length (i.e. λ_{max}) to a considerable extent.

The resonance hybrid of the anion derived from β-benzoyl-α-phenylethyltin trichloride should also increase the value of λ_{max} than that of the corresponding non ionised structure. The compounds that absorb light of wave length between 400-800 nm (visible light) appear coloured to human eye, the precise colour being a complicated function of which wave lengths of the compounds subtract from white light. Progressive absorption from 400 nm upwards leads to progressive darkening through yellow, orange, red, green, blue, violet and ultimately black as the observed colour of the compounds. All these appeared colours of the compounds are complementary colours left after subtraction of colours corresponding to the wave lengths at which those compounds absorb maximum in the visible range from the white light.

The slow change of colour from light yellow to orange in case of β-benzoyl-α-phenylethyltin trichloride is possibly due to greater λ_{max} value for the resonance hybrid of the ion derived from the compound by the elimination of H^+.

The change in colour was also observed on keeping the compound β-acetyl-α-phenylethyltin trichloride for a period of time. The explanation for such colour change is possibly the same.

In aliphatic compounds there was every limited scope of stabilisation of anion derived by the elemination of H^+ by resonance, hence comparable estertin chlorides did not show any colour change gradually with time.

REFERENCES

1. C.E. Moore, Atomic Energy Levels, Circular 467, National Bureau of Standards, Vol. 1, Government Printing Office, Washington D.C. (1949)

2. R.C. Poller, J. Organometal. Chem. 3, 321 (1965)

3. M. Gielen and N. Sprecher, Organometal. Chem. Rev., 1, 455 (1966)

4. I.P. Beletskaya, K.P. Butin, A.N. Ryabtsev and O.A. Reutov, J. Organometal. Chem., 59, 1-44 (1973)

5. I.R. Beattie, Quart. Rev., 17, 382 (1963)

6. I.R. Goldshetein, E.N. Guryanova, E.D. Deleneskaya and K.A. Kocheskov, Dekl. Akad. Nauk. S.S.S.R. 136, 1079 (1961)

7. J.L. Wardell, J. Organometal. Chem., 9, 89(197); 10, 53 (1967)

8. A. Cassol and R. Barbieri, Ann. Chem., 55, 606 (1965)

9. R.G. Pearson, Am. Chem. Soc., 85, 3553 (1963)

10. B. Saville, Angew. Chem. Intern. Ed., England, 6, 928 (1967)

11. T.F. Bolles and S.R. Drago, J. Am. Chem. Soc., 87, 5015 (1965); 88, 3921 (1966)

12. K.A. Elegbede and R.N.A. McLean, J. Organometal. Chem., 69, 405 (1974)

13. R.W.J. Wood and J.R. Sams, Can. J. Chem., 48, 71 (1970)

14. V.G. Kumar Das, J. Inorg. Nucl. Chem., 38, 1241 (1976)

15. French Patent, 1,389,821, Feb. 19,1965 /Chem. Abs., 63, 1816e (1965) /

16. Y. Kawasaki, M. Hori and K. Uneka, Bull. Chem. Soc., Japan, 40, 2463 (1967)

17. J.P. Clark, V.M. Longford and C.J. Wilkins, J. Chem. Soc. (A), 792 (1967)

18. V.G. Kumar Das and W. Kitching, J. Organometal. Chem., 13, 523 (1968)

19. J. Buckle and P.G. Harrison, J. Organometal. Chem., 77, C22 (1974)

20. T.F. Bolles and R.S. Drago, J. Am. Chem. Soc., 88, 3921 (1966)

21. D.L. Alleston and A.G. Davies, J. Chem. Soc., 2050 (1962)

22. D. Blake, G.E. Coates and J.M. Tate, J. Chem. Soc., 756 (1961)

23. J.E. Fergusson, W.R. Roper and C.J. Wilkins, J. Chem. Soc., 3716 (1965)

24. G. Eng, K.L. Rechie and L. May, Inorg. Chem. Acta., 43(2), 233-5 (1980)

25. F.E. Smith and E.L. Khoo, J. Inorg. Nucl. Chem., 43(8), 1917-18 (1981)

26. T.N. Srivastava and P.C. Kamboj, J. Ind. Chem. Soc., 56(9), 857-9 (1979)

27. T.N. Srivastava and P.C. Kamboj, Ind. J. Chem. Sect A, 19A(2), 167-9(1980)

27. T.N. Srivastava and P.C. Kamboj, Ind. J. Chem. Sect A, 19A (2), 167-9 (1980)

28. T.N. Srivastava, B. Bera and P.C. Srivastava, Ind. J. Chem. Sect. A, 16A(2), 164-5 (1978)

29. R.C. Paul, R.K. Sharma, R. Walia and S.P. Narula, Ind. J. Chem. Sect. A, 16(6), 544-6(1978)

30. F.E. Smith and B.V. Liengme, J. Organometal. Chem., 91, C31 (1975)

31. I.R. Beattie and G.P. McQuillan, J. Chem. Soc., 1519 (1963)

32. W.D. Honnic, M.C. Hughes, C.D. Jr. Schaeffer and J.J. Zuckerman, Inorg. Chem., 6, 2017 (1967)

33. A.S. Mufti and R.C. Poller, J. Chem. Soc., 5055(1965)

34. F.W.B. Einstein and B.R. Penfold, Chem. Commun., 780 (1966)

35. F.W.B. Einstein and B.R. Penfold, J. Chem. Soc.(A), 3019 (1968)

36. D.V. Naik and W.R. Scheidt, Inorg. Chem., 12, 272 (1973)

37 R.C. Poller and D.L.B. Toley, J. Chem. Soc. (A), 1578 (1967)

38. W.R. Mewhinnic, R.C. Poller, J.N.R. Ruddick and M.J. Thevarsa, J. Chem. Sec (A), 2327 (1969)

39. T.N. Srivastava and B. Misra, J. Organometal. Chem., 32, 331 (1971)

40. M.A. Mullins and C. Curran, Inorg. Chem., 6, 2017 (1967)

41. N.W. Issacs, C.H.L. Kennard and W. Kitching, Chem. Commun., 820 (1968)

42. L. Coghi, M. Nardelli, C. Pelizzi and G. Pelizzi, Gazz. Chem. Ital., 105, 1187 (1975)

43. L. Coghi, C. Pelizzi and G. Pelizzi, Gazz. Chem. Ital., 104, 873 (1974)

44. T.N. Srivastava, D.C. Rupainwar and J.S. Gaur, J. ~~Inrg~~ Inorg. Nucl. Chem., 36, 733 (1974)

45. K.L. Jaura, S.K. Bhalla, B.D. Gupta and V.K. Verma, Ind. J. Chem., 11, 49 (1973)

46. F.E. Smith, D.H. Grant and S. Gray, J. Inorg. Nucl. Chem., 4115, 629-31 (1979)

47. A.G. Davies, L. Smith and P.J. Smith, J. Organometal. Chem., 23, 135 (1970)

48. P.R. Palan, Ph.D. Thesis, Lond. Univ. 1967

49. R.J.H. Clark, A.G. Davies and D.F. Martin, J. Chem. Sec. (A), 1828 (1968)

50. S.P. Narula and R.K. Sharma, Ind. J. Chem. Sec (A), 17A(1), 98-100 (1979)

51. G. Matsubayashi, T. Tanaka, S. Nishigaki and K. Nakatsu, J. Chem. Soc., Dalton Transc., 3, 501-5 (1979)

52. D. Cunningham, M. Little and K. McLoughlim, J. Organometal. Chem., 165(3), 287-94 (1979)

53. W.N. Aldridge and J.E. Cremer, Analyst., 82, 57 (1957)

54. H. Irving and J.J. Cox, J. Chem. Soc., 1470 (1961)

55. G.C. Ghosh and A.K. Ghosh, Ind. J. Chem. Soc., 21, 524-526 (1982)

56. G.C. Ghosh, Ph.D. Thesis, North Bengal University, India (1978)

57. A.K. Mallick, Ph.D. Thesis, North Bengal University, India (1982)

58. D. Pal Choudhuri, Ph.D. Thesis, North Bengal University, India (1983)

59. W.H. Nelson and D.F. Martin, J. Inorg. Nucl. Chem., 27, 89 (1965)

60. K. Kawakami and R. Okawara, J. Organometal. Chem., 6, 249 (1966)

61. W. Gerrad, E.F. Mooney and R.G. Rees, J. Chem. Soc., 740 (1964)

62. W.H. Nelson and D.F. Martin, J. Organometal. Chem., 4, 67 (1965)

63. R.C. Poller and J.N.R. Ruddick, J. Chem. Soc(A), 2273 (1969)

64. T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, J. Organometal. Chem., 1, 484 (1964)

65. H.G. Langer, U.S. 3, 120, 550, Feb. 4 (1964) /Chem. Abs., 60, 12051b (1964) /

66. I. Foldesi and G. Straner, Acta. Chim. Acad. Sci., Hung., 45, 313 (1965) /Chem. Abs., 64, 3591h (1966) /

67. J.M. Holmes, R.D. Peacock and J.C. Tatlow, J. Chem. Soc. (A), 150 (1966)

68. E.O. Schlemper, Inorg. Chem., 6, 2012 (1967)

69. F. Alavi-Moghadam, G. Ayrey and R.C. Poller, Eur. Polym. J., 11, 649 (1975)

70. C.D. Barsode, P. Umpathy and D.N. Sen, J. Ind. Chem. Soc., LIII (8), 761 (1976)

71. F. Huber and R. Kaiser, J. Organometal. Chem., 6, 126 (1966)

72. M. Wada, K. Kawakami and R. Okawara, J. Organometal. Chem., 4, 159 (1965)

73. M.A. Mullins and C. Curran, Inorg. Chem., 7, 2584 (1968)

74. A.H. Westlake and D.F. Martin, J. Inorg. Nucl. Chem., 27, 1579 (1965)

75. G. Faraglia, L. Roncucci and R. Barbieri, Ric. Sci. Rend. Sez. A , 8(2), 205 (1965)

76. D. Dutta, Ph.D. Thesis, North Bengal University, India (1970)

77. M. Komura and R. Okawara, Inorg. Nucl. Chem. Letters, 2, 93 (1966)

78. D.P. Gaur, G. Srivastava and R.C. Mehrotra, Ind. J. Chem., 12, 399 (1974)

79. L. Roncucci, G. Faraglia and R. Barbieri, J. Organometal. Chem., 1, 427 (1964)

80. D. Datta, B. Majee and A.K. Ghosh, J. Organometal. Chem., 30, 43-51 (1971)

81. T.N. Srivastava, M.P. Agarwal and K.L. Saxena, J. Inorg. Nucl. Chem., 35, 306 (1973)

82.(a) C.D. Barsode, P. Umapathy and D.N. Sen, J. Ind. Chem. Soc., 52, 942 (1975)

82(b) C.D. Barsode, P. Umapathy and D.N. Sen, J. Ind. Chem. Soc., LIII (8), 761 (1976)

83. C.D. Barsode, P. Umpathy and D.N.Sen, J. Ind. Chem. Soc., 54(12), 1172-77 (1977)

84. V.G. Kumar Das, Ng. Seik. Weng, J. Singh, P.J. Smith and R. Hill, J. Organometal Chem., 214(2), 183-90 (1981)

85. T.S. Basu, B. Majee and A. Roy, Abs. Symposium on "Modern trends in Co-ord. Chem.", Oct. 6-8, 1980, p. 58, Inorg. Chem. Div., Inst. of Sci., Bombay.

86. B. Majee and T.S. Basu, Abs. Third Nat. Symposium on "Elemento-Org. Compols. in Chem. Synth", Feb. 22-25, 1982, Dept. of Chem., Univ. of Rajasthan, India.

87. B. Majee, T.K. Chattopadhyay, T.S. Basu and M.N. Halder, Abs. Symposium on "New Vistas in Organometal. Chem", Feb. 10-13, 1983, p. 17, Dept. of Chem., Univ. of Rajasthan, India.

88. D. Maughan, J.L. Wardell and J.W. Burley, J. Organometal. Chem., 212, 59-70 (1981)

88a. R.A. Howie, E.S. Paterson, J.L. Wardell and J.W. Burley, J. Organometal. Chem., 259 (1), 71-8 (1983).

88b. RA. Howie, E.S. Paterson, J.L. Wardell and J.W. Burley, J. Organometal. Chem., 304 (3), 301-8 (1986).

89. M.V. Garad, S. Gopinathan and C. Gopinathan, Z. Anorg. Allg. Chem., 465, 204-8 (1980)

90. M.V. Garad, S. Gopinathan and C. Gopinathan, Ind. J. Chem. Sec. A, 20A, 412-14 (1981)

91. V.G. Kumar Das, Ng. Seik. Weng and P.J. Smith, Inorg. Chim. Acta, 49(2), 149-52 (1981)

92. M.A. Wassef, S. Hessin, Commun. Fac. Sci. Univ. Ankara, Ser. B 27(11), 141-52 (1981)

93. M.A. Wassef and S. Hessin, Egypt. J. Chem. 24(1-3), 97-107 (1982)

94. K.S. Siddiqui, R.I. Kureshy, P. Khan and S.A.A. Zaidi, Indian J. Chem. Sect. A., 22A(7), 616-17 (1983)

95. J. Otera, T. Yano and K. Kusakabe, Bull. Chem. Soc. Jpn. 56(4), 1057-9 (1983)

96. M.V. Ga~~r~~rad, Inorg. Chim. Acta, 87(1), 79-81 (1984)

97. E.J. Gabe, F.L. Lee, F.E. Smith, Inorg. Chim. Acta, 90(2), L11-L13 (1984)

98. J.J. Bonire, Chem. Chron. 15(1), 3-12 (1986)

99. J.N. Spencer, R.B. Belser, S.R. Moyer, R.E. Haines, M.A. Distravalo and C.H. Yoder, Organometallics, 5(1), 118-20 (1986)

100. J.C. Trehan, R.K. Sharma and C.P. Sharma, Polyhedron, 5(6), 1227-31 (1986)

101. B.K. Deb and A.K. Ghosh, Z. anog. allg. Chem., 229-238 (1986)

102. B.K. Deb and A.K. Ghosh, Polyhedron, 5(3), 863-870 (1986)

103. B.K. Deb and A.K. Ghosh, Can. J. Chem., 65, 1241 (1987)

104. V.G. Kumar Das, C.K. Yap and P.J. Smith, J. Organometal. Chem., 327(3), 311-26 (1987)

105. B.N. Biddle, J.S. Gray and A.J. Crowe, Appl. Organomet. Chem., 1(3), 261-5 (1987)

106. R.C. Poller, The Chemistry of Organotin Compounds, Logos Press Limited, Great Britain. 1970

107. A.K. Sawyer, Organotin Compounds, Vol. 1, Ch. 3. 1971

108. H. Zimmer and J.J. Miller, Naturwissenschaften, 53, 38 (1966)

109. R.D. Taylor and J.L. Wardell, J. Organometal. Chem., 94, 15 (1975)

110. D.J. Peterson, M.D. Robins and J.R. Hansen, J. Organometal. Chem., 73, 237 (1974)

111. J.L. Wardell and J.M. Wigzell, J. Organomet. Chem., 244 (3), 225-33 (1983)

112. H.A. Olszowy and W. Kitching, Organometallics, 3(11), 1670-5 (1984)
ibid. 3(11), 1676-83 (1984)

113. D.W. Hawker and P.R. Wells, Organometallics, 4(5), 821-5 (1985)

114. S.V. Medvedev and A.V. Yatsenko, Zh. Obshch. Khim. 56(9), 2166 (1986)

115. O. Buchman, M. Grosjean, J. Nasielski and B. Wilmet-Devos, Helv. Chim. Acta., 47, 1688 (1964)

116. S. Laosooksathit, Warasan Songkhla Nakkharin, 5(4), 365-6 (1983)(Through C.A. 101 (21), 192092 e, 1984

117. R.J. Gillespie, R. Kapoor and E.A. Robinson, Can. J. Chem., 44, 1197 (1966)

118. C. Eaborn and J.A. Waters, J. Chem. Soc., 542 (1961)

119. C. Eaborn, J.A. Treverton and D.R.M. Walton, J. Organometal. Chim., 9, 259 (1967)

120. A. Henderson and A.K. Holliday, J. Organometal. Chem., 4, 377 (1965)

121. S. Chandrasekhar, S. Latour, J.D. Wuest and B. Zacharie, J. Org. Chem., 48(21), 3810-3 (1983)

122. D.W. Hawker and P.R. Wells, J. Organomet. Chem., 266(1), 37-44 (1984)

123. E. Murayama, T. Kikuchi, H. Nishio, M. Uematasu, K. Sasaki, N. Saotome and T. Sato, Nippon Kagaku Kaishi, (3), 350-61 (1985)

124. S. Boue, M. Gielen and J. Nasielski, J. Organometal. Chem. 9, 443 (1967)

125. R.E. Dessy and W. Kitching, Advances in Organometallic Chemistry, Academic Press, New York and London, 4, 267 (1966)

126. M. Gielen and J. Nasielski, J. Organometal. Chem., 1, 173 (1963)

127. M. Gielen and J. Nasielski, J. Organometal. Chem., 7, 273 (1967)

128. D.F. Martin, P.C. Maybury and R.D. Walton, J. Organometal. Chem., 7, 362 (1967)

129. D.F. Martin and R.D. Walton, J. Organometal. Chem., 5, 57 (1966)

130. K. Ramaiah and D.F. Martin, Chem. Comm. 130 (1965)

131. S.V. Ponamarev, E.V. Machigin and I.F. Lutsenki, Zh. Obshch. Khim., 36, 548 (1966)

132. O. Schmitz-Dumont, G. Mueller and W. Schaal, Z. Anorg. Allgen. Chem., 332, 263 (1964)

133. C. Eaborn, H.L. Hornfield and D.R.M. Walton, J. Chem. Soc. (B), 1036 (1967)

134. C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 4, 217 (1965)

135. V.I. Bregadze and O. Yu. Okhlobystin, Izv. Akad. Nauk. S.S.S.R., Ser. Khim., 2084 (1967)

136. P. Dembech, G. Seconi and C. Eaborn, J. Chem. Soc. Parkin Trans 2 (3), 301-3 (1983)

137. D. Seyferth and M.A. Weiner, Chem. and Ind. 402 (1959); J. Am. Chem. Soc., 83, 3583 (1961)

138. D. Seyferth, R. Suzuki and L.G. Vaughan, J. Am. Chem. Soc., 88, 286 (1966)

139. D. Seyferth and T.F. Jula, J. Organometal. Chem., 8, P. 13 (1967)

140. D. Seyferth, L.G. Vaughan and R. Suzuki, J. Organometal. Chem., 1, 437 (1964)

141. W. Tochterman, Angew. Chem. Interm. Edit. Engl. 5, 351 (1966)

142. M.D. Curtis and A.L. Allred, J. Am. Chem. Soc., 87, 2554 (1965)

143. E.J. Corey and R.H. Wollenberg, J. Am. Chem. Soc., 96, 5581 (1974)

144. K. Niedenzu, Organometal. Chem. Rev., 1, 305 (1966)

145. L.G. Sharanina, V.S. Zavgorodnii and A.A. Petrov, Zh. Obshch. Khim., 36, 1154 (1966)

146. T. Chivers and P. David, J. Organometal. Chem., 10, p35 (1967)

147. R.D. Chambers and T. Chivers, J. Chem. Soc., 3933 (1965)

148. A.J. Leusink, W. Drenth, J.G. Noltes and G.J.M. Van der Kerk, Tetrahedron Letters, 1263 (1967)

149. D. Seyferth and J.M. Burlitch, J. Organometal. Chem., 4, 127 (1965)

150. V.I. Adveeva, G.S. Burlachenko, Yu. I. Baukov and I.F. Lutsenko, Zh. Obshch. Khim., 36, 1679 (1966)

151. I.F. Lutsenko, Yu. I. Baukov and G.S. Burlachenko, J. Organometal. Chem., 6, 496 (1966)

152. V.S. Zavgorodnii, L.G. Sharanina and A.A. Petrov, Zh. Obshch. Khim., 38, 1150 (1968)

153. G.S. Burlachenko, B.N. Khasapov, L.I. Petrovskaya, Yu. I. Baukov and I.F. Lutsenko, Zh. Obshch. Khim., 36, 512 (1966)

154. I.F. Lutsenko, Yu. I. Baukov, G.S. Burlachenko and B.N. Khasapov, J. Organometal. Chem., 5, 20 (1966)

155. Yu. I. Baukov, G.S. Burlachenko, I.Yu. Belavin and I.F. Lutsenko, Zh. Obshch. Khim., 36, 153 (1966)

156. Yu. I. Baukov, G.S. Burlachenko and I.F. Lutsenko, J. Organometal. Chem., 3, 478 (1965)

157. Yu. I. Baukov, G.S. Burlachenko and I.F. Lutsenko, Zh. Obshch. Khim., 35, 757 (1965)

158. P.M. Treichel and R.A. Goodrich, Inorg. Chem., 4, 1424 (1965)

159. D.W.A. Sharp and J.M. Winfield, J. Chem. Soc., 2278 (1965)

160. O. Buchman, M. Grosjean and J. Nasielski, Helv. Chim. Acta., 47, 1679 (1964)

161. Z.S. Novikova, M.V. Proskurnina, L.I. Petrovskaya, I.V. Bogdanova, N.P. Galitskova and I.F. Lutsenko, Zh. Obshch. Khim., 37, 2080 (1967)

162. H. Hartmann, Annalen, 714, 1 (1968)

163. E.A. Besolova, V.L. Foss and I.F. Lutsenko, Zh. Obshch. Khim. 38, 1574 (1968) (Chem. Abs. 1968 69, 106849)

164. K. Koenig and W.P. Neumann, Tetrahedron Letters, 495 (1967)

165. R.G. Mirskov and V.M. Vlasov, Zh. Obshch. Khim., 36, 562 (1966)

166. W.P. Neumann and F.G. Kleiner, Annalen, 716, 29 (1968)

167. D. Seyferth and T.F. Jula, J. Am. Chem. Soc., 90, 2938 (1968)

168. K.A. Kocheshkov, Chem. Ber., 62, 996 (1929)

169. K.A. Kocheshkov, Chem. Ber., 66, 1661 (1933)

170. K.A. Kocheshkov, J. Gen. Chem. U.S.S.R., 4, 1359 (1934)

171. K.A. Kocheshkov, J. Gen. Chem. U.S.S.R., 5, 211 (1935)

172. K.A. Kocheshkov and M.M. Nad, Chem. Ber., 67, 717 (1934)

173. K.A. Kocheshkov, M.M. Nad and A.P. Alexandrov, Chem. Ber., 67, 1348 (1934)

174. S.D. Rosenberg and A.J. Gibbons, J. Am. Chem. Soc., 79, 2138 (1957)

175. D. Seyferth and F.G.A. Stone, J. Am. Chem. Soc., 79, 515 (1957)

176. K.V. Vyayraghavan, J. Indian Chem. Soc., 22, 135 (1945)

177. W.J. Jones, W.C. Davies, S.T. Bowden, C. Edwards, V.E. Davis and L.H. Thomas, J. Chem. Soc., 1446 (1947)

178. W.P. Neumann and G. Burkhardt, Ann. Chem., 663, 11 (1963)

179. D. Seyferth, J. Am. Chem. Soc., 79, 2133 (1957)

180. D. Seyferth, Naturwissenschaften, 44, 34 (1957)

181. H. Siebert, Z. Anorg. Allgem. Chem., 268, 177 (1952)

182. Z.M. Manulkin, J. Gen. Chem., U.S.S.R., 20, 2004 (1950)

183. Yu. A. Aleksandrov, V.N. Glushakova and B.A. Radbil, Tr. Khim. Khim. Tekhnol, 69 (1967) (Chem. Abs. 1968, 69, 27506)

184. Yu. A. Aleksandrov and B.A. Radbil, Zh. Obschch. Khim., 37, 2345 (1967)

185. N.S. Vyazankin, G.A. Razuvaev and T.N. Brevnova, Zh. Obshch. Khim., 35, 2033 (1965)

186. P.H. De Ryck, L. Verdonck and G.P. Van der Kelen, Bull. Soc. Chim. Belg., 94(9), 621-9 (1985)

187. N. Soundarurajan and M.S. Platz, Tetrahedron Letter, 28(25), 2813-16 (1987)

188. J.J. Zuckerman, Organotin Compounds: New Chemistry and Applications, Advances in Chemistry Series, Am. Chem. Soc., New York (1976), p. 113-122.

189. H.C. Clark and C.J. Willis, J. Am. Chem. Soc., 82, 1888 (1960)

190. A.B. Evnin and D. Seyferth, J. Am. Chem. Soc., 89, 952 (1967)

191. M. Buschhoff, W.P. Neumann, Eur. Pat. Appl. EP 158, 163 (Cl. CO 7F7/100) 16 Oct. 1985, DE Appl. 3,411,834, 30 Marc 1984, 18pp.

192. P.C. Srivastava, S.K. Srivastava and S.B. Sharma, Can. J. Chem. 63(2), 329-31 (1985)

193. J.C. Podesta, A.B. Chopa, A.D. Ayala and L.C. Koll, J. Organometal. Chem., 333(1), 25-36 (1987)

194. D. Seyferth, H. Dertouzos, R. Suzuki and J. Yick-Pui Mui, J. Org. Chem., 32, 2980 (1967)

195. D. Seyferth, J. Yick-Pui Mui, M.E. Gordon and J.M. Burlitch, J. Am. Chem. Soc., 87, 681 (1965)

196. D. Seyferth, F.M. Armbrecht, B. Prokai and R.J. Cross, J. Organometal. Chem., 6, 573 (1966)

197. M. Pereyre, G. Colin and J. Valade, Compt. Rend., 264, 1204 (1967)

198. H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, Tetrahedron Letters, 5493 (1966)

199. Dao-Huy-Giao, Compt. Rend., 260 (Groupe 8), 6937 (1965)

200. E.A. Puchinyan and Z.M. Manulkin, Tr. Tashkent Farmatsevt. Inst., 4, 354 (1966) (Chem. Abs., 1968, 68, 78382)

201. D. Seyferth, C. Sarafidis and A.B. Evnin, J. Organometal. Chem., 2, 417, 437 (1964)

202. D. Seyferth and A.B. Evnin, J. Am. Chem. Soc., 89, 1468 (1967)

203. L. Spialter, G. Buell and C.W. Harris, J. Org. Chem., 30, 375 (1965)

204. R.P. Kozyrod and J.T. Pinhey, Tetrahedron Letter, 24(12), 1301-2 (1983)

205. S. Kerschl et al, Z. Naturforsch, B. Anorg. Chem. Org. Chem., 39B(8), 1037-41 (1984)

206. X. Wang and Z. Cheng, Huaxue Shiji, 8(6), 350-5 (Ch) (1986)

207. R.E. Hutton and J.W. Burley, 156, 369-382 (1978)

208. I.L. Finar, "Problems and their solution in Organic Chemistry", E.L.B.S. Edition (1973) p. 346. Longman Group Limited, London.