PART I

INTRODUCTION

Organotin chemicals are at present widely used in industry and represent a significant and growing outlet for tin. Historically, organotin compounds were among one of the first organometallic species to be investigated. Extensive research at different institutes are currently aimed to have a better understanding of the structural and mode of action of these compounds.

The basic studies in the field of organotin compounds have been developed due to the success of a large number of modern techniques applied to the organotin compounds. Tin possesses, for example, two spin of one-half isotopes, ^{117}Sn and ^{119}Sn which become important in nuclear magnetic resonance studies. Tin has stable isotopes, which allow the easy identification of the tin-bearing fragments in the mass spectrometer. Mossbauer resonance from the ^{119}Sn nucleide can be easily recorded. Further tin-carbon stretching frequencies in the infrared and Raman spectra can be assigned in most cases.The availability of two stable oxidation states, tin (II) and tin (IV), with contrasting chemistries and a wide variety of structural types have afforded a large scope for diverse studies in organotin compounds. Tin (IV) derivatives alone encompass four-, five-, six-, seven- and eight coordination at tin centre in neutral, cationic and anionic species, with intra and intermolecular association to give dimer and higher polymers with one, two and three dimensional lattice in the solid state, which have provided much interest in extensive studies in these areas.

The annual industrial production of organotin compounds was less than 50 tons per annum in 1950s. But this figure (1) gradually increased to 35000 tons in 1983. The conservative estimate for the current years will be not less than 40,000 tons per annum.

Therefore the preparation of organotin compounds find increasing importance.

The history of organotin compounds began with the isolation of some organotin halides by Frankland and Löwig (2-4). Thereafter organotin chemistry started to develop as a regular research subject. The development of organotin chemistry during the first fifty years was rather slow because of the lack of efficient and attractive methods for their preparations. The situation changed around the turn of the century when the organomagnesium halides became easily available as alkylating and arylating reagents. Through Grignard reagents, a wide variety of organotin halides could be prepared.

The development of organotin chemistry was extended by Kocheshkov (5) in 1929 who developed a new method of preparation of organotin halides. The method was based on redistribution reaction between the compounds of the type

R_4Sn and SnX_4 (R = alkyl or aryl group and X = halogen).

Krause and Von Grosse (6) published the first comprehensive review covering the literature upto 1935. Ingham, Rosenberg and Gilman (7) extended the literature work upto 1959. Weiss (8) compiled an exhaustive list of organotin compounds covering the literature from 1937 to 1964. Since 1964, a number of literature of organotin chemistry has been published in annual surveys (9-24). The "Tin" annual survey covering the year 1978 has been published by Harrison (24). Apart from these review articles, several books (25-29) have been published.

The patents granted in 1940 and 1943 to Ungve (30) describing the utility of certain dialkyltin derivatives as heat stabilisers for PVC, were a new step in the field of organotin compounds, though their full industrial significance did not become apparent until 10 to 15 years later.

The major application of organotin compounds primarily centres around PVC stabilisation, though uses in catalytic activity for polyurethane formation, epoxy resin curing, olefin polymerisation may become highly significant in near future.

The most effective heat stabilisers are certain organotin compounds of the type R_2SnX_2 where R is methyl, n-butyl, n-octyl and X is a carboxylic acid ester (usually the ester of maleic acid) or a mercapto carboxylic acid ester (usually an iso-octyl ester of mercapto acetic acid).

Though monoalkyltin derivatives have no such PVC stabilising property, yet their addition in small amounts (5-10%) to the dialkyltin PVC stabilisers are very often useful since such an addition has found synergistic effect on stabilising effectiveness, which allow the manufacture of PVC articles with perfect colourlessness and clarity. Recently a new variety of functionally substituted dialkyltin dihalide ("Estertins") (31) has been found to possess good PVC stabilisation property.

Apart from the above properties, organotin compounds, particularly the triorganotin compounds, exhibit a large number of biological properties like antifungal antibactrial, anthelmintic, molluscicidal, insecticidal and related activities.

From environmental point of view, the organotin compounds have an advantage over many other compounds because they degrade to totally non-toxic tin species. Recent development in understanding the mode of toxic action of di- and tri- organotin compounds have been reviewed by Smith (32). Seldon (33) suggested a generalised degradation scheme of trialkyltin derivatives.

Trialkyltin compounds as wood preservatives were first proposed by Van der Kerk and Luijten (34) in 1954. The use of tributyltin compounds in wood preservation upto

1970 has been reviewed by Richardson (35) and later by Crowe et al (36).

As pesticides, the use of organotin compounds is quite promising since organotin pesticides do not accumulate in the soil with successive applications. These are metabolised readily in animals and soils into inorganic tin compounds, which are not taken up by the plants.

Though the industrial applications of organotin compounds were mainly confined to diorganotin and triorganotin compounds (37-40), Several attempts have been made in recent years to find applications for monoorganotin (41) and tetra-organotin(42) compounds. Recently monoorganotins have been found to be effective as water repellants for fabrics and building materials, ~~and~~ mineral flotation agents depending on their hydrophobicity, as PVC stabiliser synergists and as industrial esterification catalysts. Mixture of mono- and di-alkyltin compounds are also used in the production of thin transparent surface films of tin dioxide or glass (43). Recently monoalkyltin compounds are used to provide scratch resistant stannic oxide film (44); as homogeneous catalyst they show no problem of corrosion of the stainless steel vessels (45) and used as active hydrophobic agents (46,47) for building materials and cellulosic substrates. Few monophenyltin derivatives were reported to have fungicidal activity (48). Tetraorganotin compounds find also some important application

They are used to assess as anti-wear additive antioxidants for lubricating oils and delayed action biocides.

So far, we have tried to give an outline about the different types of activities of organotin compounds and some of their current and potential uses. In view of such discussions, it may be said that the preparation of new organotin compounds and their detailed studies will be of increasing interest.

Organotin halides represent one of the most important group of organotin compounds. The preparation of the majority of organotin halides can be carried out under the following types of reactions.

(a) Direct synthesis involving tin and alkyl or aryl halide:

In general the reaction can be represented as

$$Sn + 2RX \longrightarrow R_2SnX_2$$

where R = alkyl or aryl group and X = Cl, Br, I.

Historically Frankland (2) prepared the first organotin halide in 1849 by this route from the reaction between ethyl iodide and metallic tin at 160°C. In 1852 Löwig (4) also synthesised triethyltin bromide. Several other organotin halides (49-53) were prepared by heating tin and alkyl halide in a sealed tube in the temperature range 130°-220°C for 20-40 hours. In this type of reaction, the compounds of the types R_2SnX_2 and R_3SnX were found to form simultaneously in almost all the reactions but in different amounts.

By applying similar method Kocheshkov (54) prepared methyltin trichloride and methyltin tribromide. The organotin halide $(C_2H_5OOCCH_2)_2SnBr_2$ was also prepared (55) by the reaction of tin and $BrCH_2COOC_2H_5$.

In 1953 Smith and Rochow (56) prepared a mixture of dimethyltin dichloride and methyltin trichloride by passing gaseous methyl chloride into molten tin at 350-450°C. They also prepared a number of similar compounds. In general the order of reactivity of the alkyl halide was found $RI > RBr > RCl$. The method was further modified (57-59) by using different catalysts.

Sometimes the role of solvent is very much significant in above reactions. Sisido et al (60) reported that with benzyl chloride in non-polar solvent like benzene, the predominant product was dibenzyltin dichloride but with the same benzyl chloride in polar solvent like butanol, water, the main product was tribenzyltin chloride.

Irmscher et al (61) heated tin powder and methyl bromide with some methanol in an autoclave at 100°C to prepare dimethyltin dibromide.

Following the same procedure, similar other compounds (62-66) were also prepared. Oakes and Hutton (67,68) obtained dibutyltin diiodide in satisfactory yield by refluxing butyl iodide with tin in an open system by using lithium or lithium bromide as catalysts and suitable solvents e.g. butanol. ~~considerably lower yields were~~

~~reported for dibutyltin dibromide and dioctyltin dibromide.~~ Considerably lower yields were reported for dibutyltin dibromide and dioctyl tin dibromide. Sisido et al (69,70) prepared dibutyl tin dibromide, dibutyl tin dichloride $(nPr)_2SnBr_2$ by using suitable catalyst. Simple primary amines were used as effective catalysts in many of such reactions (71). Two or three-component catalyst systems were also successfully used in some cases. These were Lewis bases with a metallic salt (72), tetrabutylammonium iodide with diethyleneglycol diethyl ether (73), an organic disulphide or thiol with magnesium and iodine (74). Dialkyltin dibromide and di-or tri-benzyltin chlorides could however be prepared without the use of catalyst (75). Following similar methods several substituted alkyl halides such as X_2Sn (p-iso-pr $C_6H_4CH_2)_2$, $XSn(p\text{-iso-}PrC_6H_4CH_2)_3$, $X_2Sn(CHRCHR'CONHCH_2CO_2Et)_2$, $X_2Sn(CH_2CHMeCONRR')_2$, $X_2Sn(CHMeCH_2CONRR')_2$ for X = Br, I and R, R' = H, Me were prepared (76,77,78).

Kocheshkov and his co-workers (79-82) prepared several higher alkyl halides by irradiating the mixture of tin and alkyl halide with γ radiation. Wyant et al (83-87) also studied large number of similar reactions. Beside these the preparations of alkyltin halides were also carried out by other workers (viz. 88, 89, 90).

Some of the alkyltin halides were prepared (91,92) by the electrolysis of alkyl halide in suitable solvent medium by using magnesium cathode and soluble tin anode.

Löwig (4) isolated a mixture of $(C_2H_5)_2SnI_2$, $(C_2H_5)_3SnI$, $(C_2H_5)_4Sn$ and $(C_2H_5)_2Sn$ from the reaction of tin-sodium alloy and ethyl iodide. Cahours (49) and Ladenburg (93) carried out the same reaction by using methyl iodide. In 1954 Van der Kerk and Luijten (94) prepared $(C_2H_5)_3SnBr$ and $(C_2H_5)_3SnCl$ together, with $(C_2H_5)_4Sn$ and $(C_2H_5)_2SnX_2$ (X = Cl, Br) by using tin-magnesium alloy. Faulker (95) used small amount of either mercury or mercury salts as catalyst in the similar reaction and prepared compound of the type R_3SnCl. Laine et al (96) synthesised R_3SnBr and R_2SnBr_2 by following the same procedure (R = n-propyl, n-butyl). Harada (97-99) activated tin-sodium alloy with zinc in the formation of R_3SnI and R_4Sn ($R = CH_3$, C_2H_5, C_3H_7). The compounds of the type R_3SnCl, R_4Sn (R = n-propyl, n-butyl, n-amyl) were also prepared by the same method (100).

In most of such reactions specially in case of substituted alkyl or aryl tin halides the presence of catalyst was found to be essential (25) (where R = alkyl or aryl group and X = Cl, Br, I).

Many of the alkyl as well as aryl tin halides could be synthesised successfully by the halogenation of tetraorganostannanes by halogens. The replacement of first two organic groups in the tetraorganotin could be effected under appropriate reaction conditions but on further halogenation formation of tin (IV) halides was observed (106). The preparation of diphenyltin dichloride from the reaction of tetraphenyltin with chlorine was reported as early as in 1878 by Aronheim (107). Later, several investigators (108-110) also studied these reactions in detail. Krause et al (111, 112) prepared $(CH_3)_3SnBr$ and $(CH_3)_2SnBr_2$ by bromination of $(CH_3)_4Sn$ with bromine under appropriate reaction conditions. Seyferth (113) prepared $(CH_3)_3SnI$ by iodination of $(CH_3)_4Sn$. Harada (98) prepared several other tri- and di- alkyl halides. Manulkin (106, 114) studied several of such reactions in ether medium and observed decreasing reactivity with increasing carbon atoms in alkyl or aryl group of the tetraalkyl or tetraaryltin. He also found that by using boiling toluene, better results could be obtained. Following this method several workers obtained quite good results during their preparations of organotin halides. The successful synthesis was carried out for R_3SnX /̅X = Cl, Br, I and R = p-tolyl (115, 116), o-toly, p-xylyl (116)_7, R_3SnX and R_2SnX_2 /̅X = Br, I and R = C_6H_{11} (117)_7, R_3SnX /̅X = F, Cl, Br, I_7.

Von Rumohr et al (101) synthesised $(CH_3)_2SnCl_2$ starting from methyl chloride and molten tin using $NaAlCl_4$ as catalyst. The reaction was stated not to proceed directly but via an addition of methyl chloride to stannons chloride forming CH_3SnCl_3, which was then reduced by the tin metal and followed by another addition of methyl chloride.

A systematic review of methods for the catalysed synthesis of organotin (IV) halides from tin metal and alkyl halides with 163 references was made by Kizlink Juraj in 1984 (102).

In 1985 the compound $Br_2Sn(CH_2COOC_2H_5)_2$ was prepared by Bogatskii (103) by refluxing tin powder and $BrCH_2COOC_2H_5$ in a molar ratio 1:2. The process was run in two stages by heating the reaction mixture at 60-70°C for 10-15 minutes and then refluxing 5-15 minutes in presence of catalytic amount of Crown ether 15-Crown-5. Bogatskii et al (104) also synthesised dialkyltin dibromide by heating tin at 90-100°C in the presence of Crown ether (15-Crown-5 ether) and then treating with alkyl bromide at reflux condition for 45-60 minutes. In the same year Glosky (105) prepared methyltin chlorides. Dimethyltin dichloride was prepared by reacting methyl chloride with $Sn/SnCl_2$ at ∽200°C in the presence of pentavalent organophosphorus dihalide catalyst. A mixture of $(C_4H_9)_3PCl_2$, Sn and $SnCl_2$ in the molar ratio 1:1:1 was heated to 185-190°C and then treated with methyl chloride until no further reaction was observed (∽2.5 hours). Crude methyltin trichloride and dimethyltin dichloride were separated and then tin metal and methyl chloride were added at 185-190°C. After four such cycles, the products were found a mixture of ∽82% dimethyltin dichloride and ∽18% methyltin trichloride with the overall yield of 90% organotin chloride.

(b) Cleavage reactions:

The synthesis of organotin halides by cleavage reaction involves two types viz. the cleavage of Sn-C bond and the cleavage of Sn-Sn bond. Halogen and hydrogen halides are effective in cleaving Sn-C bond whereas Sn-Sn bond may be cleaved by halogen, hydrogen halide, alkyl halide, mercuric chloride or alkyl mercuric chloride.

(i) Cleavage of tin-carbon bond:

The general reactions under this heading are as follows:

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

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

$$R_2SnX_2 + 2X_2 \longrightarrow SnX_4 + 2RX$$

$$R_4Sn + HX \longrightarrow R_3SnX + RX$$

$$R_3SnX + HX \longrightarrow R_{''}SnX_2 + RX$$

and R = CH_2CH_2CN (118), $(p\text{-}FC_6H_4)_3SnBr$ (119), $(p\text{-}ClC_6H_4)_3SnBr$ (120), $(p\text{-}ClC_6H_4)_2SnBr_2$. By bromination of $[C_6H_5C(CH_3)_2CH_2]_4Sn$, Reichle (121) obtained impure monobromide. Tetranaphthyltin and tetramesityltin were apparently found inactive during bromination and iodination with bromine and iodine respectively (122). Such halogenation of organostannanes was studied by different investigators (52, 113, 123-139) in different solvents and also by changing other reaction parameters. Different organotin iodides were prepared by starting with the compound of the type R_3SnR' (R and R' being different) and carrying out the reactions in different solvents and different temperatures (113, 140, 141).

Van der Kerk and Noltes (142) studied few halogenation reactions involving functionally substituted organic groups. ~~He~~ They found that in α-substituted organotin nitriles and esters, the functionally substituted groups were most easily removable groups whereas in β-substituted organotin compounds or in compound with substituent in a position more distant than β-position, generally non substituted alkyl or aryl groups were found to split off from the organotin molecules. The reactivity of organotin halides were also found to depend on the nature of the substitution. Thus α-thienyl group (143) and alkyl group (135) were found to be more reactive than phenyl. The reactivity of the organotin halide involving cyanomethyl group (144) cyanoethyl group (145), 1-cyclopentadienyl group (146), neopentyl group (147) was also studied. The bromination of diethyl cyclopentamethylenetin $(C_2H_5)_2(CH_2)_5Sn$ brought out the cleavage of the ring with the formation of $(C_2H_5)_2SnBr(CH_2)_5Br$ (128).

Beside these many other organotin halides were prepared by the halogenation with halogen acids. Manulkin (148) obtained $(CH_3)_3SnCl$ by the reaction of tetramethyl stannane and hydrogen chloride in boiling chloroform. A series of compounds with the composition R_3SnCl [R = C_6H_5 (149), n-dodecyl, n-tetradecyl, and n-octadecyl (150)] were prepared by this method at room temperature. Adjusting the relative amounts of hydrogen chloride with the tetraorganostannane, several diorganotindichlorides such as diphenanthryl and diphenyl-2-tin dichloride were successfully prepared. The reactivity of Sn-C bond for cleavage by hydrogen halide was studied in few cases. The vinyl group was found to have same relative reactivity toward hydrogen chloride and hydrogen bromide as that of iodine (137). $(C_2H_5)_2Sn(CH_3)_2$ and $(C_2H_5)_2Sn(n\text{-}C_3H_7)_2$, the compounds were formed by simultaneous replacement of two different groups by gaseous hydrogen chloride at 100-140°C (151). From $(CH_3)_3SnC_2H_5$ only one methyl group could be split off by hydrogen chloride (148) in boiling chloroform. In tribenzylethyltin, a benzyl group could be replaced by iodine but ethyl group was found to be replaced by chlorine on treatment with hydrogen chloride (152).

Not only the halogens and halogen acids were found effective for halogenation but also some metallic halides could bring about such halogenation reactions to yield organotin halides. Thus in alkaline medium, mercuric chloride was reported to successively replace the phenyl groups in tetraphenyltin by chlorine (153,154). With tetracyclopropyl-

-tin and mercuric chloride, tricyclopropyltin chloride and with mercuric bromide, the corresponding bromide were obtained (155). Manulkin (156) investigated the reaction between aluminium chloride and tetraphenyltin, tetraethyltin, tetrabutyltin and obtained the reaction products stannic chloride, diethyltin dichloride and a mixture of tributyltin chloride and dibutyltin dichloride respectively. With ferric chloride, tetraethyltin yielded triethyltin chloride (156). Several metal halides and metaloid halides were found suitable to conduct such halogenation reactions (91,138,157-164).

The cleavage of tin-carbon bond in tetraorganostannanes could also be carried out by halogen transfer agents like acyl chloride (108,165,166), chlorosulphuric acid (139), benzene sulphonyl chloride, sulphuryl chlorides (108, 166), and even with alkyl halides (108,165,167,168) using appropriate reaction conditions. In all cases the reaction products were of the form R_3SnX or R_2SnX_2 or a mixture of both.

In 1983, Surin Laosooksathit (169) treated $(C_6H_5)_3Sn(C_4H_9)$ and $(C_6H_5)_3Sn(CH_2)_4Sn(C_6H_5)_3$ separately with HBr/CH_2Cl_2 at $-78^{o}C$ and obtained $(C_6H_5)_2Sn(C_4H_9)Br$ and $(C_6H_5)_2SnBr(CH_2)_4Sn(C_6H_5)_2Br$ respectively. At the same year Wardell et al (170) found that reactions of $(C_6H_5)_3Sn(CH_2)_nSOC_6H_4(CH_3)$p, (n = 3 or 4) with iodine, bromine or mercuric chloride all formed $(C_6H_5)_2XSn(CH_2)_nSO_mC_6H_4(CH_3)$-p (X = iodo, bromo or chloro; m = 1,2).

The halodephenylation of $(C_6H_5)_3SnX$ (X = NCO, NCS and N_3) with IX' (X' = Cl and/or Br) to yield $(C_6H_5)_2Sn(X)X'$ and C_6H_5I was reported by Srivastava et al (171) in 1985.

(ii) Cleavage of tin-tin bond:

The general reactions under this heading are as follows:

$$(R_3Sn)_2 + X_2 \longrightarrow 2R_3SnX$$

$$(R_2Sn)_n + nX_2 \longrightarrow nR_2SnX_2$$

$$(R_3Sn)_2 + HX \longrightarrow 2R_3SnX + H_2$$

$$(R_2Sn)_n + nHX \longrightarrow nR_2SnX_2 + nH_2$$

$$(R_3Sn)_2 + 2RX \longrightarrow 2R_3SnX + R_2$$

$$(R_3Sn)_2 + R'X \longrightarrow R_3SnX + R_3SnR'$$

$$(R_2Sn)_n + nRX \longrightarrow nR_3SnX$$

$$(R_3Sn)_2 + HgCl_2 \longrightarrow 2R_3SnCl + Hg$$

$$(R_2Sn)_n + nHgCl_2 \longrightarrow nR_2SnCl_2 + nHg$$

$$(R_3Sn)_2 + RHgCl \longrightarrow R_3SnCl + R_4Sn + Hg$$

The halogenation of $(R_3Sn)_2$ and $(R_2Sn)_n$ by using halogens (4,147,172-175) proper alkyl halide (175-178) and by using halogen acids (175, 179) /̲R = alkyl, aryl group and X = Cl, Br, I _7 were carried out successfully by different investigators from time to time. Use of mercuric chloride or alkyl mercury chloride for halogenation of organostannanes was also reported (180,181).

The reaction between stannic chloride and $[(C_2H_5)_3Sn]_2$ (182) yielded tin, triethyltin chloride, diethyltin dichloride and tetraethyltin, but with $[(C_6H_5)_3Sn]_2$ (175) the products were stannous chloride and triphenyltin chloride. Nasielski et al (183) studied the kinetics of several such reactions.

(c) Redistribution reaction:

The treatment of a tetra- alkyl or aryl tin compound with the requisite amount of stannic halide is widely used procedure for the preparation of organotin halides and the process has the advantage over the halogen cleavage method is that none of the organic groups is lost.

The reaction types may be represented as follows:

$$3R_4Sn + SnX_4 \longrightarrow 4R_3SnX$$
$$R_4Sn + SnX_4 \longrightarrow 2R_2SnX_2$$
$$R_4Sn + 3SnX_4 \longrightarrow 4RSnX_3$$
$$R_3SnX + RSnX_3 \longrightarrow 2R_2SnX_2$$
$$R_2SnBr_2 + Br_2 \longrightarrow RSnBr_3 + RBr$$

In the first three reactions, the chlorides are formed more readily than the bromides, stannic iodide usually reacts so slowly that the method is rarely used for the preparation of iodides.

Kocheshkov (184-189) first introduced this method for the preparation of R_3SnX, R_2SnX_2 and $RSnX_3$ type of compounds, /‾R = C_6H_5, $C_6H_4CH_3$, CH_3, C_2H_5, n-C_3H_7 _7. Rosenberg and his co-worker (136) carried out the similar reaction where they used the compound having $CH_2 = CH-$ group for R. Vyayraghavan prepared (191) compound where R stood for $CH_3-CH = CH-$ group.

Among the other compounds obtained by redistribution reactions, dicyclopropyltin dichloride and dibromide (192) and $(C_6F_5)_3SnCl$, $(C_6F_5)_2SnCl_2$ (193) may also be mentioned.

The fourth and fifth reactions among the mentioned reactions were carried out in recent years. Max Buschhoff (194) in 1984 prepared the compounds R_nSnX_{4-n} (R = alkyl, aryl, aralkyl, cycloalkyl; X = halogen; (n = 1,2,3), useful as plastic stabiliser were prepared from a redistribution of appropriate alkyltin halides in presence of SnF_2 catalyst at temperatures varying in the range of 140-210°C. Thus $(C_4H_9)_2SnCl_2$ was prepared in 97% yield from $(C_4H_9)_3SnCl$ and $C_4H_9SnCl_3$ by heating at a temperature of 160°C.

Medvedev and Yatsenko (195) in 1985 prepared $RSnBr_3$ (R = C_2H_5, C_4H_9) in about 70% yield by bromination of R_2SnBr_2 in the absence of a solvent.

(d) Displacement of one halogen by other by using appropriate halogen acids:

The method is best way for the synthesis of other organotin halides which can not be obtained in pure form or in good yield by other classical methods (196).

$$R_3SnX + MOH \longrightarrow R_3SnOH + MX$$
$$R_3SnOH + HX' \longrightarrow R_3SnX' + H_2O$$

$$R_2SnX_2 + 2MOH \longrightarrow R_2Sn(OH)_2 + 2MX$$
$$R_2Sn(OH)_2 + 2HX' \longrightarrow R_2SnX'_2 + 2H_2O$$

$$RSnX_3 + 2H_2O \longrightarrow RSnOOH + 3HX$$
$$RSnOOH + 3HX' \longrightarrow RSnX'_3 + 2H_2O$$

(where R = alkyl or aryl group and X = F, Cl, Br, I).

The reaction of sodium fluoride in alkaline aqueous solution with organotin oxide is an excellent method for the preparation of organotin fluorides (117, 120, 173, 197-199). Not only in the case of preparation of organotin fluoride, the preparation of other organotin halides also was carried out by the halogenation of organotin hydroxides (prepared by the alkaline hydrolysis of suitable organotin halides) by appropriate halogen acids (196).

The direct replacement of one halogen by another was also reported in many case (117,120,129,173,197,199-204).

Thus dimethyltin dichloride could be converted to dimethyltin diiodide with sodium iodide and $(n\text{-}Bu)_2SnCl_2$ to $(n\text{-}Bu)_2SnF_2$ with sodium fluoride.

Recently in 1985, conversions of dibenzyldichlorostannane (i.e. dibenzyltin dichloride) to dibutyldichlorostannane (i.e. dibutyltin dichloride) was carried out by B. Mahieu et al by using tributylaluminium.

(e) Reactions involving Grignard reagent and other metal alkyl or metal aryl:

Use of Grignard reagent or other metal alkyl (or metal aryl) is one of the important method for the synthesis of tetraalkyl (or aryl) tin) Alkyl (or aryl)tin halides are generally obtained along with R_4Sn.

The general scheme of the reaction may be represented as follows:

$$RMgX + SnX_4 \longrightarrow RSnX_3 + MgX_2$$
$$2RMgX + SnX_4 \longrightarrow R_2SnX_2 + 2MgX_2$$
$$3RMgX + SnX_4 \longrightarrow R_3SnX + 3MgX_2$$

$$R_3Al + SnX_4 \longrightarrow R_3SnX + AlX_3$$
$$2R_3Al + 3SnX_4 \longrightarrow 3R_2SnX_2 + 2AlX_3$$
$$R_3Al + 3SnX_4 \longleftrightarrow 3RSnX_3 + AlX_3$$
$$3(cyclo\text{-}C_6H_{11})_2AlCl + 2SnCl_4 \longrightarrow 2(cyclo\text{-}C_6H_{11})_3SnCl + 3\ AlCl_3$$

where R = alkyl or aryl grpup; X = Cl, Br, I.

Many of the organotin halides could be successfully prepared by using Grignard reagent and tin (IV) halides (196). Such reactions were found to form mixture of several alkyl (or aryl) tin halides and tetraalkyl (or aryl)tin (193,205-207). The use of Grignard reagent was found very helpful for linking large organic groups, such as 1-naphthyl (120), 2-diphenyl (122) and neophyl (208) to tin. Perfluorophenyltin halides were obtained from stannic chloride and corresponding Grignard reagent (202, 209, 210). The use of organolithium reagents (211) and organo mercury reagents (209,212) were also reported to be used instead of Grignard reagent.

The preparation of dibutyltin dichloride was reported from the reaction of Würtz type of reaction (213) and also from the reaction of butyl sodium and stannic chloride (214). Synthesis of diphenyltin dichloride was reported from the reaction of diphenyl mercury and stannic chloride by Aronheim (215).

Recently in 1985, Jiauxi (216) prepared tetraphenanthryl-(9)-tin and diphenanthryl-(9)-tin dichloride by Grignard reaction method with 86% yield with slight modification of the process. Grignard reaction of 9-phenanthryl bromide with stannic chloride in benzene was performed at room temperature. Tetra-9-phenanthryltin formed was then converted to di-9-phenanthryltin dichloride in chloroform by hydrogen chloride gas in 80% yield.

Since 1960 several workers (217-225) used aluminium alkyls and tin (IV) halides for the preparation of organotin halides. In recent years one of the important synthesis by this route was the preparation of R_3SnCl (R = cyclohexyl) in 1984 by Gavrilenko et al (226). The yield was found 80%.

(f) Alkylation of stannous chloride:

Tin (II) chloride has been found to form organotin (IV) compounds with certain suitable alkylating agents. Of course this route is limited in application.

Nesmeyanov and Kocheshkov (227) used stannous chloride and diphenyl mercury for the preparation of diphenyltin dichloride. The reaction was successfully performed with different diaryl mercury where aryl groups were phenyl, benzyl, p-tolyl, α-naphthyl, β-naphthyl (227) and p-chloro-, p-bromo- and p-iodophenyl (228). Instead of diaryl mercury, aryl mercury halides were also used in some cases for such reactions. Diethyl lead dichloride and stannous chloride were used by Kocheshkov and Freidlina (200) for the synthesis of diethyltin dichloride. Similarly dimethyltin dichloride and diphenyltin dichloride were synthesised. Analogous reactions were reported with R_2TlX (229,228). Relatively small yields of methyltin trichloride and methyltin triiodide were obtained from the reaction of stannous chloride and methyl chloride or methyl iodide respectively. Few modifications of such processes for the preparation of different alkyl or aryl tin halides were also successfully attempted (230,231).

(g) Hydrostannation route:

One of the widely used route to functionally substituted organotin compounds is hydrostannation reaction. A review by Leusink (232) demonstrated the importance of this approach. The hydrostannation route was previously limited to the synthesis of tetraalkyltin compounds and trialkyltin halides.

Addition of an organotin hydride to a carbon-carbon double bond was first demonstrated by Van der Kerk and his co-workers in 1956 (233) and the reaction type was

$$R_3SnH + CH_2 = CHX \longrightarrow R_3SnCH_2CH_2X$$

where X was different substituents. The route was established as a major method for forming tin-carbon bonds. With few exceptions (234-236), the reaction could be successfully used in the preparation of large number of important organotin compounds (237-252). With triorganostannane sometime hydrostannolysis also occurs.

$$R_3SnH + R'X \longrightarrow R_3SnX + R'H$$

(R = alkyl or aryl group; R' = alkyl, aryl, substituted alkyl or substituted aryl group; X = Cl, Br, I) (236,252).

With the carbonyl compounds the reactions of organostannanes were found to take place ~~in the following manner~~ (253-255).

The reactions of organostannanes with other suitable organotin halides or hydrogen halides are capable of forming organotin halohydride.

$$R_2SnH_2 + R_2SnX_2 \rightleftharpoons 2R_2SnXH$$

(where R = butyl group; X = F, Cl, Br, I) (256)

With dihydride and dichloride having different groups attached to tin, the following equilibria was found to exist (257).

$$R_2SnH_2 + R'_2SnCl_2 \rightleftharpoons R_2SnCl + R'_2SnClH \rightleftharpoons R_2SnCl_2 + R'_2SnH_2$$

The organotin halohydrides can also be prepared by the action of hydrogen halide on the organostannanes.

$$C_2H_5SnH_3 + HBr \longrightarrow C_2H_5SnBrH_2 + H_2$$

(258)

$$(C_6H_5)_3SnH + HBr \longrightarrow (C_6H_5)_2SnBrH + C_6H_6$$

$$(C_4H_9)_2SnH_2 + HCl \longrightarrow (C_4H_9)_2SnClH + H_2$$

(258 a)

The reactions of monohydride and dichloride (259) were also studied.

$$R'_3SnH + R_2SnCl_2 \longrightarrow R'_3SnCl + R_2SnClH$$

(where R' = butyl grpup; R = alkyl group).

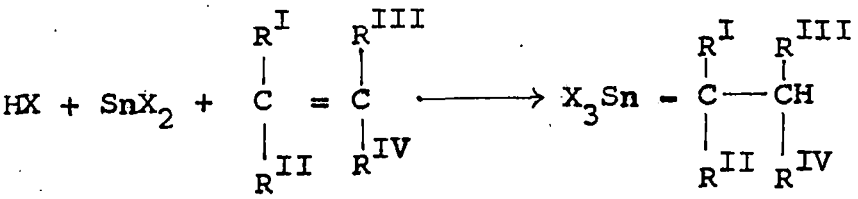
The organotin halohydrides were found not very stable (258a). Though unstable yet these compounds could be made to undergo certain reactions where the products were substituted alkyl-tin halides.

$$(C_2H_5)_2SnClH + Hg(CH_2COOCH_3)_2 \longrightarrow$$
$$\longrightarrow (C_2H_5)_2Sn(Cl)CH_2COOCH_3 \quad (260)$$
$$+ Hg + CH_3COOCH_3$$

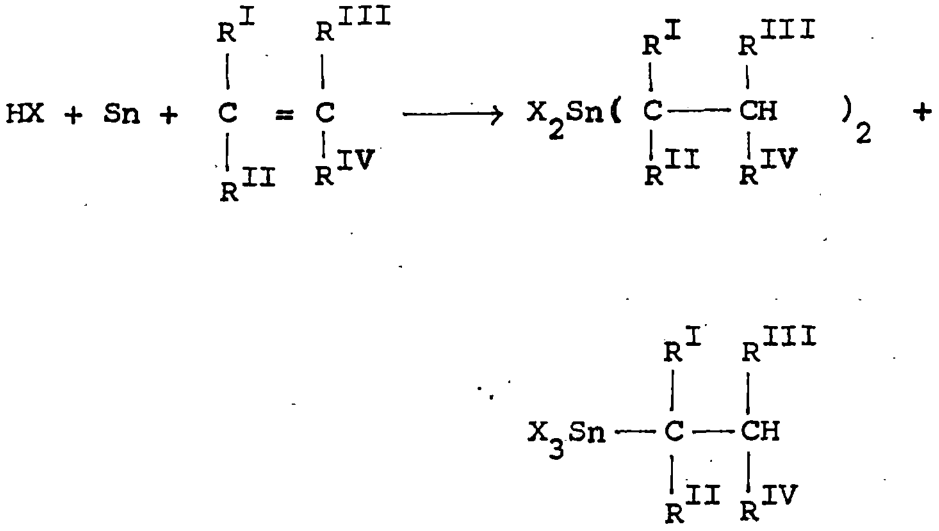
$$(i\text{-}C_4H_9)_2SnClH + CH_2 = CHCN \longrightarrow (i\text{-}C_4H_9)_2Sn(Cl)CH_2CH_2CN \quad (261)$$

The reaction involving di-isobutyltin chlorohydride and acrylonitrile is similar to addition of triorganostannane to terminal alkenes (262-264).

Hydrostannation route was used by Hutton et al (265-268) to prepare a quite large number of functionally mono- and di- substituted organotin halides. They carried out the reaction between hydrogen halides, stannous halides and α,β-unsaturated carbonyl compounds to yield β-substituted alkyltin trihalides and the reactions between hydrogen halides, tin and the α,β-unsaturated carbonyl compounds to give largely bis - (β-substituted alkyl) tin dihalides in substantial amount. The following equations represent the overall reactions.



$$HX + SnX_2 + R^{I}R^{II}C{=}CR^{III}R^{IV} \longrightarrow X_3Sn{-}CR^{I}R^{II}{-}CHR^{III}R^{IV}$$



$$HX + Sn + R^{I}R^{II}C{=}CR^{III}R^{IV} \longrightarrow X_2Sn(CR^{I}R^{II}{-}CHR^{III}R^{IV})_2 + X_3Sn{-}CR^{I}R^{II}{-}CHR^{III}R^{IV}$$

(X = Cl, Br, I; R^{I}, R^{II} and R^{III} are H or CH_3; R^{IV} organic groups containing $-\overset{O}{\overset{\|}{C}}-$).

The reactions were found highly specific and proceed in high yield at convenient temperatures and atmospheric pressure. A wide variety of activated olifins were used by Hutton et al which were largely α,β-unsaturated esters, α,β-unsaturated ketones, acids and amides etc. Exceptions to these were maleic acid esters and isophorone.

In most of the reactions hydrogen halide used by them was hydrogen chloride. Addition of excess of dry gaseous hydrogen chloride to anhydrous stannous chloride in dry diethyl ether medium at a temperature below 25°C form a pale yellow lower layer, previously characterised as $HSnCl_3 \cdot (C_2H_5OC_2H_5)_2$ was also used by them (269) in some cases. Above 30°C the complex was found to be unstable decomposing to hydrogen chloride, stannous chloride and diethyl ether.

$$HSnCl_3 \cdot (C_2H_5OC_2H_5)_2 \rightleftharpoons SnCl_2 + HCl + 2(C_2H_5)_2O$$

The Table 1 and Table 2 represent some of the successful attempts by them. They observed that during the preparation of disubstituted alkyltin dichlorides the formation of mono- substituted alkyltin trichloride can be minimised by slow passage of hydrogen chloride which prevents the formation of stannous chloride. The more sterically hindered monomers tend to have a reduced rate of reaction but still give high yields. In every case only the β-adduct was isolated as shown by NMR spectroscopy. Any solvent which does not react with hydrogen halide may be used. With certain monomers, e.g. butyl acrylate, the monomer acts as its own solvent and complexing agent. The yield of organotin halide is lowered because of hydrolysis by the moisture present in the system. Hydrohalogenation of monomer also sometime lowers the yield of organotin.

Table 1

The reaction between hydrogen halide, Sn(II) halide and α,β-unsaturated carbonyl compound in diethyl ether.

Organic compound	Reaction temperature (^{o}C)	Reaction time (hours)	Conversion of $SnCl_2$ (%)	Organotin compound	Melting point (^{o}C)	(C=O) in cm^{-1}
$CH_2 = CHCOOCH_3$	25	3.5	98	$Cl_3SnCH_2CH_2COOCH_3$	69	1660
$CH_2 = CHCOOCH_3$	20	1	72	$Br_3SnCH_2CH_2COOCH_3$	75	1655
$CH_2 = CHCOOC_2H_5$	15	1	79	$Cl_3SnCH_2CH_2COOC_2H_5$	68	1665
$CH_2 = CHCOOC_4H_9$	20	2	92	$Cl_3SnCH_2CH_2COOC_4H_9$	46	1659
$CH_2 = CHCOOC_6H_5$	20-25	5	89	$Cl_3SnCH_2CH_2COOC_6H_5$	177	1686
$CH_2 = C(CH_3)COOCH_3$	25	3.5	62	$Cl_3SnCH_2CH(CH_3)COOCH_3$	86	1660
$(CH_3)_2 = CHCH_3$	25	2	80	$Cl_3SnC(CH_3)_2CH_2COCH_3$	123	1665
$CH_2 = CHCOOH$	25	4	99	$Cl_3SnCH_2CH_2COOH$	123-127	1665
$CH_2 = CHCONH_2$	20	10	<20	$Cl_3SnCH_2CH_2CONH_2$		
$CH \equiv CCOOH$	20-25	2	~ 60	$Cl_3SnCH = CHCOOH$		1623
$CH \equiv CCOOCH_3$	20	6	60	$Cl_3SnCH = CHCOOCH_3$		

Table 2

The reaction between hydrogen halide, tin powder and α,β-unsaturated carbonyl compound in diethylether at 20°C (with Sn/Monomer ½).

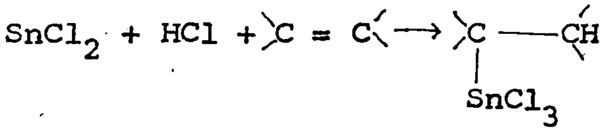
Organic compound	Reaction time (hours)	Conversion of tin (%)	Diorganotin dihalide	% Mono organotin trihalide	% Diorganotin dihalide	Melting point (°C)	(C=O) in cm^{-1}
$CH_2 = CHCOOCH_3$	14	94	$Cl_2Sn(CH_2CH_2COOCH_3)_2$	3.5	94	132	1677
$CH_2 = CHCOOCH_3$	12	100	$I_2Sn(CH_2CH_2COOCH_3)_2$	7	2		1677
$CH_2 = CHCOOC_2H_5$	25	100	$Cl_2Sn(CH_2CH_2COOC_2H_5)_2$	15	60		1677
$CH_2 = CHCOOC_4H_9$	20	100	$Cl_2Sn(CH_2CH_2COOC_4H_9)_2$	9.5	Pure product ~10 could not be isolated		1676
$CH_2 = C(CH_3)COOCH_3$	13	45	$Cl_2Sn(CH_2CH(CH_3)COOCH_3)_2$	50	25	111	1676
$C(CH_3)_2 = CHCOCH_3$	10	100	$Cl_2Sn(C(CH_3)_2CH_2COCH_3)_2$	22	46	158	1671
$CH_2 = CHCOCH_3$	14	100	$Cl_2Sn(CH_2CH_2COCH_3)_2$	~47	Purification was not possible	107-108	1672

Contd..

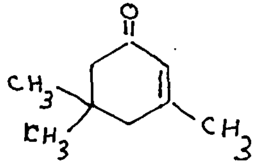
Table 2 (Contd..)

$CH_2 = CHCONH_2$	23	82	$Cl_2Sn(CH_2CH_2CONH_2)_2$	< 3	79	240-250	1669
$CH_2 = CHCOOH$	6.5	66	$Cl_2Sn(CH_2CH_2COOH)_2$	< 3	70	157	1676
$CH_2 = CHCN$	15	66	$Cl_2Sn(CH_2CH_2CN)_2$	< 3	14	173	

Table 3



$$SnCl_2 + HCl + \rangle C = C\langle \longrightarrow \underset{\overset{|}{SnCl_3}}{\rangle C} - CH\langle$$

Reactive Monomers	Unreactive monomers
Acrylate $CH_2 = CHCOOR$	Acrolein $CH_2 = CHCHO$
Methacrylates $CH_2 = CHCOOR$	Alpha Olefins $CH_2 = CH-R$
	Allyl chloride $CH_2 = CHCH_2Cl$
Crotonates $CH_3 = CHCOOR$	Allyl alcohol $CH_2 = CHCH_2OH$
Acrylic acid $CH_2 = CHCOOR$	Styrene $C_6H_5.CH = CH_2$
Methacrylic acid $CH_2 = C(CH_3)COOH$	Isophorone 

Contd..

Table 3 (Contd..)

Acryloyl chloride $CH_2 = CHCOCl$

Vinyl ketone $CH_2 = CHCOR$

Phorone $(CH_3)_2C=CHCOCH=C(CH_3)_2$

Propiolic acid $CH = CCOOH$

Acrylamide $CH_2 = CHCONH_2$

Diethyl Ethylidene Malonate

$CH_3CH = C(COOC_2H_5)_2$

Vinyl acetate $CH_3COOCH = CH_2$

Acetylene $CH = CH$

Furan 

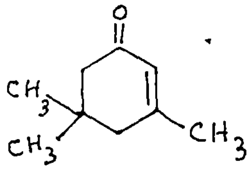
Maleic Acid Ester

$ROOCCH = CHCOOR$

Phenyl Acetylene $C_6H_5\ C \equiv CH$

Table 4

$$Sn + 2HCl + 2 \;{>}C = C{<} \longrightarrow ({>}CH - \overset{|}{\underset{|}{C}}-)_2SnCl_2$$

Reactive Monomers	Unreactive Monomers
Acrylates $CH_2 = CHCOOR$	Alpha olefins $CH_2 = CHR$
Methacrylates $CH_2=C(CH_3)COOR$	Styrene $C_6H_5CH = CH_2$
Crotonates $CH_3CH=CHCOOR$	Isophorone 
Acrylic Acid $CH_2=CHCOOR$	Maleic Acid
Acryloyl Chloride $CH_2 = CHCOCl$	$HOOCCH = CHCOOH$
Methyl Vinyl Ketone $CH_2 = CHCOCH_3$	Maleic Acid Esters $ROOCCH = CHCOOR$
Phrone $(CH_3)_2C = CHCOCH=C(CH_3)_2$	
Propiolic Acid $CH \equiv CCOOH$	
Acrylamide $CH_2 = CHCONH_2$	
Diethyl Ethylidene Malonate $CH_3CH = C\ (COOC_2H_5)_2$	

halide. In the preparation of trichlorostannane, an oxygenated solvent must be used. Monomers such as sytrene which add hydrogen halide or which polymeri~~c~~se can not be used. Intramolecular carbonyl coordination to tin centre occurs in these β-substituted organotin compounds.

Hutton et al (270) suggested the limitations of the above reactions as indicated in the Table 3 and Table 4.

Burley ~~Joseph~~ et al not only prepared β-carboalkoxyethyltin trihalides and bis(β-carboalkoxyethyl)tin dihalides but also they successfully prepared and characterised some of the tris (β-carboalkoxyethyl)tin halides and tetra (β-carboalkoxyethyl)tin compounds of the same series (271).

Studying some previous experimental results

$$RX + Sn \longrightarrow RSnX_3 + R_2SnX_2 + R_3SnX$$

$$(X = Br, I;\ R = CH_3,\ C_4H_9,\ C_8H_{17})$$

(272)

$$R_2SnX_2 + M \xrightarrow[160^\circ C]{\text{Base } (+\ RX)} R_3SnX + R_4Sn$$

$$(R = C_4H_9;\ X = Cl;\ M = Zn, Sn)$$

(273)

$$RSnCl_3 + M \xrightarrow[20^\circ C]{(C_2H_5)_2O} R_2SnCl_2 + R_3SnCl$$

$$(R = CH_3,\ CH_2CH_2COOCH_3;\ M = Zn,\ Sn)$$

(274)

They were able to prepare tris (β-carboalkoxyethyl)tin halides and tetra (β-carboalkoxyethyl)tin by reacting β-carboalkoxyethyltin trihalides and zinc (or tin) under appropriate reaction condition. The overall reaction can be represented as follows:

$$X_3XnCH_2CH_2COOR + Zn \longrightarrow XSn(CH_2CH_2COOR)_3 + Sn(CH_2CH_2COOR)_4$$

$(X = Cl,\ Br;\ R = CH_3,\ C_2H_5,\ C_4H_9,\ C_6H_5)$

The reaction between bis (β-carboalkoxyethyl)tin dihalide and Zn was as follows:

$$X_2Sn(CH_2CH_2COOR)_2 + Zn \longrightarrow XSn(CH_2CH_2COOR)_3 + Sn(CH_2CH_2COOR)_4$$

(X = Cl, Br; R = alkyl, or aryl radical).

The bis (β-carboalkoxyethyl)tin dihalides were found somewhat less reactive than the corresponding trihalides and short reaction time generally found to favour the formation of tris (β-carboalkoxyethyl)tin halides. Moreover unlike the β-carboalkoxyethyltin trihalides, the dihalides could not made to react with metallic tin, they reacted only in presence of zinc. They also studied all these reactions thoroughly by changing solvent, temperature, reaction time and also by using some catalysts.

The detailed picture of few of their successful attempts are tabulated here (Table 5). Not only they prepared the compound but also they studied their properties. The structure of these compounds were also characterised with the help of spectroscopic data (IR, NMR etc).

Burley et al (275) prepared several of the ketoalkyltin trichlorides and bis(ketoalkyl)tin dichloride by following hydrostannation route under appropriate reaction conditions. In many cases specially during the preparation of bis(alkyl)tin dichloride they obtained mixtures of organotin compounds instead of getting a single compound as the major product. However, they were able to characterise and study these compounds. Few of their successful attempts were as follows. (Table 6).

Not only they attempted to prepare bis(ketoalkyl) tin dichloride but they also prepared mono(ketoalkyl)tin trichloride by the reaction of hydrogen chloride, stannous chloride and appropriate ketone in suitable solvent at proper reaction temperature. They isolated in reasonable yield $Cl_3SnC(CH_3)_2CH_2COCH_3$ from a mixture of hydrogen chloride, stannous chloride and acetone in an ethereal solution. Use of acetone in place of α,β-unsaturated ketone was explained by them as the formation of α,β-unsaturated carbonyl compound from the added ketone by acid-catalysed condensation reaction in the first step of the reaction, the condensation product simultaneously produced in reaction mixture the α,β-unsaturated carbonyl compound by

Table 5

Reactions between β-carboalkoxyethyltin compounds and zinc.

Reagent	Solvent	Zn/Organotin (Molar ratio)	Reaction time (h)	Temperature (^{o}C)	Yield(%) R'_3SnCl+ R'_4Sn	% R'_4Sn
$Cl_3SnCH_2CH_2COOCH_3$	Ether	2.63	20	22	73	
		2.95	36	Reflux	80	74
$Br_3SnCH_2CH_2COOCH_3$	Toluene	2.73	5	Reflux	58	6
$Cl_3SnCH_2CH_2COOC_2H_5$	Ether	2.00	16	Reflux	86	4
$Cl_3SnCH_2CH_2COOC_4H_9$	Ether	2.71	20	22	75	
$Cl_3SnCH_2CH_2COOC_6H_5$	Toluene	2.26	12	Reflux	47	Not determined
$Cl_2Sn(CH_2CH_2COOCH_3)_2$	Ether	1.30	36	Reflux	69	70
	Methyl acetate	1.11	2	Reflux	81	12
$ClSn(CH_2CH_2COOC_4H_9)_2$	Ether	1.37	8	Reflux	76	8
	Ether	1.03	21	Reflux	84	7
	Ether	1.37	36	Reflux	79	75

Contd..

Table 5 (Contd..)

	Toluene (100 ml) + $ClCH_2CH_2COOC_4H_9$ (8 gm)	5.49	5	Reflux	50	30
$Br_2Sn(CH_2CH_2COOC_4H_9)_2$	Toluene	1.64	5	Reflux	71	Not determined
$Cl_2Sn(CH_2CH_2COOC_6H_5)_2$	Toluene	0.99	20	Reflux	62	Not determined
$(CH_3COO)_2Sn(CH_2CH_2COOCH_3)_2$	Toluene	1.77	3	Reflux	83	95
$(CH_3COO)_2Sn(CH_2CH_2COOC_4H_9)_2$	Toluene	3.03	8	Reflux	83	100

R' = CH_2CH_2COOR; R = alkyl or aryl group.

Table 6

The reaction of dialkyl ketones RCOR' with tin and hydrogen chloride (at 35°C) (Molar ratio ketone/tin/hydrogen chloride = 4/1/2)

Ketone R	 R'	Solvent	Reaction time (h)	Number of organotin products (TLC)	Yield(%)	Mono-keto-alkyltin(%)
CH_3	CH_3	Acetone	4	2	64	30
C_2H_5	C_2H_5	Ether	168	2	29	Main product
C_3H_7	C_3H_7	Ether	144	2	32	Main product
CH_3	C_2H_5	-	12	5	22	48
CH_3	C_3H_7	Hexane	168	1	85	100
CH_3	C_4H_9	Ether	312	2	71	Main product

dehydration. Potentially, a wide range of ketoalkyltin chlorides might be produced (276) by the one step in-situ acid-catalysed condensation of simple ketones and hydrostannation of resultant α,β-unsaturated ketones since trichlorostannane is known to be moderately strong acid.

Their results may be represented in ~~the following~~ table.7.

They (277) reported several ketoalkyltin chlorides from β-hydroxy ketones. Here the principle of acid catalysed dehydration of ketols (β-hydroxy ketones) was used by them as another potential source of formation of α,β-unsaturated ketones in the reaction mixture for the formation of ketoalkyltin chlorides. (table 8) .

The temperature of the reactions was maintained at 35^{o}C and the solvent used here was ether.

However, α -hydroxy ketone such as 3-hydroxy-3-methyl-2-butanone failed to react with HCl/Sn couple to form similar organotin products.

Beside these Garad (278) also reported the reactions of β-carbobutoxyethyltin trichloride.

(h) <u>Other related methods</u>:

Few ester tin chlorides were also prepared by Hoffman et al (279) from the reaction of Sn, HCl and the compound of the type CH_2 : CHR (R = Cyano, COOH, COOR'; R' = alkyl). They obtained 94.3% yield of di-n-butoxypropyltin trichloride by heating a mixture containing Sn

Table 7

Synthesis of 3-keto-1-methyl, butyl tin chlorides.

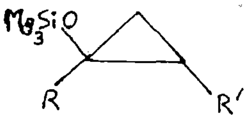
Reagents	Reaction time (h)	Products	Yield (%)	Monoketoalkyltin(%)
HCl, $SnCl_2$ $CH_3CH = CH.COCH_3$	10	$Cl_3SnCH(CH_3)CH_2COCH_3$	79	100
HCl, Sn, $CH_3CH = CH.COCH_3$	8	$Cl_3SnCH(CH_3)CH_2COCH_3$ $+ Cl_2Sn(CH(CH_3)CH_2COCH_3)_2$	55	18
HCl, Sn, $(CH_3)_2CO, CH_3CHO$	5	$Cl_3SnCH(CH_3)CH_2COCH_3$ $+ Cl_2Sn(CH(CH_3)CH_2COCH_3)_2$	67	34

Table 8

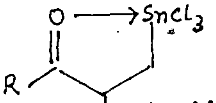
Reagents	Reaction time (h)	Products	Yield (%)	Monoketoalkyltin (%)
HCl, $SnCl_2$, $CH_3COCH_2C(CH_3)_2OH$	3	$Cl_3SnC(CH_3)_2CH_2COCH_3$	76	100
HCl, Sn, $CH_3COCH_2C(CH_3)_2OH$	9	$Cl_3SnC(CH_3)_2CH_2COCH_3$ + $Cl_2Sn(C(CH_3)_2CH_2COCH_3)_2$	44	35
HCl, Sn, $CH_3COCH_2CH_2OH$	7	$Cl_3SnCH_2CH_2COCH_3$ + $Cl_2Sn(CH_2CH_2COCH_3)_2$	79	25
HCl, Sn, $CH_3COCH(CH_3)CH_2OH$	7	$Cl_3SnCH_2CH(CH_3)COCH_3$ + $Cl_2Sn(CH_2CH(CH_3)COCH_3)_2$	60	39

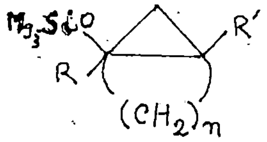
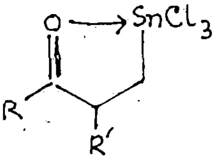
CH_2: $CHCOOC_4H_9$ and 36% HCl at 80°C for five hours in the presence of 0.3 gm of Al.

Kaufhold and his co-workers (280) prepared a series of compounds corresponding to the molecular formula $(RCH_2CH_2)_nSnCl_{4-n}$ (R = cyano, COOH, COOR'; R' = alkyl; n = 1,2) in 1983. They treated metallic tin with the appropriate organic compound at a temperature of 25-30°C for 90 minutes in presence of antimony catalyst which was then followed by addition of conc. HCl. The amount of antimony catalyst was found to range 0.01-10%.

Addition of organotin hydrides of the type $(C_6H_5CH_2)_3SnH$ to methylpropenoates followed by chlorination of the product with mercuric chloride furnished a product of the type $(C_6H_5CH_2)_2SnClCHRCHR'COOCH_3$ (R, R' = CH_3, C_6H_5) reported by Podesta et al (281). Podesta et al (282) also prepared a series of estertin compounds having the general molecular formula $R_2SnXCHR^1CHR^2COOCH_3$ ($R = CH_3$, $R^1 = R^2 = H$; $R = CH_3, C_4H_9, C_6H_5$, $R^1 = R^2 = CH_3$; $R = R^2 = H$, $R^1 = C_6H_5$; $R = C_4H_9, C_6H_5$, $R^1 = R^2 = C_6H_5$; X = chloro, iodo) using $(CH_3)_3SiX$. The yield was reported to range 54-100%. A novel synthesis of β-trichlorostannyl ketones from siloxycyclopropanes was effected by Ilhyong and his co-workers (283). Reactions of monocyclic siloxycyclopropanes 

(R = $(CH_3)_3C$,

$(CH_3)_2CH$, 1-cyclohexyl; R' = H) with stannic chloride in methylene chloride at 15°C for thirty minutes gave β-trichlorostannyl ketones  in good yields.

Also with the compounds of the type  they prepared the compound  (R, R' =H, CH_3; n = 3,4,5) in 66-84% yields.

Howie et al (284) studied the crystal structure and coordination chemistry of $Cl_3SnCH_2CH_2CH_2COOC_2H_5$. Feshin et al (285) studied thoroughly the electronic and spatial structures of estertin type of compounds. e.g. $Cl_3GeCH_2CH_2CONH_2$ and $Cl_3SnCH_2CH_2COOH$ containing donor centres were discussed in relation to ^{35}Cl NMR and crystal structure data determined in previous studies. A study of mercaptoester/chlorine exchange equilibria exhibited by β-carboalkoxyethyltin compounds was performed by Joseph and his co-workers (286). The Cl/mercaptoester exchange reactions in butyl and β-carbobutoxyethyltin compounds were found to occur readily in deuterochloroform at 35°C as confirmed by 60 MHz proton NMR data.

Several workers prepared a number of complex compounds of these estertin halides by using different complexing agents (287, 288, 289). The Lewis acidity of organotin halides will be discussed in more detail later.

Some organotin halides having unsaturation in the organic part were prepared by several investigators. Thus Ryu and his co-workers (290) in 1987 synthesised $CH_2:CRCR^1R^2CH_2SnCl_3$ [$R = H, CH_3, R^1 = R^2 = H; R = H, R^1R^2 = (CH_2)_5, R = R^2 = H, R' = CH_3$, n-heptyl] in very good yield 84-91%. They also synthesised a brominated product $BrCH_2CHBrCH_2CH_2SnCl_3$. The compounds $(C_4H_9)_2ClSnCH(CH_3)CH:CH_2$ and $(C_4H_9)_2ClSnCH_2CH:CHCH_3$ were reported to form as intermediate during the reactions between $(C_4H_9)_3SnCH_2CH:CHCH_3$ and aldehyde in presence of Lewis acids such as $(C_4H_9)_2SnCl_2$ by Boaretto et al in 1987.

Masamune et al (291) used bis (2,4-pentanedionato)tin dichloride to prepare hexakis (2,6-diethyl phenyl)cyclo tristannoxane which on treatment with concentrated hydrochloric acid formed $(2,6-(C_2H_5)_2C_6H_3)_2SnCl_2$.

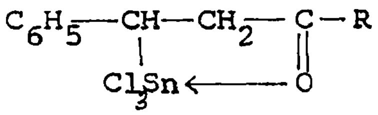
Hawker et al (292) found that treating $((CH_3)_3Sn)_4C$ with bromine, iodine or F_3CCOOH formed $((CH_3)_3Sn)_3CR$, $((CH_3)_3Sn)_2CR_2$, $(CH_3)_3SnCR_3$ ($R = Sn(CH_3)_2R'$; R' = bromo, iodo, CF_3COO) and $C(Sn(CH_3)_2R'')_4$ (R'' = bromo, iodo). In the case of bromo compound, the ultimate product was $(Br_2SnCH_3)_2C(Sn(CH_3)_2Br)_2$. Again they found that on treatment of $(CH_3)_3Sn)_3CH$ with bromine, the compound $(CH_3)_3Sn)_2CHR'''$ and $(CH_3)_3SnCHR'''_2$ and finally R'''_3CH ($R''' = Sn(CH_3)_2Br$) were formed.

In 1984 $(CH_3)_3SnI$ was prepared in 33% yield by Manders et al (293) by shaking a suspension of SnS and CH_3I in water at 60°C for 24 hours in the dark.

Besides these, few organotin halides were reported time to time by different workers to form during some organic synthetis as intermediate products. One such reported (294) organotin halide intermediate was $(CH_2 : C : CH_2)_2SnBr_2$.

SCOPE AND OBJECTIVES

Scope and Objectives

The hydroboration and hydrostannation reactions have added a new dimension in the field of organometallic and organic chemistry. Hutton et al (265-268) have extended these reactions to develop new methods of preparation of estertin chlorides (useful commercial PVC intermediates) by reacting carbonyl activated unsaturated compounds with intermediates like $HSnCl_3$ and H_2SnCl_2. But the reactions studied so far concerned primarily with aliphatic systems. It has been proposed during the current investigation to study these reactions of carbonyl activated unsaturated compounds in aromatic systems with trichlorostannane ($HSnCl_3$) intermediate. To achieve the objectives, the reaction of benzylideneacetophenone (chalcone) and trichlorostannane (i.e. a mixture of stannous chloride and hydrogen chloride) was studied under different experimental conditions. Unlike corresponding aliphatic systems the reaction presented many experimental difficulties. The organotin compounds formed were often in poor yields and a large amount of gummy material was produced during the reaction which could not be characterised properly. The gummy material contained stannous chloride along with some uncharacterised products. Though organotin compounds were formed by the addition of $HSnCl_3$ into $C_6H_5CH = CHCOC_6H_5$, such compounds are relatively unstable compared to the product obtained by the reaction of $HSnCl_3$ on $CH_3CH = CHCOCH_3$. The comparative weakness of tin-carbon bond of 

$$\begin{array}{l} C_6H_5-CH-CH_2-C-R \\ \qquad\quad | \qquad\qquad \| \\ \qquad Cl_3Sn \longleftarrow O \end{array}$$

(where R = C_6H_5 or CH_3) may lead to conversion of $C_6H_5CH = CHCOR$ to some other pure organic compounds which do not contain any tin.

It was the primary goal to isolate, characterise and study the reactions of some new organotin chlorides under current investigation. Hence the conversion reactions of unsaturated aromatic ketones by chlorostannation reactions have not so far been studied, though these reactions might prove quite interesting.

Under the present investigations the isolation of new organotin chlorides have been attempted with the following reactions under different experimental conditions.

(i) $C_6H_5CH = CHCOC_6H_5 + HSnCl_3$

(ii) $C_6H_5CH = CHCOCH_3 + HSnCl_3$

(iii) $C_6H_5CH = CHCOCH = CHC_6H_5 + HSnCl_3$

It has been possible to isolate some new organotin chlorides by studying the above reactions, the details of which will be described ~~here~~ later.

Some of the important reactions of these organotin chlorides were also studied which will be discussed in next chapter.

EXPERIMENTAL

Tin was estimated gravimetrically by converting to stannic oxide and finally to volatile stannic iodide, essentially by the method of Van der Kerk and Luijten (140).

Analyses of the compounds for carbon, hydrogen and nitrogen were carried out at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow.

The infrared spectra were taken in the range between 4000-500 cm^{-1} for most of the compounds using Beckmann IR-20 and Pye Unicam-SP-300S infrared spectrophotometer equipped with KBr optics and mulling the compounds in nujol in all cases unless otherwise mentioned. Few spectra (4000-200 cm^{-1}) were recorded using Pye-Unicam-SP-300S with KBr optics. The following abbreviations have been used to discuss the spectral part.

v.s. = very strong, s = strong, m = medium, w = weak, v.w. = very weak, b = broad, sh = shoulder, nujol had peaks at 3000-2800s, 1460s, 1376m (error limit = ± 5 cm^{-1})

The ^{1}H NMR, ^{13}C NMR and ^{119}Sn spectra of β-benzoyl-α-phenylethyltin trichloride were recorded at 360 MHz, 90.56 MHz and 134.294 MHz respectively in Brucker Spectrospin through the courtesy of Dr. Edvards Liepinsh, Institute of Organic Synthesis, Aizkraukles 21, Riga, U.S.S.R.

The ^{1}H NMR spectra of β-acetyl-α-phenylethyltin trichloride and β-styrylcarbonyl-α-phenylethyltin trichloride and ^{13}C NMR spectrum of β-styryl-α-phenylethyltin trichloride were recorded at 80 MHz (^{1}H NMR) and 20 MHz (^{13}C NMR) with Brucker WP80SY Multinuclear 80 MHz FT NMR Spectrophotometer and JEOL PMX 60 SI CW ^{1}H NMR spectrophotometers at the Department of Chemistry and Biological Chemistry, University of Essex, Colchester, U.K. through the courtesy of Dr. D.J. Greenslade.

All the NMR spectra were recorded in $CDCl_3$. For ^{1}H, ^{13}C tetramethyl silane was used as internal standard, while ^{119}Sn shift of β-benzoyl-α-phenylethyltin trichloride was recorded against tetramethyltin.

Sometime following abbreviations have been used for different groups in the molecular formula of the compound and also for naming the compound:

Methyl	Me
Ethyl	Et
Propyl	Pr
Butyl	Bu
Phenyl	Ph
8-Hydroxyquinoline (oxine)	HOx
1,5-diphenylthiocarbazone (dithizone)	H_2Dz
1,5-diphenylcarbazone	H_2DPC

All solvents viz. benzene, chloroform, methanol, ethanol, petroleum ether, diethyl ether (ether), ethyl acetate etc, used in the experiments were purified and dried according to the standard methods (296). Petroleum ether used was of boiling point range 60-80 °C. Some of the compounds used viz. anhydrous stannous chloride, dry hydrogen chloride, benzylideneacetophenone (chalcone), dibenzylideneacetone were prepared and purified and dried in the laboratory. The other compounds viz. benzylideneacetone (B.D.H) 1,5-diphenylcarbazone (E. Merck), potassium thiocyanate (B.D.H) were used after drying according to the standard methods.

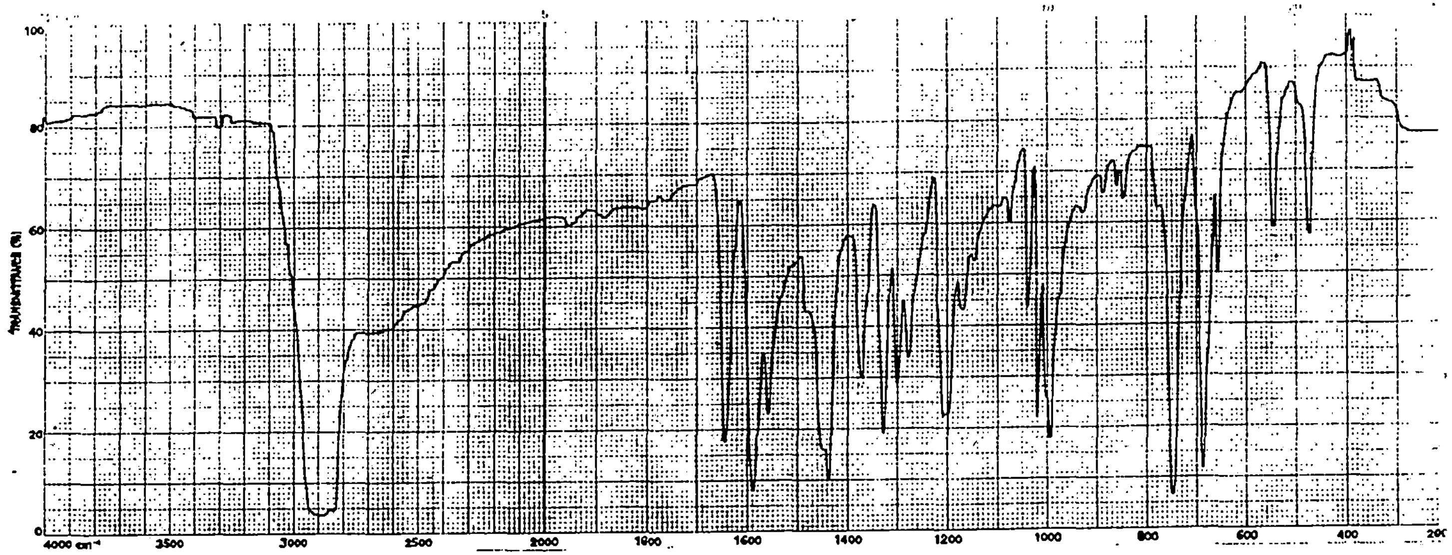


Fig. 1 IR spectrum of benzylideneacetophenone (chalcone)

Preparation of starting materials:

(a) Preparation of benzylideneacetophenone (chalcone) (296)

$$C_6H_5CHO + C_6H_5COCH_3 \xrightarrow{NaOH} C_6H_5CH = CHCOC_6H_5 + H_2O$$

A solution of 22 gms of sodium hydroxide in 200 ml of water and 122.5 ml of rectified spirit was taken in a flask fitted with a mechanical stirrer. This was placed in a bath of crushed ice. To the solution 50.5 ml of distilled acetophenone was added and then 44 ml of pure benzaldehyde was added intermitently by keeping reaction temperature at 15-30°C. The stirring was continued until the mixture became very thick. The thick solution was kept in refrigerator for overnight. The solid was then separated and ~~adn~~ washed with cold water to remove alkali. Final washing was done with 20 ml of ice-cold rectified spirit. The solid was recrystallised from warm (50°C) rectified spirit (400 ml).

The yield of pure chalcone was 70 gms.

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

Found	C	86.14	H	5.42
Calculated	C	86.54	H	5.77

Melting point 57°C

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

2960-2820s(b), 1645 vs, 1590 vs, 1560s, 1485 sh, 1455 sh, 1435 vs, 1375 s, 1330 s, 1300 s, 1280 m, 1200 s, 1170 m, 1155 w, 1075 w, 1040 s, 1020 s,

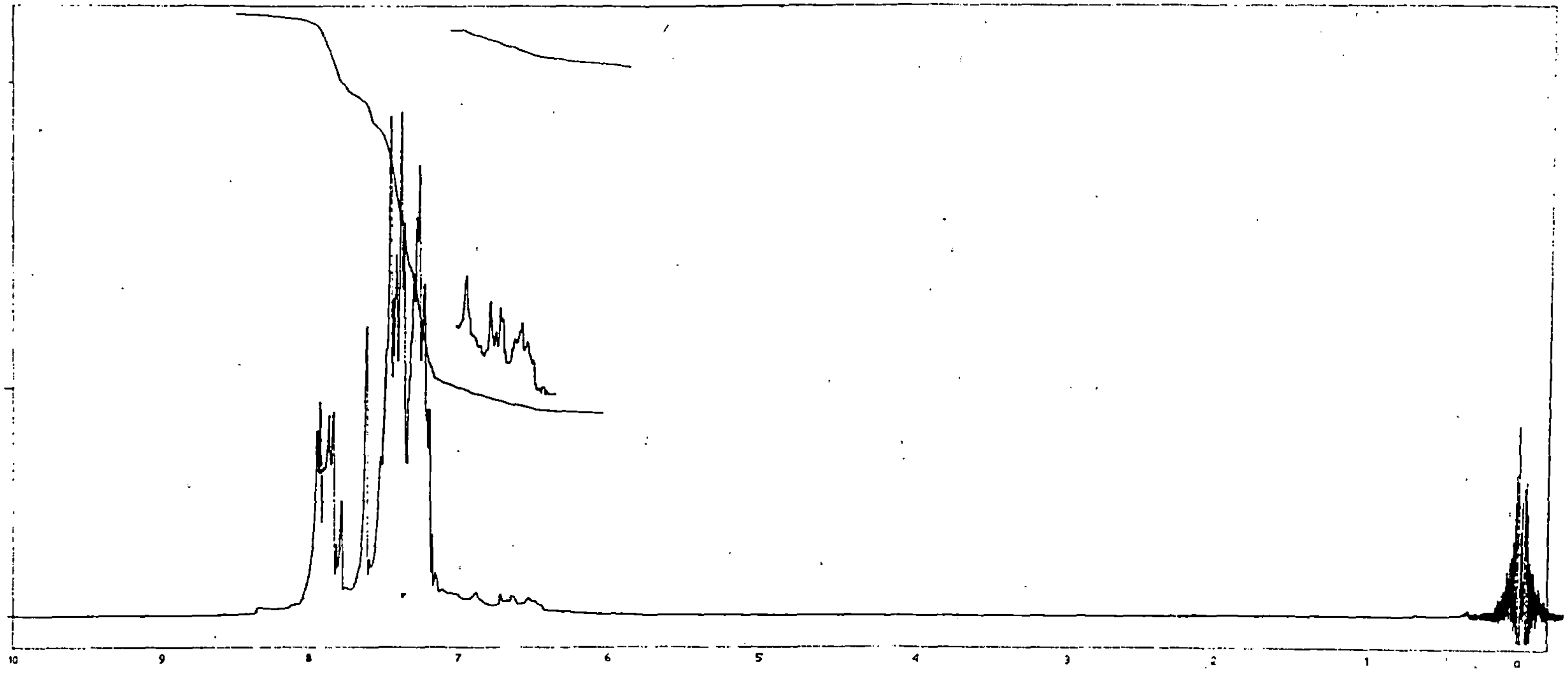


Fig. 2 ^{1}H NMR spectrum of benzylideneacetophenone (chalcone)

995 vs, 930 w, 885 w, 860 w, 845 w, 780 sh, 750 vs, 690 vs, 660 m, 545 s, 475 s.

^{1}H Nuclear magnetic resonance spectral data (Chemical shift δ)

^{1}H NMR peaks at 6.45 -7.96 (phenyl and olefinic) (Fig 2)

(b) Preparation of dibenzylideneacetone (297).

$$2C_6H_5CHO + CH_3COCH_3 \xrightarrow{NaOH} C_6H_5CH = CHCOCH = CHC_6H_5 + 2H_2O$$

A cooled solution of 100 gms of sodium hydroxide in one litre of water and 800 ml of ethanol was taken in a flask fitted with a mechanical stirrer and kept at 20-25°C. A mixture of 101.4 ml of pure benzaldehyde and 36.7 ml of pure acetone was added slowly and intermitently with continued stirring. Yellow flocculent precipitate formed was purified by recrystallisation from hot ethyl-acetate using 100 ml solvent for 40 gm of the crude dibenzylideneacetone (dibenzalacetone).

The yield of the pure compound 85 gms.

% Analysis for $C_{17}H_{14}O$

Found	C	86.78	H	5.83
Calculated	C	87.18	H	5.98

Melting point 111°C

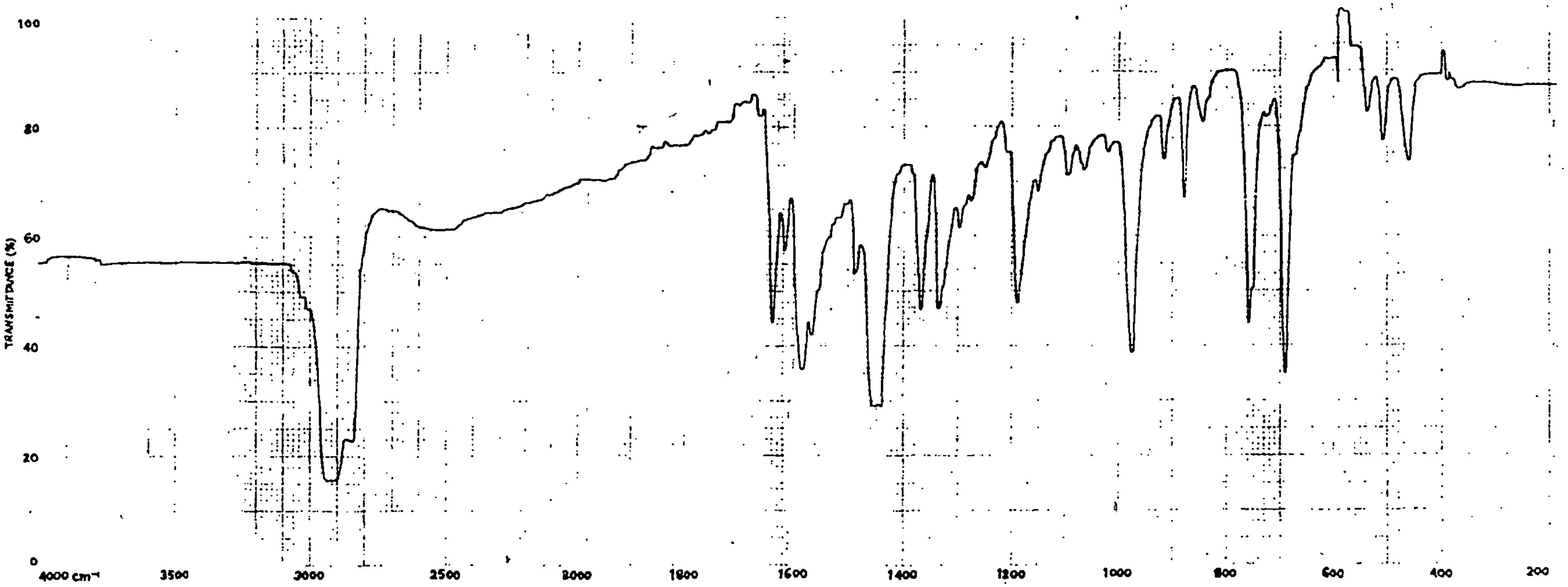


Fig. 3 IR spectrum of Dibenzylideneacetone

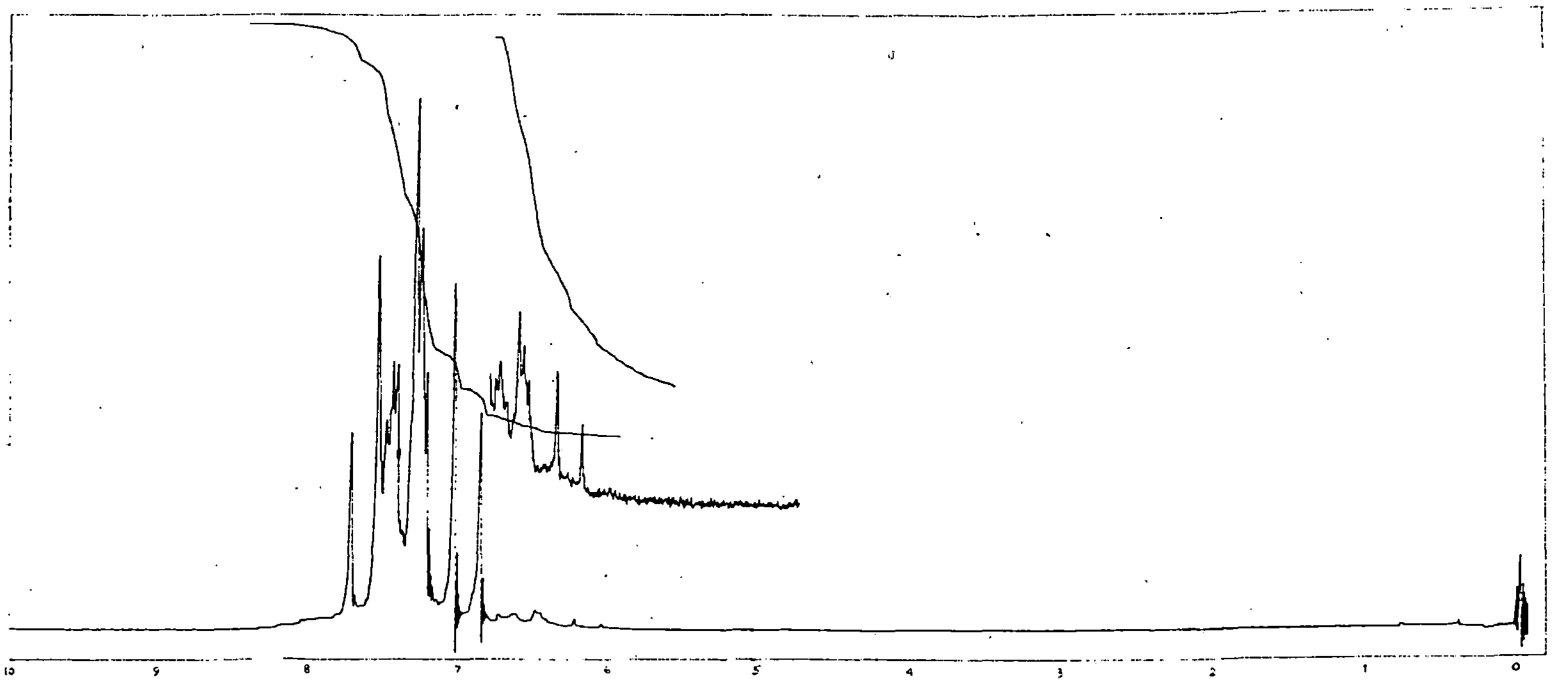


Fig. 4 ^{1}H NMR spectrum of dibenzylideneacetone

Infrared spectal data (cm^{-1}) (Fig 3)

2950-2840 vs(b), 1640 s, 1620 m, 1585 s, 1565 m, 1490 m, 1450 vs, 1370 s, 1335 s, 1300 w, 1275 w, 1190 s, 1150 w, 1095 w, 1070 w, 975 vs, 915 w, 880 m, 840 w, 760 vs, 690 vs, 535 w, 510 w, 460 m.

^1H Nuclear magnetic resonance spectral data (chemical shift δ) (Fig 4)

^1H NMR peaks at 6.05 - 7.72 (phenyl and olefinic).

(c) Preparation of anhydrous stannous chloride (296)

In a beaker 89 ml of distilled acetic anhydride was taken to which 123 gms of analytical reagent grade stannous chloride $SnCl_2.2H_2O$ was added slowly with constant stirring. Instantaneous dehydration took place with the evolution of heat. After an hour, the anhydrous stannous chloride was filtered off on a sintered glass funnel and washed free from acetic acid with 30 ml portions of anhydrous ether and dried by keeping overnight in a vacuum diseccator.

(d) Preparation of dry hydrogen chloride gas (296a)

The apparatus used is shown in the Fig. 5 . The upper funnel was of 100 ml capacity and had a capillary tube of appropriate length so as to dip into the liquid in the lower funnel whose capacity was 500 ml. The drechsel bottle (A) contained the concentrated sulphuric acid and the second bottle was the safety trap. The whole apparatus was

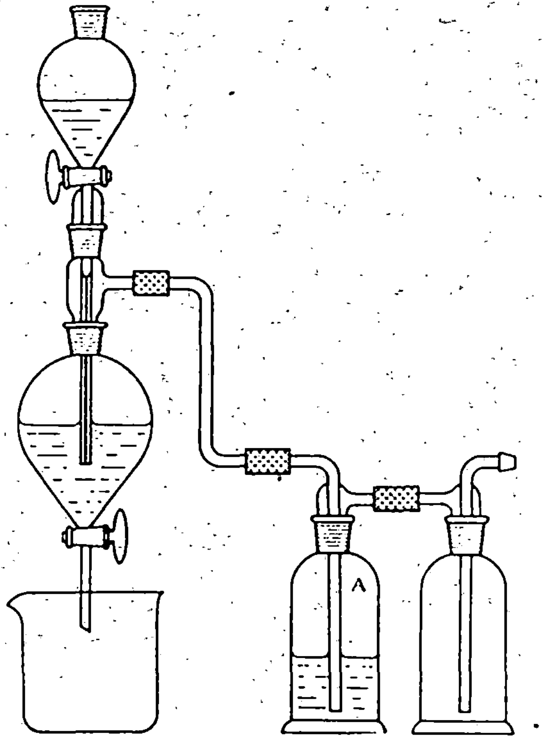


FIG 5

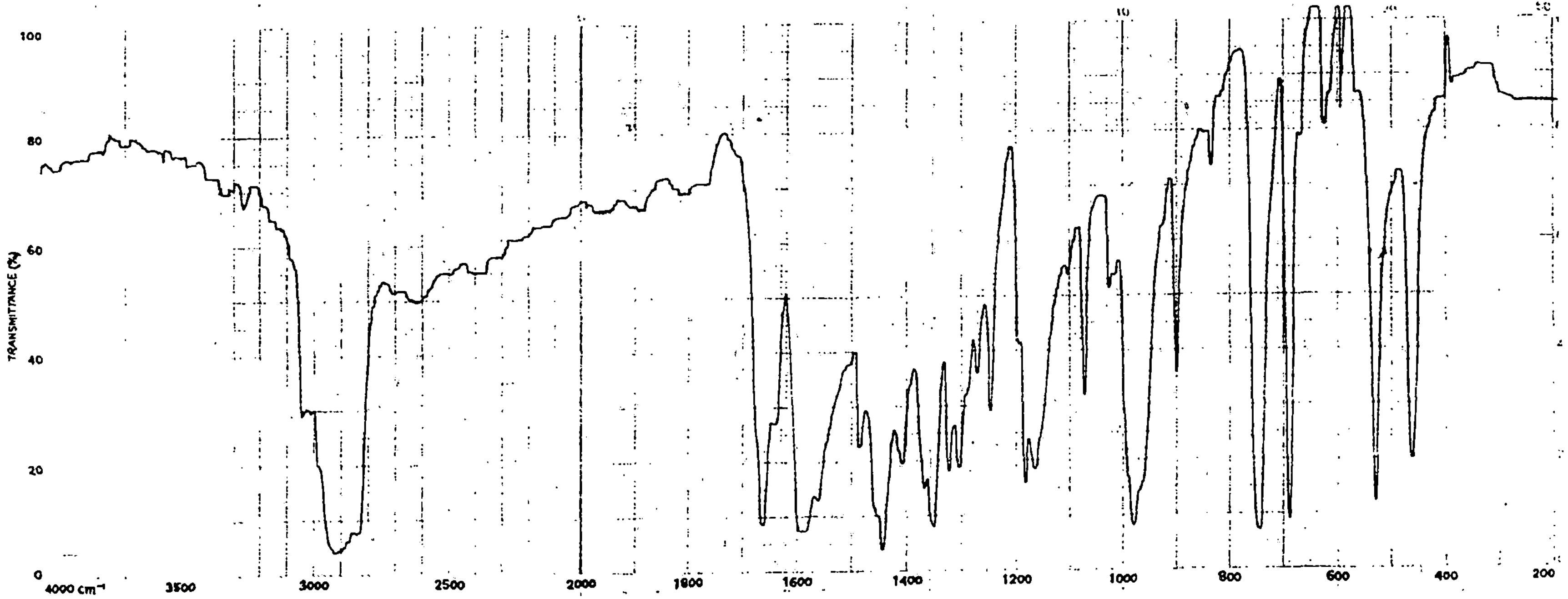


Fig. 6 IR spectrum of benzylideneacetone

mounted on a heavy stand.

About 150 ml of concentrated sulphuric acid was taken in the larger lower funnel and 100 ml of concentrated hydrochloric acid was taken in smaller funnel. The rate of flow of hydrogen chloride is controlled by regulating the supply of hydrochloric acid to the concentrated sulphuric acid in the lower funnel. The formed gas was passed through concentrated sulphuric acid contained in Drechsel bottle. The flow of hydrochloric acid was continued until a volume of hydrochloric acid equal to that of concentrated sulphuric acid had been used. The dilute sulphuric acid was then removed from the lower funnel and the apparatus was recharged where necessary.

(e) Benzylideneacetone

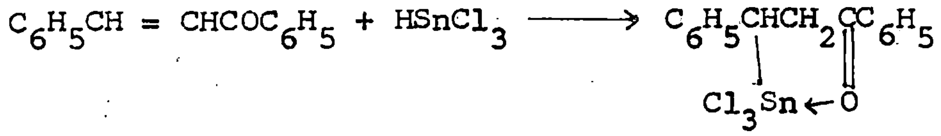
Benzylideneacetone (BDH) was used without further purification.

Melting point 39°C.

Infrared spectral data (cm^{-1}) (Fig 6)

3050-2820 vs(b), 1955 w, 1895 w, 1810 w, 1665 vs, 1640 sh, 1590 vs, 1560 sh, 1485 m, 1445 s, 1410 m, 1370 w, 1350 s, 1325 m, 1305 m, 1275 w, 1245 s, 1190 sh, 1185 s, 1165 s, 1100 w, 1075 s, 1025 m, 980 vs, 900 s, 835 w, 745 vs, 690 vs, 675 sh, 625 m, 595 w, 570 sh, 530 vs, 460 vs.

Preparation of β-benzoyl-α-phenylethyltin trichloride



$$C_6H_5CH = CHCOC_6H_5 + HSnCl_3 \longrightarrow \begin{array}{l} C_6H_5\underset{|}{C}HCH_2\underset{\|}{C}C_6H_5 \\ \qquad Cl_3Sn \leftarrow O \end{array}$$

The above reaction was studied under different experimental conditions varying temperature, time, reactant proportion and also solvent.

Method (A):

The chlorostannation of benzylideneacetophenone (chalcone) proceeds through intermediate formation of trichlorostannane ($HSnCl_3$) from anhydrous stannous chloride and dry hydrogen chloride gas. The reaction was carried out by taking 9.0 gms of anhydrous stannous chloride and 10.4 grms of recrystallised chalcone (molar proportion 1:1) in 250 ml ether (diethyl ether) in a three necked glass flask fitted with a mechanical stirrer. The flask was kept in a water bath at 20°C. Dry hydrogen chloride gas was passed continuously at medium flow rate for about five hours. The stirring was continued for another one hour by opening the stoppers of the flask to remove unreacted hydrogen chloride present in the solution as far as possible. The reaction mixture still contained some dissolved hydrogen chloride which was removed by concentrating the solution over a steam bath to about one fifth of its original volume (~50 ml). The concentrated solution was kept undisturbed overnight. The deposited solid was separated and washed with chloroform dropwise (excess of chloroform was avoided since the compound was found soluble in chloroform to some extent) to remove adhering gum as far as possible. The melting point of the crude solid was ~~was~~ 90-110°C. The impure solid was dried in air and then warmed with 150 ml of chloroform and allowed to settle. Warm chloroform fairly dissolved the solid and the clear top layer portion of the liquid was decanted. The bottom layer portion being very small in amount, could not be characterised. The decanted part of the liquid was filtered and concentrated to one third of its volume (50 ml) and few drops of petroleum ether were added to this and was allowed to stand undisturbed overnight. The light yellow crystalline product having melting point 120-125°C was obtained. The process of crystallisation was repeated several times, so that on dissolving the crystals in chloroform a homogeneous liquid phase was formed. The final crystallisation was carried out from chloroform (without adding drops of petroleum ether) which furnished very light yellow shining crystals of melting point 140°C.

The same reaction was studied under different conditions of time and temperature, the yields obtained is indicated as follows.(Table 9).

Table 9

Temperature (^{o}C)	Time (in hour)	Yield (%)
0	2.00	Nil
10	2.50	32
10	5.00	30
15	2.50	32
20	5.00	30
30	0.66	30
30	3.00	10
30	5.00	<10

The reaction when carried out between 10-20^{o}C, the yield was about 30% whether the reaction was carried out for two and half hours or five hours. But on carrying the reaction at higher temperature say at 30^{o}C, about 30% yield was obtained when reaction time was forty minutes. When the reaction time was increased, the yield was found to decrease. On carrying out the reaction at 0^{o}C with the reaction time two hours, the compound β-benzoyl-α-phenylethyltin trichloride could not be prepared instead products were gummy materials. The reaction was very much sensitive to atmospheric moisture. Reaction carried out at 10^{o}C/15^{o}C for two and half hours during heavy rainy days, practically no β-benzoyl-α-phenylethyltin trichloride could be isolated but only gummy substance and some stannous chloride could be isolated.

Changing the proportions of reactants (stannous chloride and chalcone) from 1:1 , no better yield could be obtained. Several attempts were made to carry out the same reaction with chloroform, ethanol or benzene as solvent. In most cases either no yield or very poor yield of β-benzoyl-α-phenylethyltin trichloride could be obtained.

Method (B):

Since in the previous reactions, the chlorostannation of chalcone proceeds through the intermediate formation of trichlorostannane ($HSnCl_3$), the following modification was made for the process. Instead of passing hydrogen chloride gas into ethereal solution of chalcone and anhydrous stannous chloride, trichlorostannane(265) was first prepared in ether at 0°C (———) and an ether solution of chalcone was added to trichlorostannane at 8-10°C.

Trichlorostannane ($HSnCl_3$) was prepared by taking 9.0 gms of anhydrous stannous chloride in 200 ml ether in a three necked glass flask fitted with a mechanical stirrer. The flask was kept in an ice-bath at 0°C. Dry hydrogen chloride gas was passed continuously at a moderate flow rate for half an hour. Stannous chloride changed to a white paste, which settled at the bottom of the flask. The passage of hydrogen chloride was discontinued. Then the temperature of the bath was raised to 8-10°C. A saturated solution of 10.4 gms of recrystallised chalcone (molar proportion of the reactants 1:1) in ether was added slowly intermittently through one of the side neck of the flask to the trichlorostannane (white paste in ether medium) with continuous stirring. The addition of chalcone solution was completed within an hour. The stirring was continued for another half an hour and then opening the stoppers the stirring was again continued for another hour to remove hydrogen chloride present in the solution as far as possible. The reaction mixture still contained some dissolved hydrogen chloride, which was removed by concentrating the solution over a steam bath to a gummy mass, the gummy mass was washed several times with hot petroleum ether, washings were rejected. The residue left after this was dissolved in chloroform and a little petroleum ether was added with stirring which resulted in a solid (m.p. 100-110^{o}C) product. The crude product was again dissolved in minimum quantity of chloroform with slight warming over a steam bath. On cooling, it separated into two layers. The clear upper layer was further concentrated to about one fourth of its volume and few drops of petroleum ether were added to it and then allowed to stand for an hour when solid product was separated. The process of crystallisation was repeated several times. The final crystallisation was carried out without adding drops of petroleum ether. Repeated crystallisation furnished very light yellow shining crystals of melting point 140°C. The product was found identical to that obtained by earlier method (A) as shown by mixed melting point determination and infrared spectrum of the compound. The overall yield of the pure product was about 75%.

The removal of excess hydrogen chloride in the earlier stages is essential otherwise much more gummy substance is produced reducing the final yield of the crystalline product. The isolation of the pure product must be done as quickly as possible, so that desirable yield can be obtained.

The above two-step reaction was carried out varying the temperature and the reaction time. As indicated earlier, the first step involves the preparation of $HSnCl_3$-ether complex and in the second step, a saturated solution of chalcone was added to the $HSnCl_3$-ether complex. The results obtained may be tabulated as follows. (Table 10)

Table 10

Temperature (during addition of chalcone solution) (°C)	Time (in hour)	Yield (%)
0	1	50
8-10	1	75
8-10	2	70
15-20	1	40
30	1	Nil

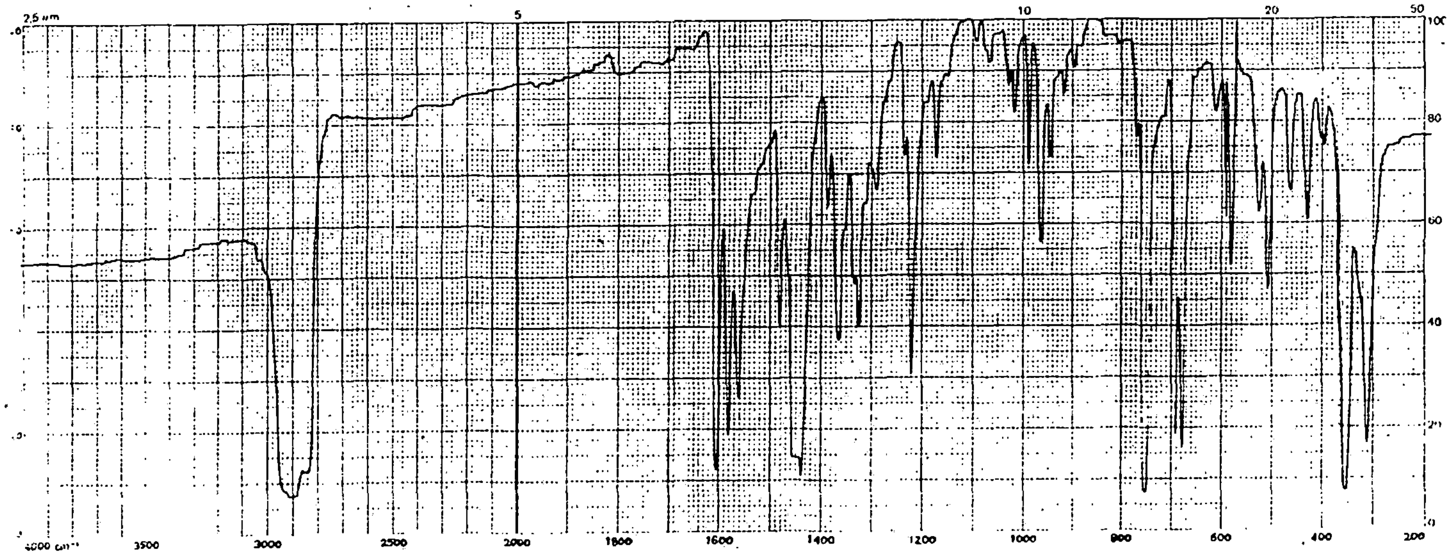


Fig. 7 IR spectrum of β-benzoyl-α-phenylethyltin trichloride

Hence the suitable method of preparing β-benzyl-α-phenylethyltin trichloride is to add within one hour a saturated chalcone solution to trichlorostannane in ether at 8-10°C.

By changing the proportions of the reactants from 1:1 or by using other solvents (chloroform, ethanol, benzene) no better results regarding the quality and quantity of the compound was found.

% Analysis for $C_{15}H_{13}OSnCl_3$

Found	C 41.90	H 3.35	Sn 27.54
Calculated	C 41.43	H 2.99	Sn 27.39

Melting point 140°C

pH (10^{-2}M solution) in chloroform or benzene ∽ 1.3.

Infrared spectral data (cm^{-1}) (Fig 7)

2960-2840 vs(b), 1605 vs, 1580 s, 1560 s, 1480 m, 1460 sh, 1440 s, 1390 m, 1365 s, 1325 s, 1310 sh, 1290 w, 1235 vw, 1220 s, 1170 m, 1070 w, 1030 w, 1020 w, 990 w, 965 s, 945 m, 920 w, 770 vw, 755 vs, 690 vs, 680 vs, 615 w, 690 m, 580 s, 530 m, 510 m, 470 m, 415 m, 350 s, 300 m.

Nuclear magnetic resonance spectral data (chemical shift δ)

^{1}H NMR peaks at 3.77 (methine), 3.85 and 4.13 (methylene) and 7.0-8.5 (aromatic). (Fig 8)

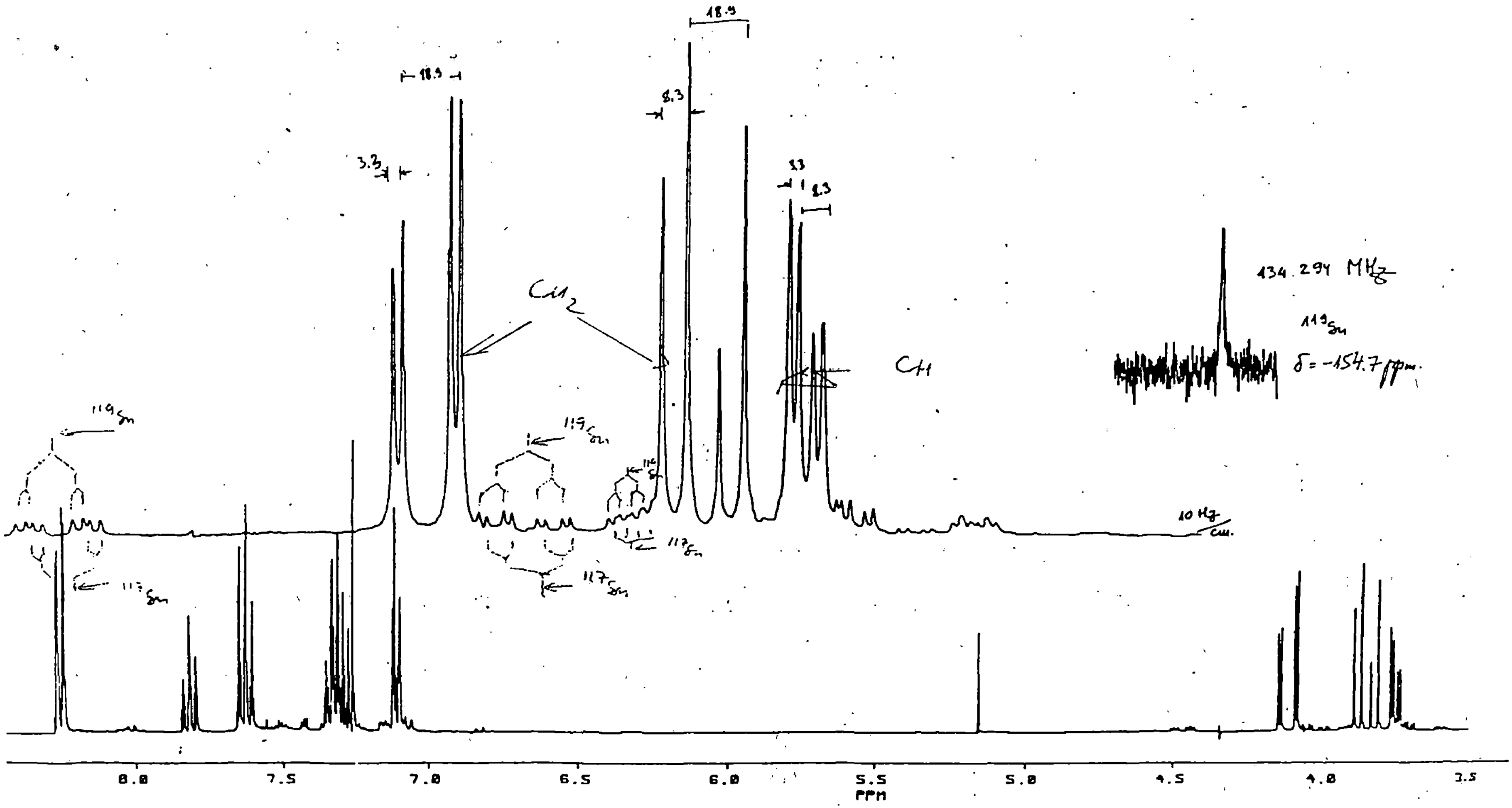


Fig. 8 ^{1}H NMR and ^{119}Sn NMR spectra of β-benzoyl-α-phenylethyltin trichloride

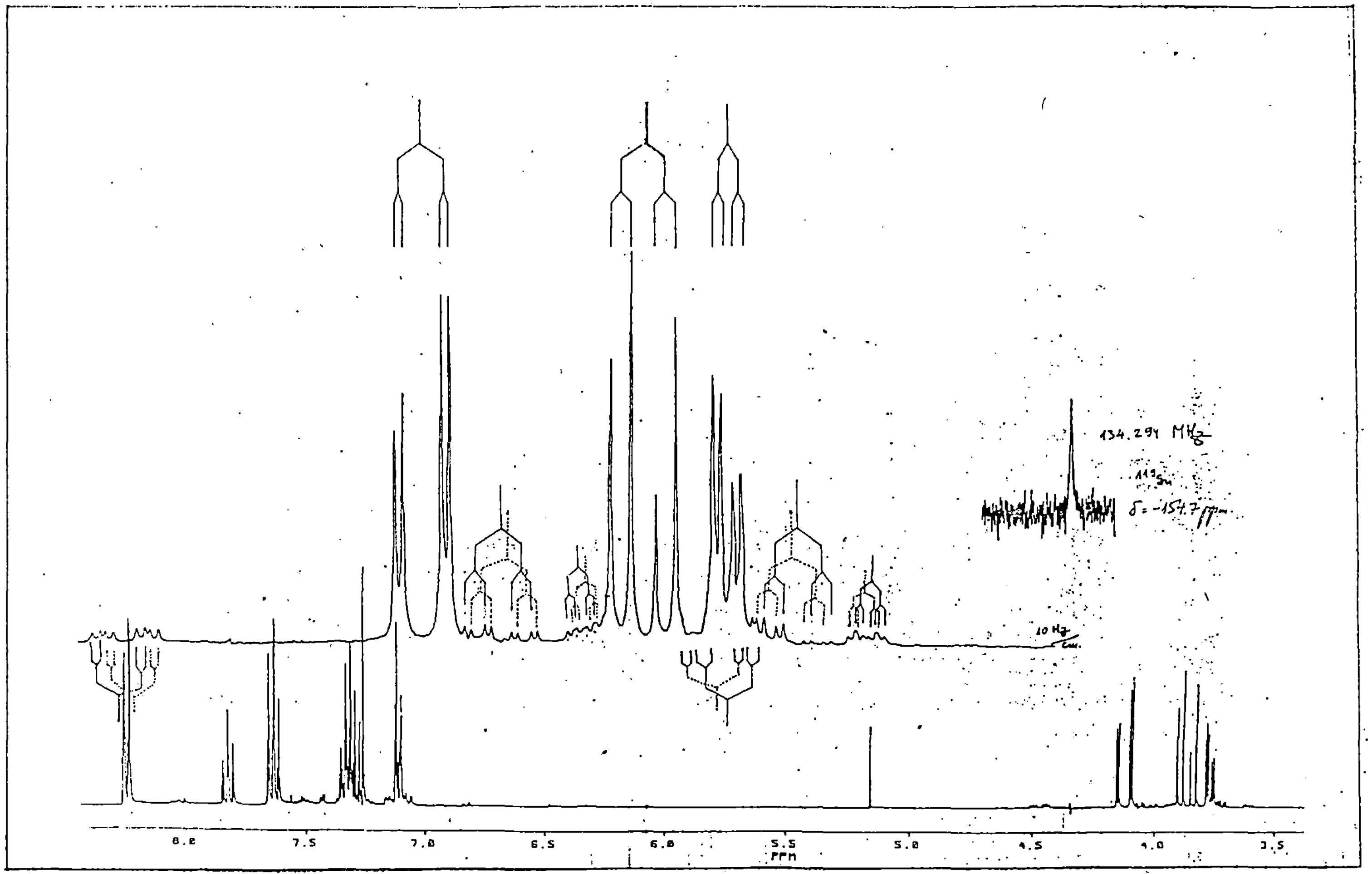


Fig. 8a ^{1}H NMR spectrum of β-benzoyl-α-phenylethyltin trichloride showing splitting of tin-signals due to interaction with proton.

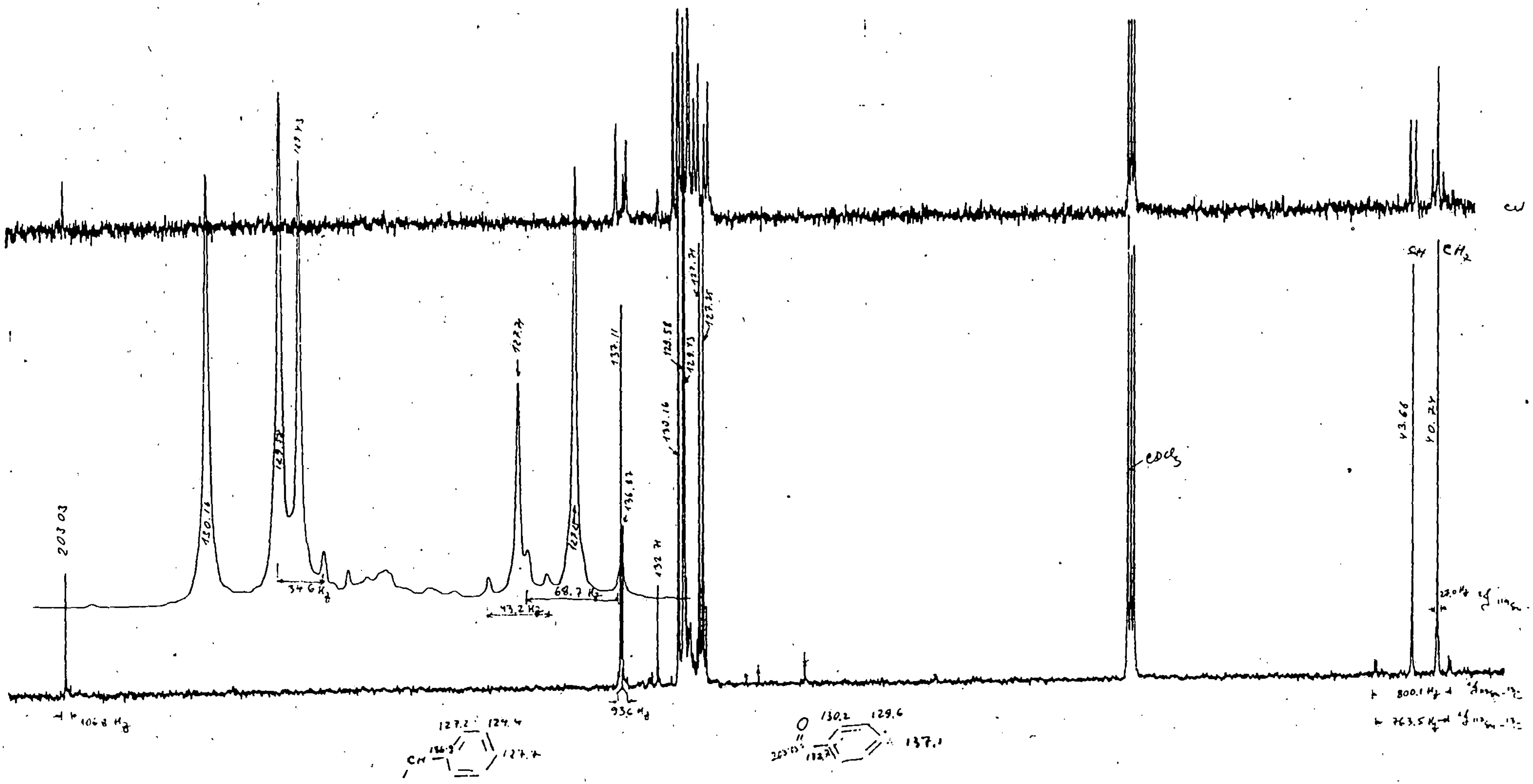


Fig. 9 ^{13}C NMR spectrum of β-benzoyl-α-phenylethyltin trichloride

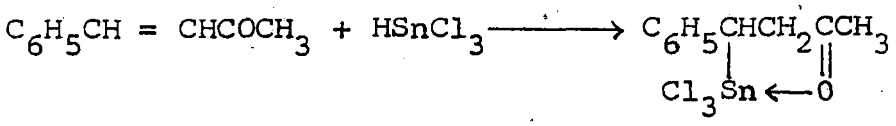
^{13}C NMR peaks at 40.74 (methylene), 43.66 (methine), 127.25-137.11 (aromatic) and 203.03 (carbonyl) (Fig 9)
^{119}Sn peak at-154.7.

The compound was found fairly soluble in chloroform, benzene, diethylether, methanol, ethanol, acetone. Its solubility in carbon tetrachloride is much less. Though the compound was fairly soluble in acetone, on evaporating acetone, some yellow gummy mass was obtained instead of the compound being dissolved.

In contact with ammonia (in the form of ammonia gas or ammonium hydroxide) and other bases like pyridine, aniline etc., the compound was found unstable.

The compound β-benzoyl-α-phenylethyltin trichloride was moisture sensitive leading to decomposition product containing chalcone, stannous chloride and other uncharacterised compounds.

Preparation of β-acetyl-α-phenylethyltin trichloride



$$C_6H_5CH = CHCOCH_3 + HSnCl_3 \longrightarrow \underset{Cl_3Sn \longleftarrow O}{C_6H_5CHCH_2CCH_3}$$

The above chlorostannation reaction was also studied under different experimental conditions varying temperature, time, reactant proportion and also solvent.

Method (A)

The chlorostannation of benzylideneacetone proceeds through intermediate formation of trichlorostannane ($HSnCl_3$) from anhydrous stannous chloride and dry hydrogen chloride gas in ether solution.

The reaction was carried out by taking 9.0 gms of anhydrous stannous chloride and 7.3 gms of benzylideneacetone (molar proportion 1:1) in 250 ml ether in a three necked glass flask fitted with a mechanical stirrer. The flask was kept in a ice-bath at 0°C. Dry hydrogen chloride gas was passed continuously at medium flow rate for about three hours. The stirring was continued for another one hour by opening the stoppers of the flask to remove unreacted hydrogen chloride present in the solution as far as possible. The reaction mixture still contained some dissolved hydrogen chloride which was removed by concentrating the solution over a steam bath to about one fifth of its original volume (~50 ml). The concentrated solution was kept undisturbed overnight. No solid was separated out of the solution. The rest portion of the solvent was then evaporated from the solution on a steam bath to form a gummy mass. The gummy mass was washed several times with hot petroleum ether and then dissolved in minimum volume of warm chloroform. After adding few drops of petroleum ether to the chloroform solution and then on keeping undisturbed twenty four hours, a brown crystalline solid was separated. The brown colour of the solid was due to adhering impurities and was largely reduced by washing the crystals with drops of chloroform (excess of chloroform was avoided since crystalline solid was also somewhat soluble in chloroform though much less than adhering brown substance). The deep brown washings were collected and concentrated which produced a brown powdery solid of melting point 110°C, which could be crystallised from chloroform-methanol mixture. It was not characterised further since it did not contain tin.

The crystalline solid (m.p. 90-96°C) was dissolved in minimum quantity of warm chloroform and allowed to stand. The liquid separated in two layers of which clear upper layer was taken and filtered and concentrated on a steam-bath and kept undisturbed overnight after adding few drops of petroleum ether to it. The bottom layer portion being very small could not be characterised. Light cream colour crystalline substance was crystallised several times until chloroform solution of it formed a homogeneous solution. The final crystallisation was carried out from chloroform solution without adding drops of petroleum ether which produced very light cream colour shining crystals having melting point 100°C. The yield was only ∽ 15%.

The yield of the above product under different conditions of time and temperature may be indicated in the following table. (Table 11).

Table 11

Temperature (°C)	Time (in hour)	Comment on the reaction product
0	2	∽15% of β-acetyl-α-phenylethyltin trichloride with uncharacterised brown solid and gummy matter.
0	3	Do
8-10	1	<10% β-acetyl-α-phenylethyltin trichloride along with brown solid and gummy material.
8-10	2	Brown uncharacterised solid and gummy matter only.
15	1	Do
15	2	Only gummy matter from which a little amount of brown solid was obtained.

When the reaction was carried out at 0°C, the yield is ∽15% whether the reaction was carried out for two hours or three hours. But if the reaction is carried out at slightly higher temperature (8-10°C), the yield of β-acetyl-α-phenylethyltin trichloride became nil provided the reaction was carried out for two hours. By decreasing the reaction time, little amount of β-acetyl-α-phenylethyltin trichloride could be isolated. But under all these conditions, large amount of uncharacterised gummy substance and brown solid (m.p. 110°C) were formed. On carrying out the reaction at still higher temperature (15°C) no β-acetyl-α-phenylethyltin trichloride was formed at all, instead gummy matter remarkably increased decreasing the amount of brown solid with increasing the reaction time.

Changing the proportion of the reactants from 1:1 did not produce any better yield of the said organotin complex. Several attempts were made to carry out the same reaction with different solvents, e.g. chloroform, ethanol or benzene. All these attempts were unsuccessful to yield β-acetyl-α-phenylethyltin trichloride.

<u>Method (B)</u>

A modification of the above process was made to improve the yield of β-acetyl-α-phenylethyltin trichloride. A stream of dry hydrogen chloride was passed through ethereal solution of anhydrous stannous chloride to form trichlorostannane at 0°C (details already described) to which a solution of benzylideneacetone in ether was added at 3-5°C.

In this method a saturated solution of 7.3 gms of benzylideneacetone was added to trichlorostannane paste (formed from 9.0 gms of anhydrous stannous chloride in 200 ml of ether at 3-5°C) with continuous stirring. The addition of benzylideneacetone was completed within forty minutes. The stirring was continued for another half an hour. Then the stoppers were opened and the stirring was continued to remove unreacted hydrogen chloride as far as possible. The reaction product still contained some dissolved hydrogen chloride which was removed by concentrating the solution over a steam-bath to a gummy mass. The gummy mass was washed several times with hot petroleum ether and the washings were rejected since it contained some uncharacterised gummy substance. The residual mass was then dissolved in minimum volume of warm chloroform to which little petroleum ether was added and vigorously stirred. A brown crystalline solid was separated from the solution. The brown crystals were washed carefully with chloroform dropwise, until the brown colour disappeared. The mass obtained was then dissolved in minimum volume of warm chloroform. The chloroform solution separated in two layers, of which the top layer was decanted and concentrated. The concentrated chloroform solution was kept undisturbed overnight after adding few drops of petroleum ether. Cream colour crystals separated out. The crystals were dissolved in minimum volume of warm chloroform and the above method of crystallisation was repeated until the chloroform solution was homogeneous in nature. In the final stage of crystallisation, petroleum ether was not added. Light cream colour shining crystals having a sharp melting point of 100°C was obtained. The overall yield was 40%. During the above process of crystallisation, the bottom part of the chloroform solution, being small in amount, was rejected. The chloroform washings of the crude brown crystals were collected together and it was then concentrated to furnish a brown powdery solid which did not contain tin. The crude brown powder had a melting point 110°C and could be recrystallised from chloroform-methanol mixture, but the compound is yet to be characterised.

Method (B) was performed for the preparation of β-acetyl-α-phenyl ethyl tin trichloride by varying the temperature of the reaction and also the time of addition of benzylideneacetone. The results obtained can be summarised as follows. (Table 12).

Table 12

Temperature (^{o}C)	Time (in hour)	Comment on the reaction product
0	0.66	Yield of the cream solid (m.p. 100°C) was 35%. Brown powdery solid and gummy product were also obtained.
0	1.5	Yield of the cream solid was 30% along with considerable amount of brown solid and gummy matter.
3-5	0.66	Yield of cream colour solid was 40%. Brown powder and gum were in lesser amount in comparison to reaction carried out with other reaction conditions.
3-5	1.5	Yield of cream solid was 32%. More of brown powder and gum were found to form than the reaction carried out with reaction time 40 minutes and temperature 3-5°C.
8-10	0.66	Yield of cream solid was 25% long with large amount of brown powdery solid and gummy substance.
8-10	1.5	Yield of cream colour solid was 18% along with large amount of brown powder and gummy matter.

Of the products, cream colour crystalline solid (m.p. 100°C), brown powdery solid (m.p. 110°C) and gummy substance, the cream colour crystalline solid could be characterised. It was found to be β-acetyl-α-phenyl ethyl tin trichloride, details of which will be described later.

Comparing the methods (A) and (B) under different experimental parameters of temperature and time, it was observed that the method (A) could not exceed more than 15% yield of β-acetyl-α-phenyl ethyl tin trichloride under any conditions so far studied. But the method (B) was found decidedly a better method of preparing such compound at a temperature range 3-5°C with the addition time of about forty minutes. About 40% yield could be obtained. The removal of free hydrogen chloride (unreacted portion of hydrogen chloride) after the addition of the unsaturated ketone to the trichlorostannane paste was found a very crucial step during carrying out the whole reaction to produce the final crystalline product. The presence of hydrogen chloride was found to increase gum content and uncharacterised brown powdery product. The reaction carried out at temperature range of 3-5°C and with shorter time of addition of unsaturated ketone was preferred as higher temperature of the reaction and longer time had a tendency to increase the quantity of gummy material and also uncharacterised brown powdery product.

Changing the proportion of the reactants (stannous chloride : benzylideneacetone) from 1:1 did not produce any better yield of β-acetyl-α-phenyl ethyl tin trichloride. Attempts to carry out the same reaction in other solvents like chloroform, ethanol and benzene also failed.

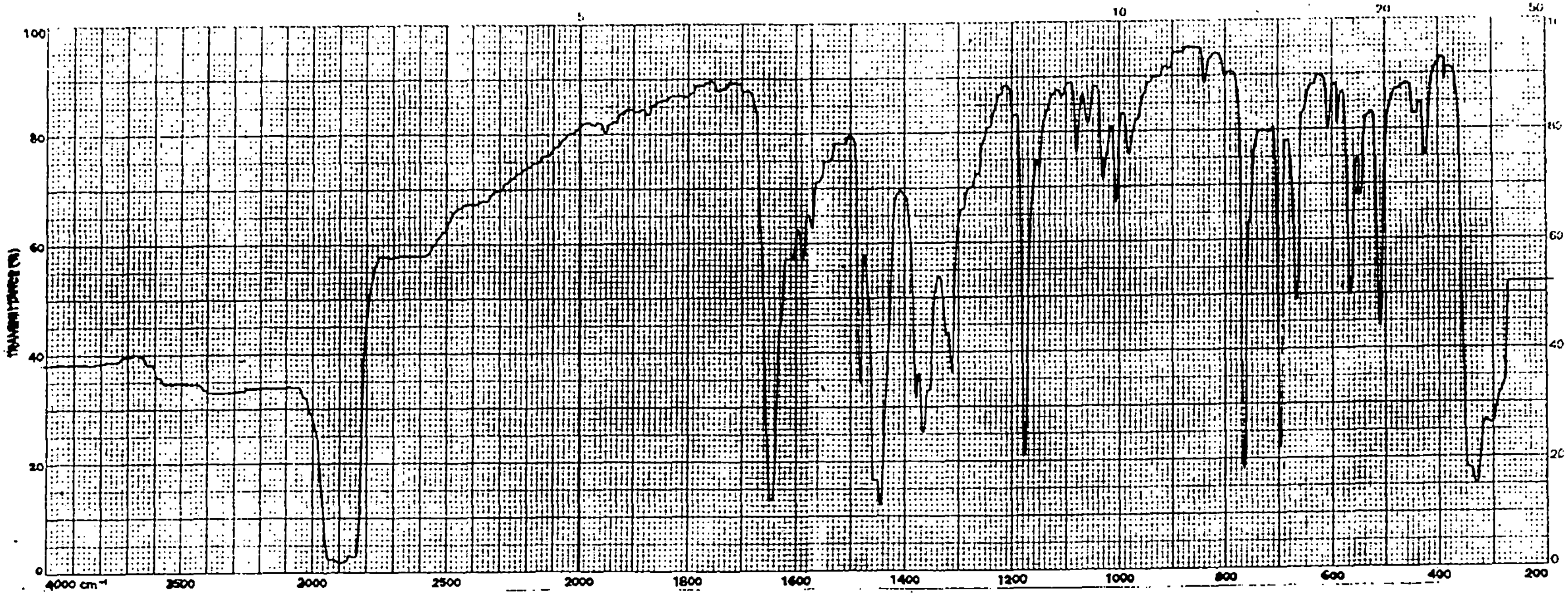


Fig. 10 IR spectrum of β-acetyl-α-phenylethyltin trichloride

In comparison with β-benzoyl-α-phenyl ethyl tin trichloride, the corresponding β-acetyl-α-phenyl ethyl tin trichloride gave poorer yield both by methods (A) and (B). In the later case, an uncharacterised brown powdery product which did not contain tin was isolated. No such product was isolated in the preparation of β-benzoyl-α-phenyl ethyl tin trichloride either by method (A) or by method (B).

% Analysis for $C_{10}H_{11}OSnCl_3$

Found	C 31.30	H 3.34	Sn 31.46
Calculated	C 32.21	H 2.95	Sn 31.95

Melting point 100°C

pH (10^{-2} M solution) in chloroform or benzene ∽1.8

Infrared spectral data (cm^{-1}) (Fig 10)

2960-2840 vs(b), 1645 vs, 1605 sh, 1590 w, 1570 vw, 1485 s, 1460 sh, 1445 vs, 1380 w, 1365 s, 1355 sh, 1325 sh, 1315 s, 1200 sh, 1175 vs, 1150w, 1080 w, 1060 w, 1030 m, 980 w, 840 w, 800 sh, 765 vs, 700 vs, 670 s, 610 w, 590 w, 565 s, 550 m, 510 s, 445 w, 425 m, 350 sh, 330 vs, 300 sh.

Nuclear magnetic resonance spectral data (chemical shift δ)

^{1}H NMR peaks at 1.7 (methyl), 2.85 (methine), (Fig 11) 2.7-3.52 (methylene) and 6.65-7.7 (aromatic).

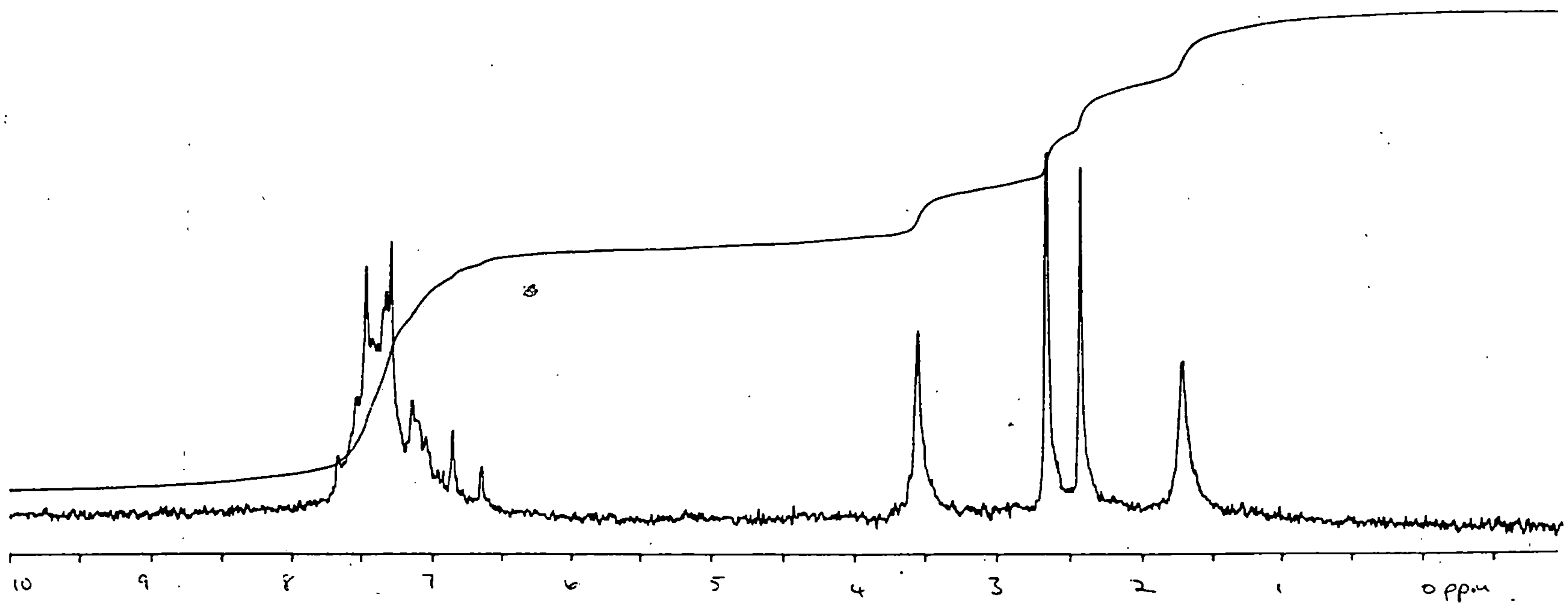


Fig. 11 ^{1}H NMR spectrum of β-acetyl-α-phenylethyltin trichloride

The compound, β-acetyl-α-phenylethyltin trichloride was found soluble in chloroform, benzene, diethylether, methanol, ethanol.

In contact with ammonia, other bases and moisture the compound was found to decompose.

Chlorostannation of dibenzylideneacetone

Method (A)

Recrystallised dibenzylideneacetone (11.7 gm) and anhydrous stannous chloride (9.0 gm) (i.e. in the molar proportion 1:1) were taken in 250 ml ether in a three necked flask fitted with a mechanical stirrer. A continuous supply of dry hydrogen chloride gas was passed into the ether solution with stirring at 20°C. The reaction was carried out for four hours and then excess of hydrogen chloride was removed as described earlier. The colour of the reaction mixture turned red and the red solution was then concentrated in a conical flask over a steam bath to a gummy material containing some red and yellow compound. [Both red and yellow compounds were soluble in chloroform but addition of petroleum ether to chloroform solution, partially deposited the red compounds, keeping the yellow compound in solution though the red compound was also partly soluble in petroleum ether. Hence the addition of petroleum ether to chloroform solution was carefully controlled so that the addition of petroleum ether did not turn top layer into reddish colour]. The gummy mass was then dissolved in chloroform and filtered. The filtrate was concentrated again over steam-bath to one fifth of the original volume and treated with petroleum ether and shaked vigorously and then allowed to settle.

The solution was separated into two layers. The top layer was separated and the bottom layer contained some gummy material. The bottom layer was redissolved in more chloroform and again controlled quantity of petroleum ether was added to the chloroform solution with vigorous shaking and allowed to settle. The process was repeated several times until the bottom layer gave red coloured residue with very little gum in it.

The yellow top layer portions were collected together and concentrated to a gummy mass and was treated as described above to completely remove the red material. After removing the red material, the chloroform-petroleum ether solution was concentrated over a steam-bath and excess of petroleum ether was added. The yellow precipitate was formed. This yellow precipitate was redissolved in chloroform and reprecipitated by excess petroleum ether. The process was repeated several times, when a sharp melting (m.p. 155°C) yellow powdery solid was obtained.

The red coloured residue contaminated with little gummy material (described earlier) was purified by dissolving in chloroform and precipitating with petroleum ether as described earlier. The gummy material was found to be unreacted stannous chloride residues. After the complete removal of gummy material, the red compound was dissolved in minimum amount of chloroform and again precipitated with excess of petroleum ether. The process was repeated several times to obtain a pure red coloured powdery compound which melted at 160°C (sharp).

The total yield of yellow and red compounds together was about 70% of the reactants used. The yellow compound was slightly more in amount than the red compound.

Similar chlorostannation experiments were carried out at 0°C, 15°C and 20°C. The final products obtained in all cases showed no remarkable differences except in a single experiment carried out at 15°C (which could not however be repeated). In the said particular experiment, a light yellow crystalline product (m.p. 120°C) was separated out from the filtrate obtained from the chloroform treatment of the gummy mass formed by evaporating the solvent from the reaction mixture after the reaction was over by adding little amount of petroleum ether with stirring. The yellow product was characterised and the details will be described later. When the reaction was carried out at 0°C, red solid was found to deposit in the inner wall of the hydrogen chloride gas inlet tube, blocking the passage of hydrogen chloride gas into the reaction mixture, causing some inconveniences, though the yield of the final products did not vary appreciably.

But if the above chlorostannation reaction was carried out varying the proportion of the reactants (Dibenzylideneacetone : stannous chloride = 2:1 instead of 1:1), then the total yield of the red and yellow compounds together reached to about 80% of the reactants used.

The same reaction was carried out with other solvents (e.g. benzene, chloroform, ethanol). Some uncharacterised gummy material containing stannous chloride was obtained but red or yellow compounds described earlier could not be isolated.

Method (B)

As followed in case of chlorostannation of benzylideneacetophenone and benzylideneacetone, the above reaction was also tried by adding dibenzylideneacetone to trichlorostannane paste at different conditions. It gave poorer yields of the products. Moreover, the reduced solubilities of dibenzylideneacetone in ether presented some inconveniences. Hence, method B was not persued further.

Light yellow crystalline compound (β-strylcarbonyl-α-phenylethyltin trichloride)

% Analysis for $C_{17}H_{15}OSnCl_3$

Found	C 44.50	H 3.66	Sn 26.53
Calculated	C 44.30	H 3.26	Sn 25.84

Melting point 120°C

pH (10^{-2}M solution) in chloroform or benzene $\sim$ 1.5.

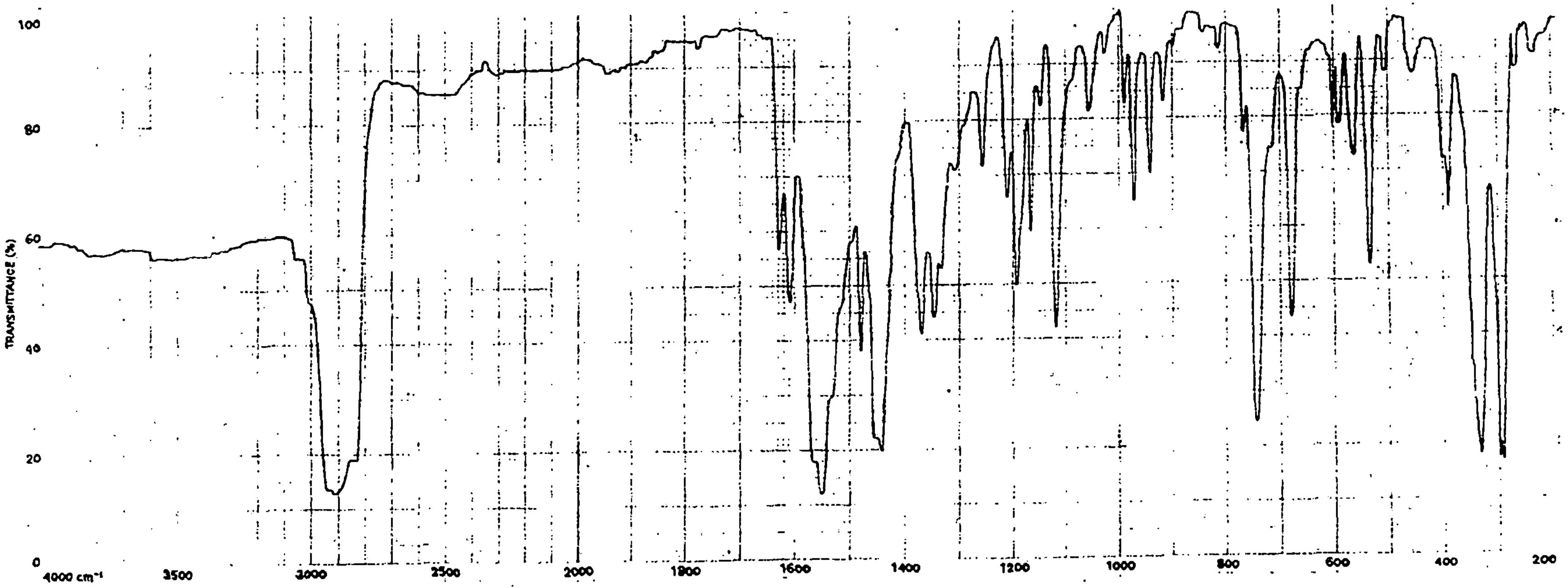


Fig. 12 IR spectrum of β-styrylcarbonyl-α-phenylethyltin trichloride

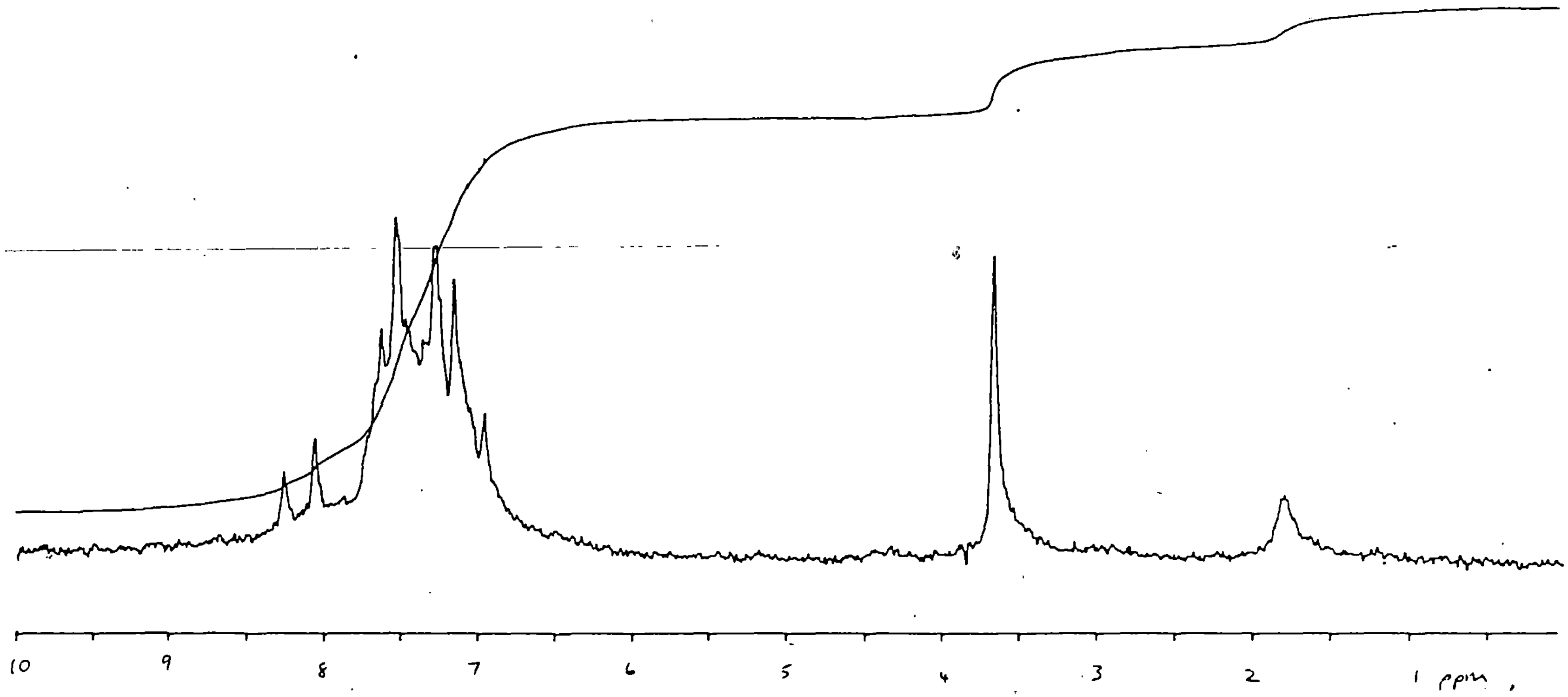


Fig. 13 ^{1}H NMR spectrum of β-styrylcarbonyl-α-phenylethyltin trichloride

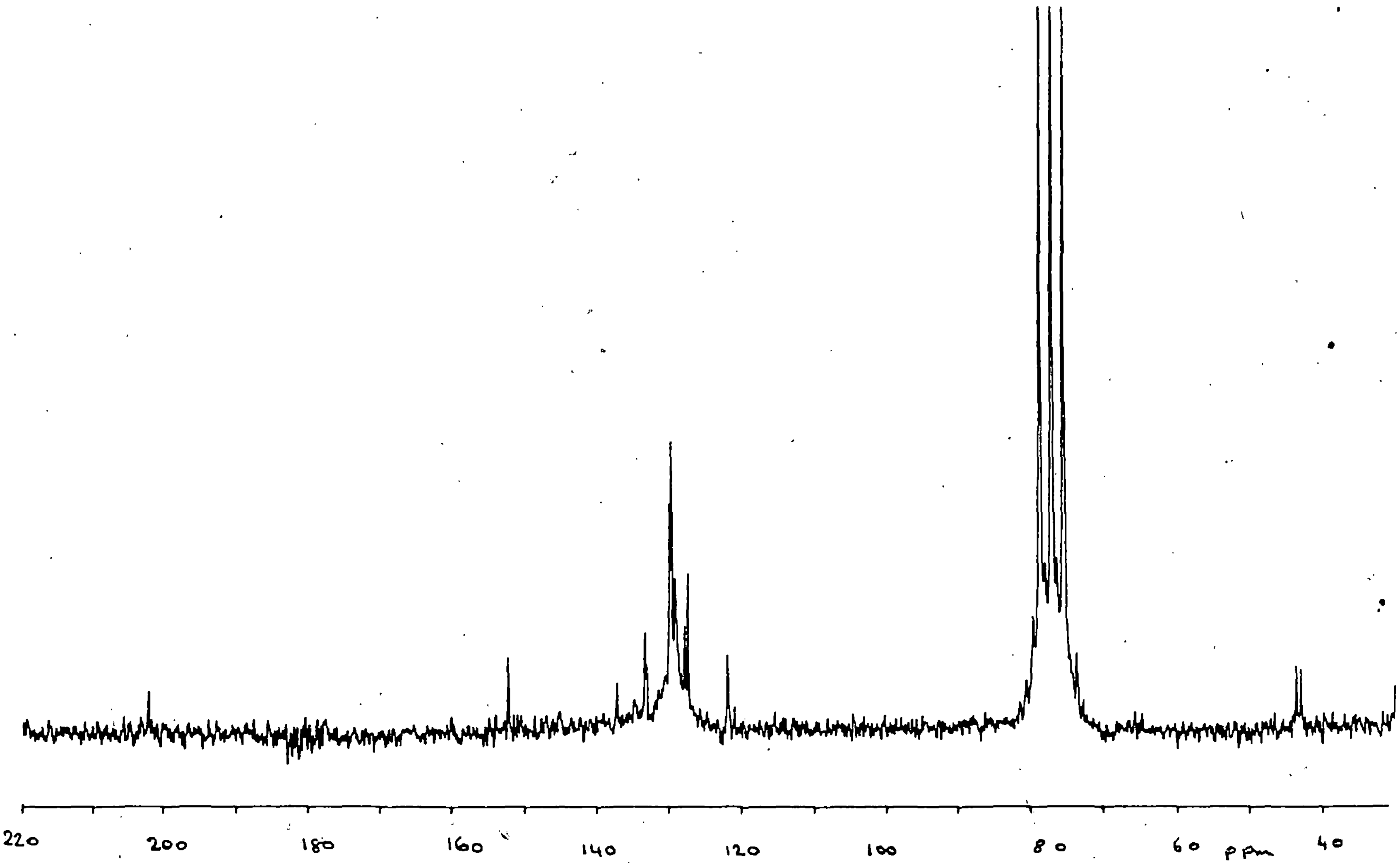


Fig. 14 ^{13}C NMR spectrum of β-styrylcarbonyl-α-phenylethyltin trichloride

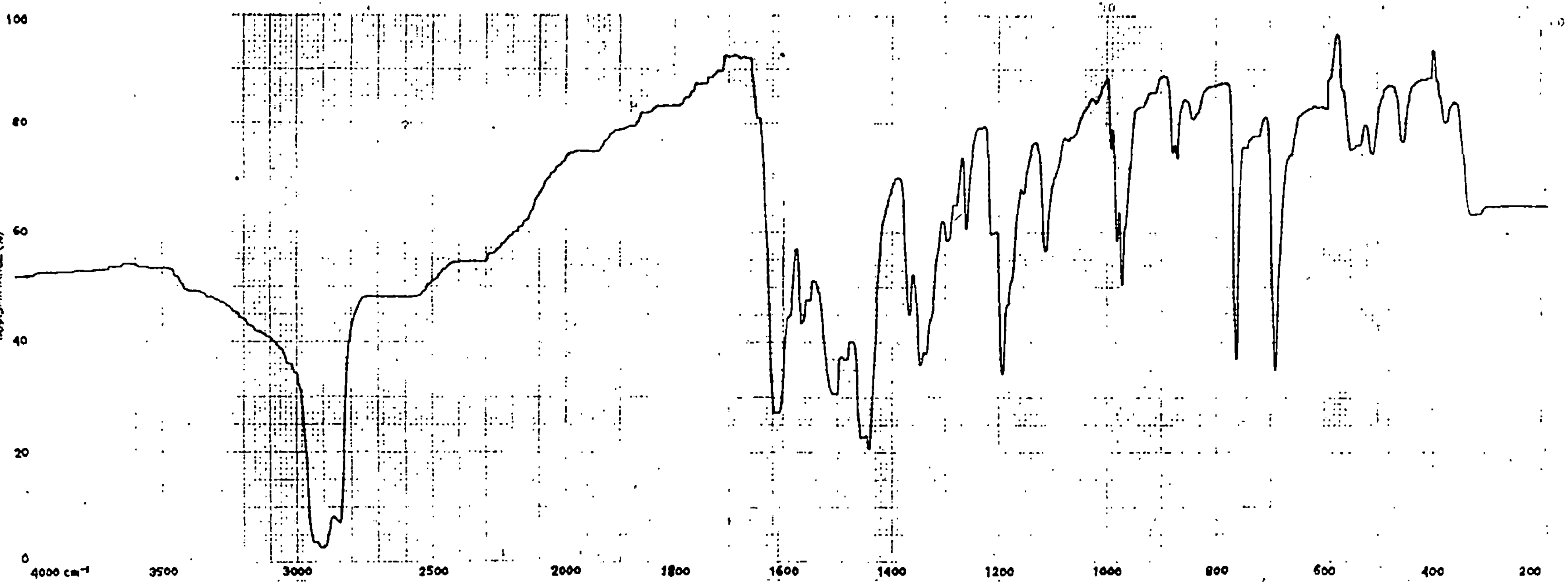


Fig. 15 IR spectrum of yellow powder from the chlorostannation reaction of dibenzylideneacetone

Infrared spectral data (cm^{-1}) (Fig 12)

2950-2830 vs(b), 1630 m, 1610 s, 1570 sh, 1550 vs, 1480 s, 1460 sh, 1440 vs, 1370 s, 1345 s, 1330 w, 1310 w, 1260 m, 1210 m, 1190 s, 1170 m, 1120 s, 1055 w, 990 w, 970 m, 940 m, 920 w, 770 w, 740 vs, 680 s, 600 w, 590 w, 565 m, 535 s, 505 w, 455 w, 390 m, 330 vs, 300 vs, 290 vs, 265 w.

Nuclear magnetic resonance spectal data (chemical shift δ)

^{1}H NMR peaks at 1.8 (methine), 3.6 (methylene) (Fig 13) and 6.9-8.25 (phenyl and olefinic).

^{13}C NMR peaks at 42.76 (methylene), 43.39 (Fig 14) (methine), 121.71-152.08 (phenyl and olefinic) and 201.99 (carbonyl).

Yellow compound

% Analysis for $C_{51}H_{41}O_3SnCl$

Found	C	72.3	H	5.27	Sn	14.28
Calculated	C	71.54	H	4.79	Sn	13.9

Melting point 155°C

Infrared spectral data (cm^{-1}) (Fig 15)

2940-2840 vs(b), 1610 vs, 1570 w, 1510 s, 1460 sh, 1440 vs, 1370 m, 1350 s, 1295 w, 1240 w, 1215 sh, 1195 vs, 1150 w, 1115 m, 990 w, 980 m, 970 s, 880 w, 870 w, 840 w, 765 vs, 690 vs, 550 m, 510 w, 450 w, 380 w.

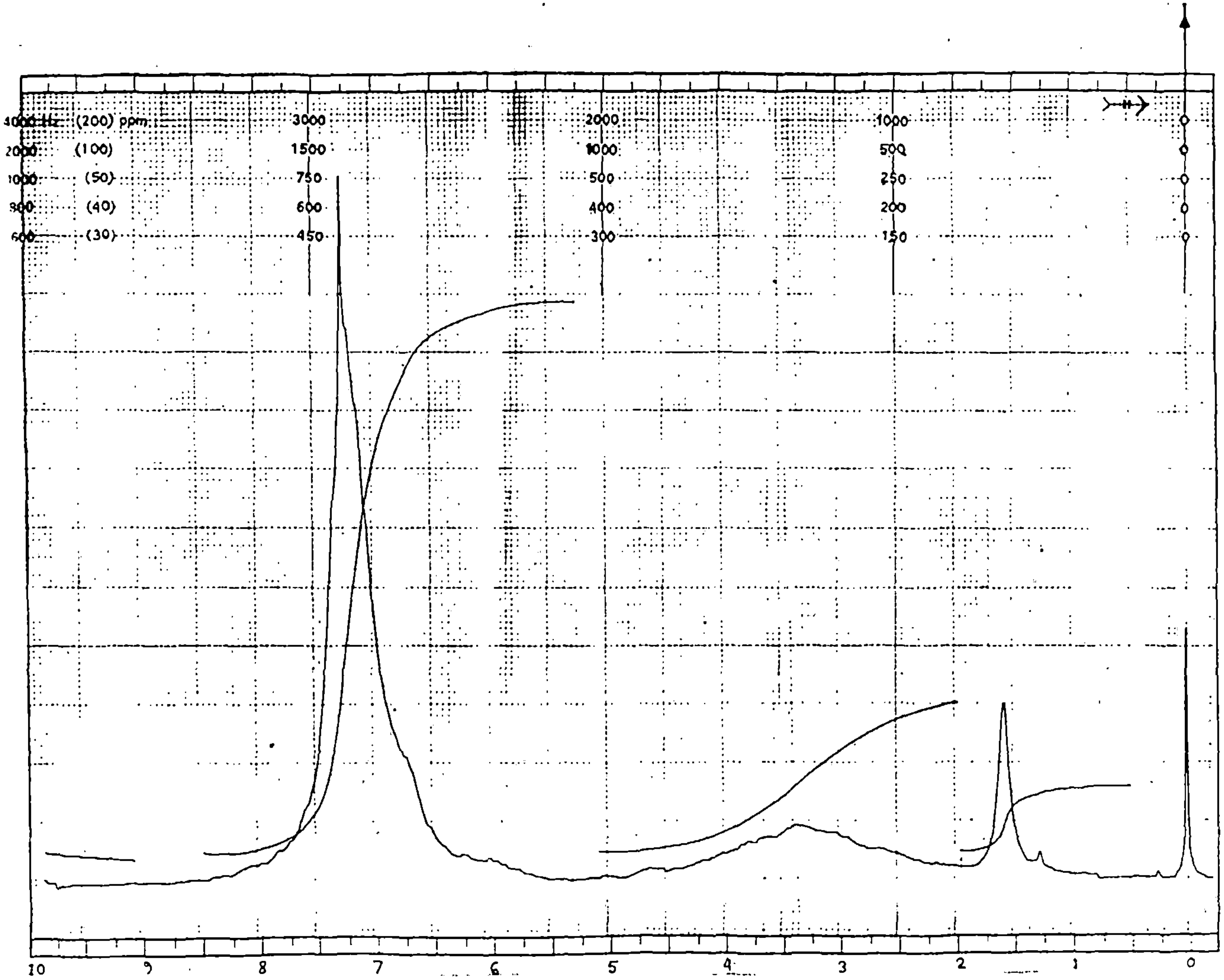


Fig. 15a ^{1}H NMR spectrum of yellow powder from the chlorostannation reaction of dibenzylideneacetone.

Red Compound

% Analysis for $C_{68}H_{54}O_4Sn_2Cl_2$

Found	C 64.75	H 4.5	Sn 18.46
Calculated	C 65.64	H 4.34	Sn 19.14

Melting point 160°C

Infrared spectral data (cm^{-1}) (Fig 16)

2800 vs(b), 1650 m, 1630 m, 1595 vs, 1470 sh, 1450 vs, 1380 m, 1350 vs, 1310 w, 1290 w, 1220 sh, 1200 vs, 1160 w, 1105 m, 1080 w, 1030 w, 990 vs, 930 m, 890 s, 860 w, 770 vs, 760 vs, 750 w, 740 w, 700 vs, 680 w, 580 m, 550 m , 505 d.

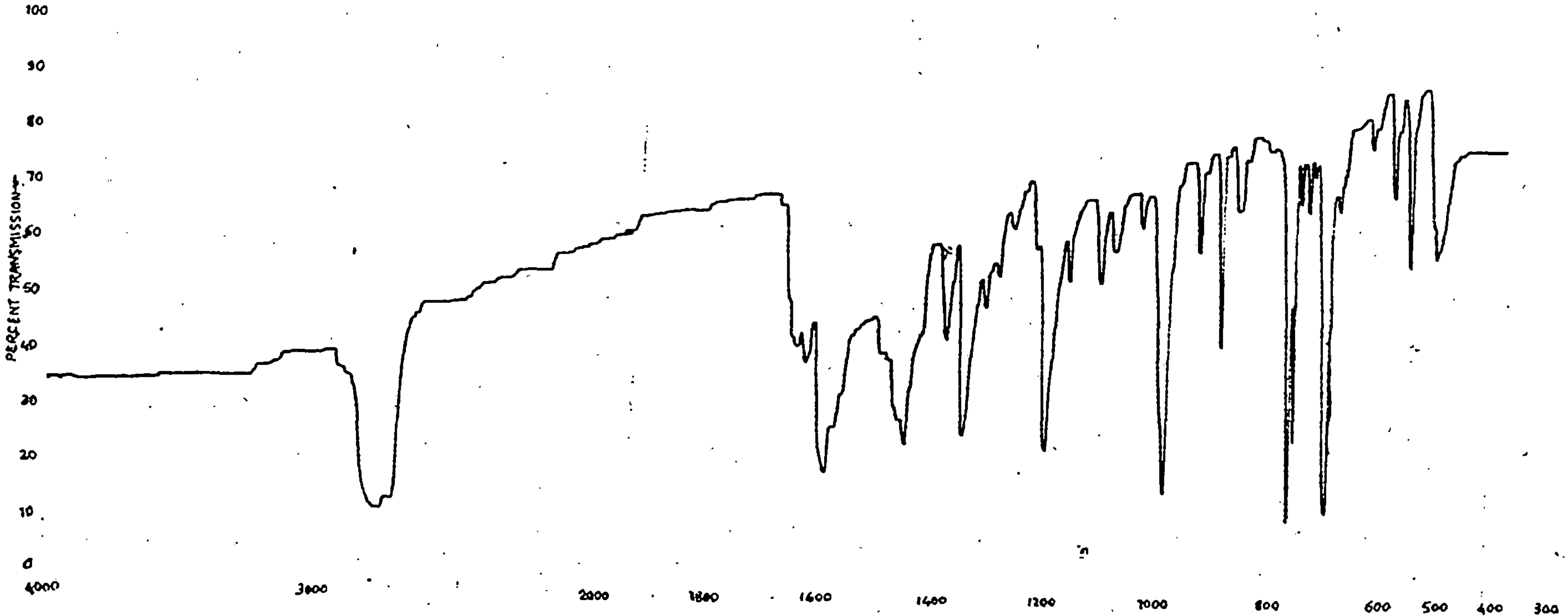


Fig. 16 IR spectrum of red powder from the chlorostannation reaction of dibenzylidene

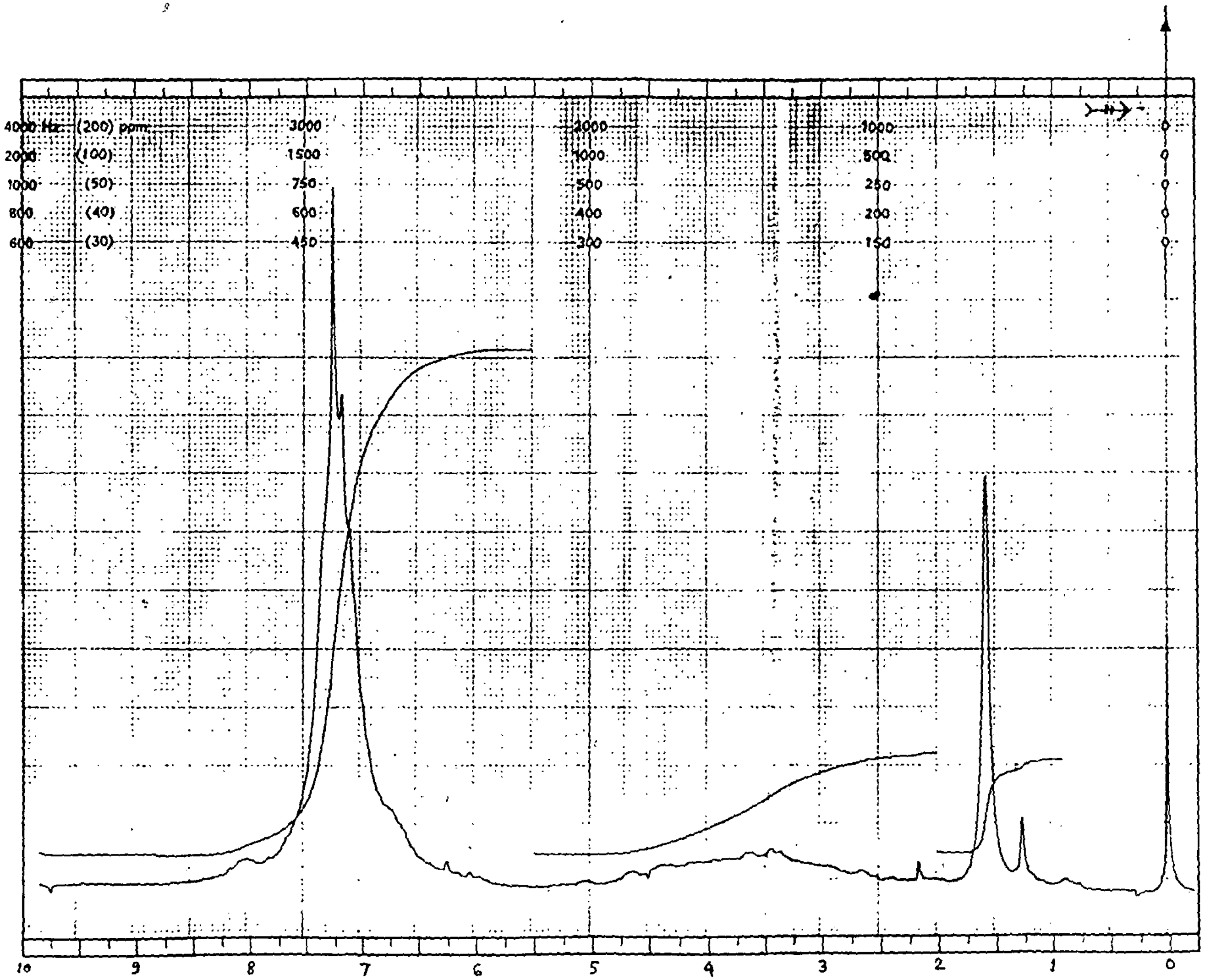


Fig. 16a ^{1}H NMR spectrum of red powder from the chlorostannation reaction of dibenzylideneacetone.

Attempts were made to prepare some derivatives of both red and yellow compounds. In case of the yellow compound, it was found possible to prepare a thiocyanato and a 1:5 diphenyl carbazonate derivative while no such derivative could be obtained from the red compound.

Thiocyanate derivative of the yellow compound

The yellow compound (from the reaction of dibenzylideneacetone, stannous chloride and hydrogen chloride) by reacting with potassium thiocyanate produced thiocyanate derivative of that compound. The reactants were taken in the molar proportion 1:1 on the basis of the proposed molecular composition for the yellow compound.

Firstly 1.709 gm of that yellow compound was dissolved in 100 ml hot ethanol by stirring with a magnetic stirrer at 60°C for about ten minutes. Then a suspension of 0.194 gm of potassium thiocyanate in 50 ml hot ethanol was added slowly with stirring continued. After completing the addition, the stirring was still continued for one hour at 60°C. It was cooled to room temperature and filtered to separate potassium chloride formed. The filtrate was evaporated almost to dryness on a steam-bath and the residue was extracted with 50 ml of chloroform and filtered. The filtrate was concentrated to a very small volume (one tenth of its original volume) and kept undisturbed overnight.

Concentrated solution furnished red crystalline solid which was purified by repeated crystallisation from minimum volume (~20 ml) of methanol. Finally deep red crystals having sharp melting point 75°C was obtained.

(Yield - 60%)

The same reaction was carried out by changing the molar proportion of the reactants (i.e. from 1:1 to 1:2 with the said yellow compound : potassium thiocyanate), but no different reaction product could be isolated suggesting the presence of only one replaceable chlorine atom in the molecule of the yellow compound.

%Analysis for $C_{52}H_{41}O_3SNSn$

Found	C 72.1	H 5.4	N 1.28 Sn 14.4
Calculated	C 71.07	H 4.67	N 1.59 Sn 13.55

Melting point 75°C

Infrared spectral data (cm^{-1}) (Fig 17)

2920-2820 vs(b), 2030 vs, 1610 s, 1580 sh, 1570 sh, 1480 sh, 1455 s, 1380 m, 1335 m, 1190 m, 1100 m, 980 m, 770 m, 700 s, 600 sh, 575 m.

Solubility of the compound

The compound was found to be soluble in ether, chloroform, ethanol, methanol, benzene.

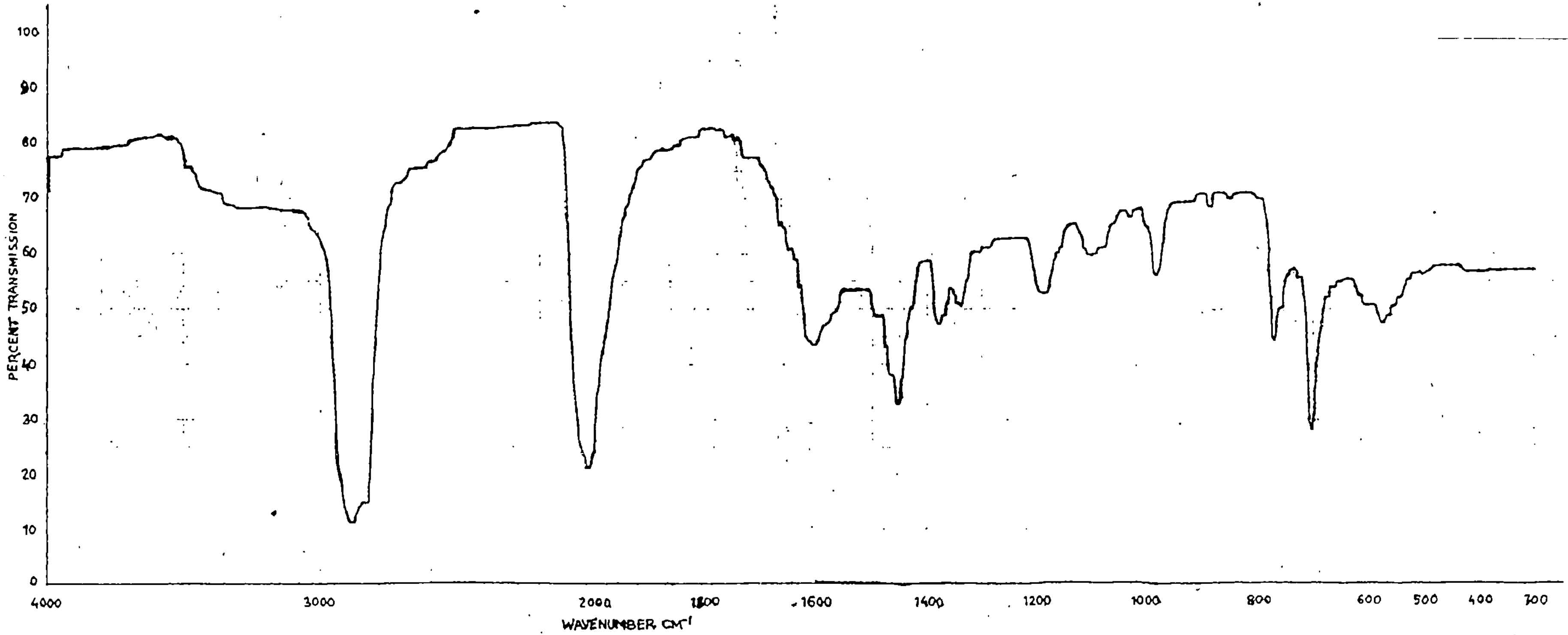


Fig. 17 IR spectrum of thiocyanate derivative of yellow powder

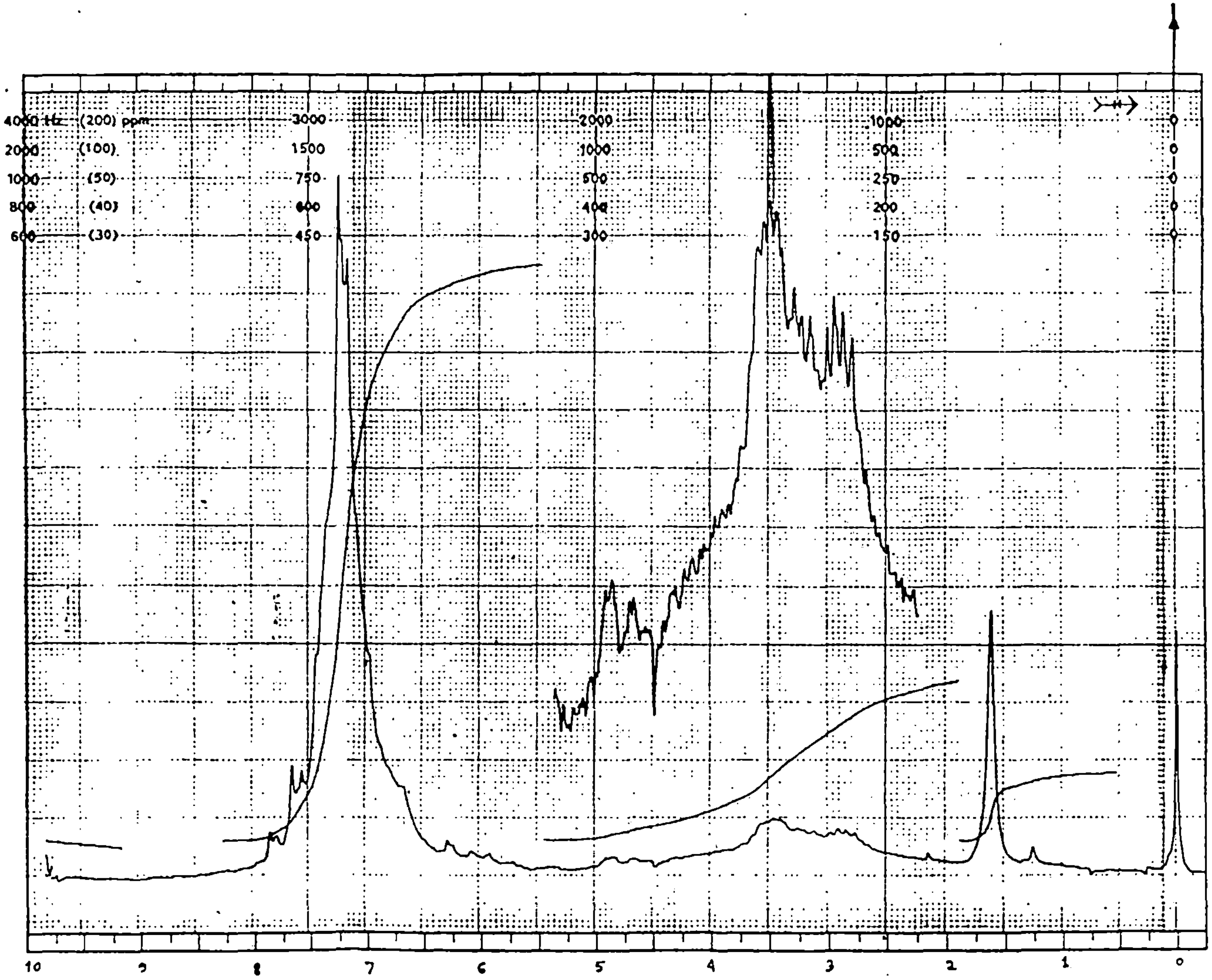


Fig. 17a ^{1}H NMR spectrum of thiocyanate derivative of yellow powder.

Diphenyl carbazone derivative of the yellow compound

The yellow compound (from the reaction of dibenzylideneacetone, stannous chloride and hydrogen chloride) and 1,5-diphenylcarbazone reacted in the molar proportion 1:1 and produced corresponding diphenylcarbazone derivative of the said yellow compound.

The yellow compound (1.709 gm) and 1,5-diphenylcarbazone (0.480 gm) were separately dissolved in 100 ml portions of hot chloroform. Two solutions were then mixed with occasional shaking. The reaction mixture was then heated on a steam bath for about fifteen minutes and then cooled to room temperature. About three drops of concentrated ammonia solution was then added to this with shaking. Ammonia (17N) neutralised the liberated hydrogen chloride. During the addition of ammonia solution, the colour of the reaction mixture was sharply changed from green to blue-violet. It was then filtered to separate ammonium chloride formed. The filtrate was then refluxed for three hours. After refluxing the reaction mixture was filtered again and the filtrate was concentrated to a small volume (∽10 ml) on a steam-bath. Equal volumes of dry ethanol was added to this concentrated filtrate and was kept undisturbed for three days. Fine greenish fluorescent deep violet crystals were separated. The compound was recrystallised from chloroform-ethanol (1:1) mixture. The melting point of the crystals was 120°C.

(Yield - 40%)

The same reaction was carried out by changing the molar proportion of the reactants (i.e. from 1:1 to 1:2 and also 1:3 with the said yellow compound; 1,5-diphenylcarbazone) but no other diphenylcarbazone derivative except the described one could be isolated. Moreover with increased amount of diphenylcarbazone, the yield of the said diphenylcarbazone derivative was found to decrease and large amount of unreacted diphenylcarbazone was recovered from the reaction mixture. This was also in favour of presence of one replaceable chlorine atom in the molecule of the yellow compound.

% Analysis for $C_{64}H_{52}O_4N_4Sn$

Found	C	72.45	H	5.05	N	6.02	Sn	10·08
Calculated	C	72.5	H	4.85	N	5.3	Sn	11·25

Melting point 120°C

Infrared spectral data (cm^{-1}) (Fig 17b)

3350 m, 2920-2850 vs(b), 1670 s, 1610 s, 1590 sh, 1505 s, 1460 s, 1385 m, 1315 m, 1300 w, 1260 m, 1215 w, 1190 m, 1150 w, 1110 w, 1080 w, 1030 w, 980 m, 910 w, 835 w, 820 w, 780 s, 770 s, 705 s, 600 w, 560 w, 520 m.

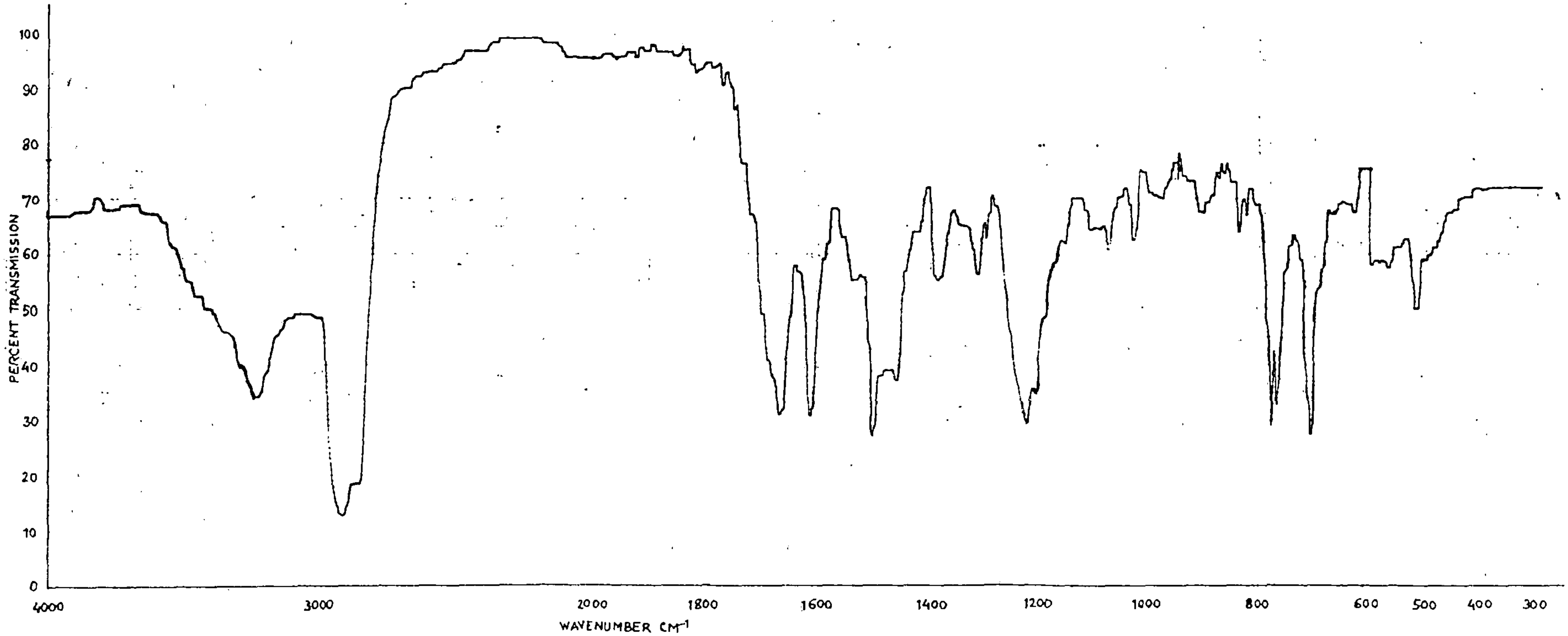


Fig. 17b. IR spectrum of 1,5-diphenylcarbazonate derivative of yellow powder

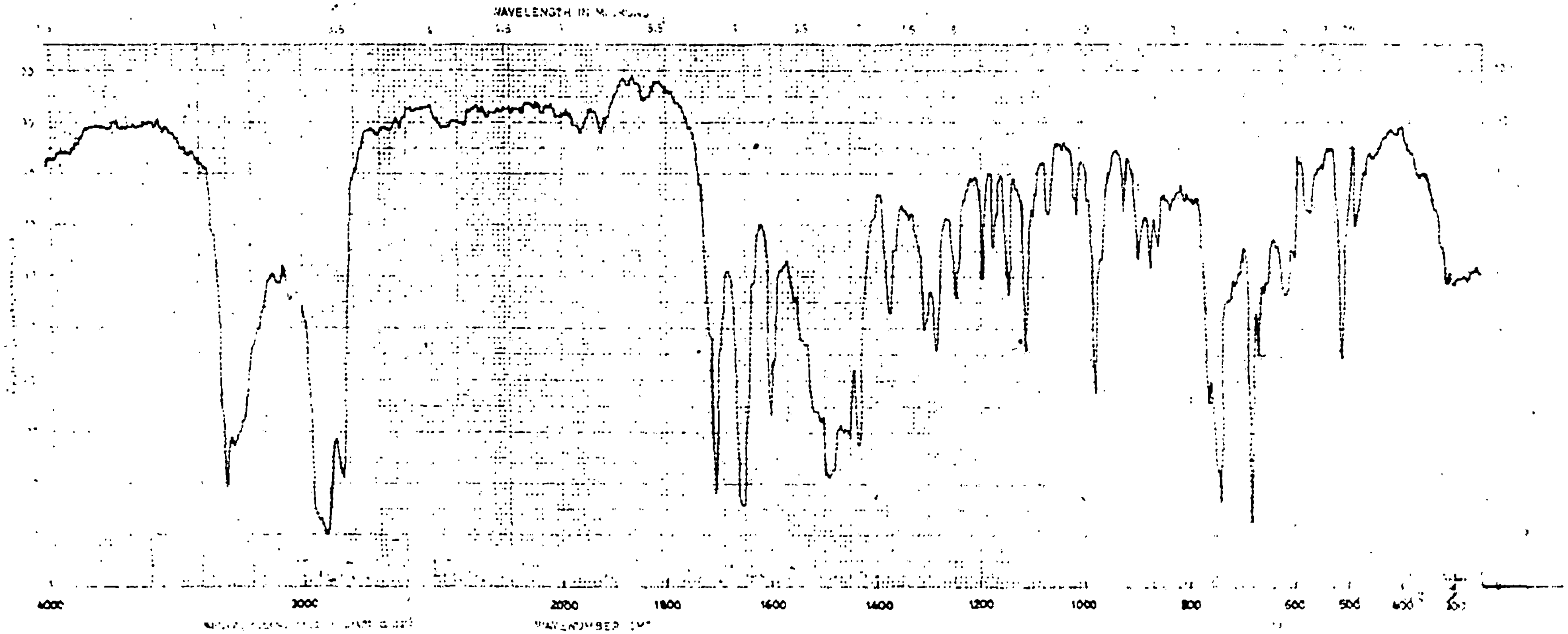


Fig17c IR spectrum of 1,5-diphenylcarbazone

All the three compounds prepared during the reactions of dibenzylideneacetone, stannous chloride and hydrogen chloride were found to dissolve fairly in common organic solvents like, chloroform, benzene, diethylether, methanol, ethanol. Their solubility in carbon tetrachloride, was much less. The ~~two of the~~ derivatives, the thiocyanate derivative and 1,5-diphenylcarbazone derivative of the yellow powder (m.p. 155°C) indicated more or less similar solubility in these solvents.

DISCUSSIONS

In course of the present investigation, few β-ketoorganotin chlorides have been prepared **and** studied as far as possible. The structural aspects of these compounds were found to have several characteristic features. A brief discussion about their molecular structures has ~~also~~ been attempted.

Structural Aspects

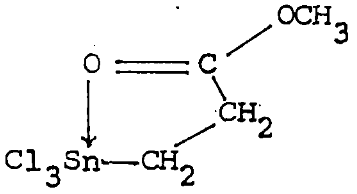
In absence of X-ray crystal structure determination facilities, we would like to discuss the structural aspects of these compounds from the IR and NMR data, though these suggestions might be somewhat tentative in nature.

The mass spectra of the compounds like β-benzoyl α-phenyl ethyl tin trichloride and the red and yellow compounds obtained from the reaction of dibenzylidene acetone and stannous chloride and anhydrous hydrogen chloride were attempted through the courtesy of Dr. D.A. Bravo-Zhirotovskii of Institute of Organic Compounds at Irkurtsk, U.S.S.R. The mass spectrum of β-benzoyl-α-phenylethyltin trichloride did not give any molecular ion peak due to low volatility of the compound even at 270°C. At 300°C, the compound decomposed, however, in the fragmentation pattern a peak corresponding to $SnCl_3^-$ ion could be detected.

The mass spectra of both red and yellow products corresponding to empirical formulae $C_{68}H_{54}O_4Sn_2Cl_2$ and $C_{51}H_{41}O_3SnCl$ respectively were also attempted. But none of these had enough volatility even at 320°C to give molecular ion peaks. At this temperature, both the compounds decomposed giving some peaks corresponding to mass numbers 780, 790 and 916 for red compound and mass numbers 700, 780, 790 for the yellow compound.As a result, we could not get any tangible benefit from the mass spectra determination of these compounds.

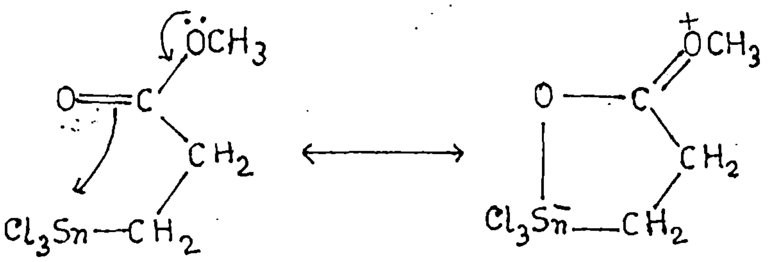
Molecular weight determination of β-benzoyl-α-phenyl ethyl tin trichloride by osmometric method gave erratic results probably due to unstable nature of the compound in solution phase. Hence, our suggestion about the structural aspects of these compounds are mainly based on IR and NMR data and therefore should be considered somewhat tentative in nature. Before suggesting the structural aspects of these compounds, it may be somewhat relevant to discuss the structural aspects of estertin compounds prepared by similar type of reactions by Hutton et al (265).

They observed that with a very few exceptions the carbonyl stretching frequencies in most of the mono-substituted alkyltin trichlorides lie between 1655 and 1665 cm^{-1} roughly 80 cm^{-1} lower the frequency than the saturated analogues of the parentα,β-unsaturated carbonyl compound. The ester methyl ^1H NMR signal in $Cl_3SnCH_2CH_2COOCH_3$ in situated down field from the corresponding signal in $CH_3CH_2COOCH_3$ and a similar effect is observed for the methyl signals in $Cl_3SnCH_2CH_2COCH_3$ and $CH_3CH_2COCH_3$. These spectroscopic effects are consistent with carbonyl coordination to Sn, since this phenomenon reduces the C = O bond order (265) (and hence the carbonyl stretching frequency) and also the perturbation of the electron distribution causes a deshielding effect on the relevant protons. Since the carbonyl stretching frequency for any compound is unaffected by dilution in toluene or ethereal solvents, the carbonyl coordination to Sn is almost certainly intramolecular in origin. For example, the structure of β-carbomethoxyethyltin trichloride can be represented as (I)



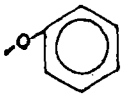
I

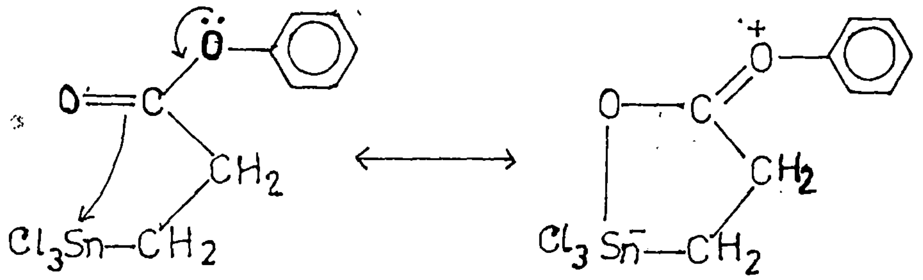
The IR spectrum of $Cl_3SnCH_2CH_2COOCH_3$ and $CH_3CH_2COOCH_3$ shows that ν(C-O) for the ester group in $Cl_3SnCH_2CH_2COOCH_3$ lies some 63 cm^{-1} to higher frequency than the same vibration in $CH_3CH_2COOCH_3$ (1270 cm^{-1} vs 1207 cm^{-1}). Possibly the methoxy oxygen lone-pair electrons are also involved in the delocalisation of the ester carbonyl electron density to Sn. The intramolecular coordination may, therefore, be represented as follows (II).



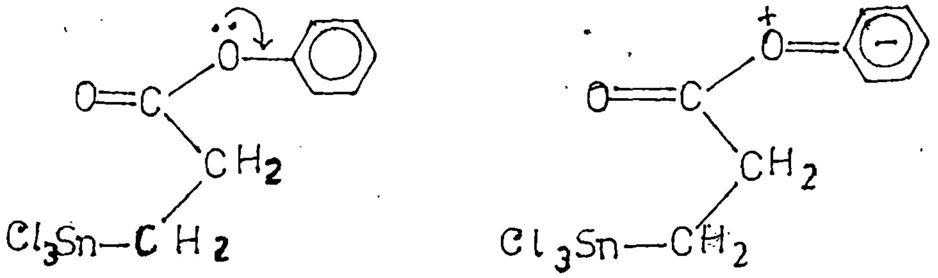
II

Intramolecular carbonyl coordination of the type described above is significantly stronger in the esters and ketones than that in the corresponding dialkyltin compounds (265).

The disturbance of normal electron density distribution by the presence of phenyl group was also reported by Hutton et al (265). They noticed the relatively high frequency carbonyl absorption (1680 cm^{-1}) in the case of phenyl ester ($Cl_3SnCH_2CH_2COOC_6H_5$) as compared to the other substituted organotin compounds. They suggested that the phenyl group probably withdraws electron density from the oxygen atom of the  group and hence diminishes delocalisation of electron density on to Sn atom. The resonance hybrid of the said phenyl ester can be represented as follows (III abd IV).



III



IV

Since the IR spectra of the starting materials and the products obtained are rather complex in nature it is not possible to assign all the bands present in the spectra. Therefore we will restrict our discussion with some characteristic bands only.

In the IR spectra of estertin type of compounds, one of the most interesting aspect was the shifting of carbonyl stretching frequency due to coordination from carbonyl oxygen atom to tin compared to that of the starting organic moiety. For β-benzoyl-α-phenylethyltin trichloride carbonyl (Fig. 7) stretching frequency, $\nu(C = O)$ is found at 1605 cm^{-1}, which is at lower frequency than that of the corresponding α,β-unsaturated carbonyl compound (benzylideneacetophenone i.e. chalcone of which $\nu(C = O)$ is at 1645 cm^{-1}) and also from saturated analogue of chalcone (i.e. hydrochalcone). This observation suggests the intramolecular carbonyl coordination to tin in similar compounds. Hutton et al (265) also suggested such intramolecular carbonyl coordination to tin in similar compounds.

The out of plane $\nu(C-H)$ bending vibrations, which appear are far more useful than the in-plane bands. The extremely intense absorptions, resulting from strong coupling with adjacent hydrogen atoms can be used to assign the position of the substituents on the aromatic ring.

In mono-substituted aromatic compounds, this substitution pattern always gives a strong absorption near 690 cm^{-1}. A second strong band usually appears near 750 cm^{-1}. In the spectrum of β-benzoyl-α-phenylethyltin trichloride there are strong bands at 750 (sh) cm^{-1}, 755 cm^{-1}, 690 cm^{-1} and 680 cm^{-1} indicating the presence of two different mono substituted phenyl rings within the molecule. These bands are also found in the IR spectrum of chalcone itself which is also expected.

Both ν(Sn-C) and ν(Sn-O) vibrations are expected to absorb in the range $\sim$400-600 cm^{-1}. ν(Sn-C) is probably rather weak in these complexes show in addition to Sn-C stretching modes, one other strong absorption band at $\sim$520-540 cm^{-1}. Two bands are found at 510 cm^{-1} and at 530 cm^{-1} in the IR spectrum of the present tin complex which are absent in the starting material chalcone may be attributed to ν(Sn-C) and ν(Sn-O) vibrations respectively.

The bands obtained in the spectrum of β-benzoyl-α-phenylethyltin trichloride in the region $\sim$350-290 cm^{-1} (two strong bands are at 350 cm^{-1} (ν_{as}) and at 300 cm^{-1} (ν_s) may be attributed to ν(Sn-Cl) vibrations.

The IR spectrum of β-acetyl-α-phenylethyltin trichloride (Fig. 10) shows all the characteristics of typical esterin type of compounds to a satisfactory extent.

For β-acetyl-α-phenylethyltin trichloride the carbonyl stretching frequency, ν(C = O) is found at 1645 cm^{-1} (as indicated by a very strong absorption band) which is at lower frequency than that of the corresponding α,β-unsaturated carbonyl compound, the benzylideneacetophenone of which ν(C = O) is at 1665 cm^{-1}. This observation suggests the intramolecular carbonyl coordination to tin which was also suggested by Hutton et al in the similar type of compounds. Of course with the present compound the extent of carbonyl absorption frequency shifting is comparatively small than in case of similar compound β-benzoyl-α-phenyltin trichloride suggesting some lesser extent of such intramolecular coordination.

The out of plane ν(C-H) bending vibrations, which appear are more useful than the in-plane bands. The extremely intense absorptions resulting from strong coupling with adjacent hydrogen atoms can be used to assign the position of the substituents on the aromatic ring. In mono-substituted aromatic compounds, this substitution gives two strong bands at ~690 cm^{-1} and at ~750 cm^{-1}. In β-acetyl-α-phenylethyltin trichloride two very strong absorption bands are found at 700 cm^{-1} and 765 cm^{-1} respectively indicating the presence of monosubstitution in the phenyl ring in the compound. In the corresponding starting compound benzylideneacetone the strong bands are found at 690 cm^{-1} and at 745 cm^{-1} indicating the presence of ~~same~~ monosubstituted phenyl ring in the molecule of the compound. Both are in favour of the proposed most probable molecular structure of β-acetyl-α-phenylethyltin trichloride.

Both ν(Sn-C) and ν(Sn-O) vibrations are expected to absorb in the range $\sim$400-600 cm^{-1}. ν(Sn-C) is probably rather weak in these complexes. In addition to ν(Sn-C) stretching modes, one other strong absorption band should found at $\sim$520-540 cm^{-1}. In the present compound a strong absorption band at 570 cm^{-1} and a medium band at 550 cm^{-1} are found and may be attributed to absorptions due to ν(Sn-O) and ν(Sn-C) vibrations respectively. Beside these a strong absorption band is seen at 510 cm^{-1} which is possibly due to ν(Sn-C) stretching modes. The said bands at 510 cm^{-1}, 550 cm^{-1} and at 570 cm^{-1} are found absent in the starting material benzylideneacetone which is also expected.

The spectrum of β-acetyl-α-phenylethyltin trichloride recorded with the help of potassium bromide disc provides some assignment for ν(Sn-Cl) absorption frequencies. The two strong absorption bands at 300 cm^{-1} (ν_s) and at 325 cm^{-1} (ν_{as}) may be assigned for absorption due to ν(Sn-Cl) since ν(Sn-Cl) is found to absorb in the region $\sim$290-350 cm^{-1}. These two bands are found absent in benzylideneacetone which is expected.

The products obtained from the reaction of dibenzylideneacetone, stannous chloride and hydrogen chloride could not be characterised conclusively. However some indications about their structure could be suggested from the studies carried out so far. Like the products obtained from the reaction of benzylideneacetophenone or benzylideneacetone with stannous chloride and hydrogen chloride, a light yellow crystalline product having a melting point 120°C was isolated in small quantity in one of the experiment which however could not be repeated in other experiments. That particular light yellow product gave an elemental analyses corresponding to a molecular composition of $C_{17}H_{15}OSnCl_3$. The infrared spectrum of the compound (Fig. 12) gave some characteristic bands in addition to a number of bands, which could not be conclusively assigned.

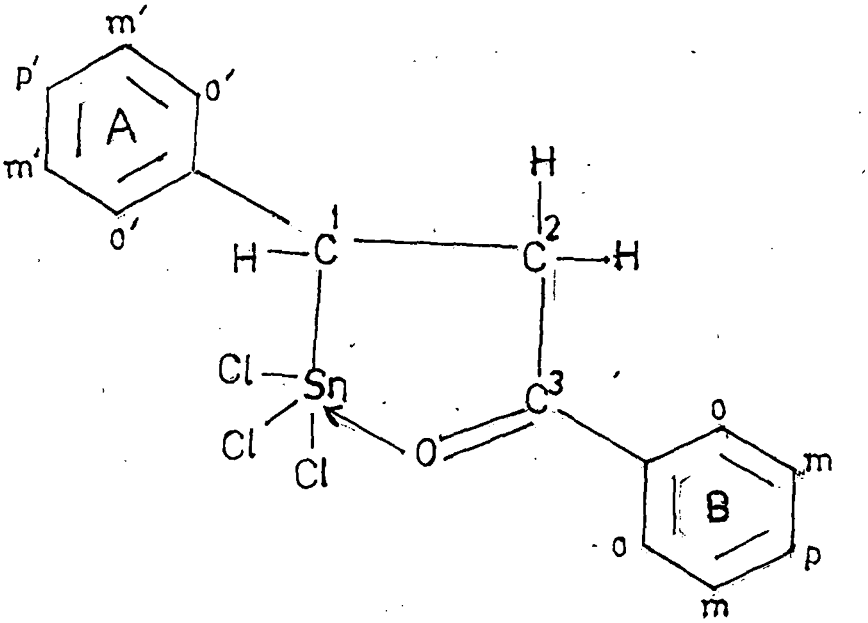
In the IR spectrum of the compound the absorption bands at 1610 cm^{-1} and 1630 cm^{-1} indicate the presence of CH = CH group, whereas a strong band at $\sim$1550 cm^{-1} shows the presence of coordinated carbonyl group. The strong bands at 680 cm^{-1} and 740 cm^{-1} are due to phenyl group deformation modes. The band at 560 cm^{-1} indicates the presence of ν(Sn-C) absorption bands whereas band at 590 cm^{-1} may be due to ν(Sn-O) absorption. There are three bands at 290 cm^{-1}, 330 cm^{-1} and 390 cm^{-1} which indicate the presence of ν(Sn-Cl) bands present in the compound $C_{17}H_{15}OSnCl_3$.

The main products from the above reaction were one yellow powder (m.p. 155°C) and the other red powdery product (m.p. 160°C). On the basis of elemental analyses, the yellow product had a molecular formula of $C_{51}H_{41}O_3SnCl$ while the red product corresponded to $C_{68}H_{54}O_4Sn_2Cl_2$.

The IR spectra of these two compounds give some indications of olefinic double bonds. In the spectrum of yellow compound (Fig. 15) the absorption at ~1650 cm^{-1} (sh) probably has been merged with the strong carbonyl absorption at 1610 cm^{-1}. In the spectrum of red compound (Fig. 16) there are two bands at 1630 cm^{-1} and at 1645 cm^{-1} in addition to a strong band due to carbonyl absorption at 1595 cm^{-1}. The strong phenyl deformation modes are found to appear at usual positions (with the yellow compound at 690 cm^{-1}, 765 cm^{-1} and with the red compound at 700 cm^{-1}, 760 cm^{-1} and 770 cm^{-1}). The ν(Sn-O) band appears at 580 cm^{-1} and at 550 cm^{-1} for the yellow and red compounds respectively. The yellow compound shows two bands for ν(Sn-Cl) absorption at 320 cm^{-1} (ν_s) and 380 cm^{-1} (ν_{as}).

The IR spectra of thiocyanate derivative of the yellow product obtained from the reaction of dibenzilideneacetone and $HSnCl_3$ are closely similar except the thiocyanate derivative has a strong band at 2030 cm^{-1} for SCN group. The 1670 cm^{-1} peak of diphenyl carbazonate indicated the fission of coordinated carbonyl group of the original yellow chloride.

From the ^{1}H NMR spectrum (Fig. 8) at 360 MHz of β-benzoyl-α-phenylethyltin trichloride the following observations can be made. For convenience the aliphatic carbons are marked as C^1, C^2, C^3 and two phenyl rings as ring A and ring B (V).



V

The methine proton (C'H) appears at δ3.77 which has vicinal coupling with the two adjacent magnetically non equivalent methylene protons (C^2Hs) with the coupling constants (J values) 8.3 and 3.3 Hz respectively. Such a coupling of methine proton results doublets of a doublet in its final form.

Similarly one of the two magnetically non equivalent methylene protons (C^2Hs) appears at δ 3.85 which has geminal coupling with other methylene proton and also vicinal coupling with methine proton (C'H) with the coupling constants (J values) 18.9 and 8.3 Hz respectively. Here also coupling results doublets of a doublet in the splitting pattern.

The other methylene proton appears at δ 4.13 and such a proton faces geminal coupling with rest of the methylene proton (C^2H) and also vicinal coupling with methine proton (C^1H) with the coupling constant values (J values) 18.9 and 3.3 Hz respectively. As stated in case of other methylene proton, in this case also net splitting pattern in the spectrum is the resultant of two doublets formed from a doublet during the course of coupling.

In this ^1H NMR spectrum, ten protons of the two phenyl rings occupy the region 7-8.5. Of these phenyl protons, five are present in the ring A and the other five are in ring B.

Since the ring B protons are adjacent to carbonyl group, hence these protons should be found in down field in comparison to the protons of the ring A. Therefore from the splitting pattern for aromatic protons in the spectrum, the three sets at 8.26, 7.83, 7.63 are attributed to ortho, para and meta protons of the ring B.

The doublet at δ8.26, is integrated for two ortho protons and the coupling constant for each is ∽8.1 Hz (being ortho coupled). The splitting pattern at δ 7.83 shows like a triplet which is possibly resulted from doublets of a doublet by merging two of the middle fragments of the said doublets of a doublet. The intensity of the middle fragments of this set also support this interpretation. The coupling constants (J values) for this interaction for this interaction is ∽8.1 Hz for each ortho coupling. Again the set at δ 7.63 shows like that of a triplet which is again due to net result of coupling due to meta protons (ortho coupling) of the ring B by merging the middle two fragments of the doublets of a doublet with the coupling constant value ∽8.1 Hz for each. The set for meta protons is integrated for two protons. Thus a total of five protons, two ortho, one para and two meta of the ring B is accounted. The resultant intensity of these sets are also in the order 2(o) : 1(p) : 2(m) which are also in good agreement with our interpretations. Each of the ortho splitting is also associated with very fine meta splitting.

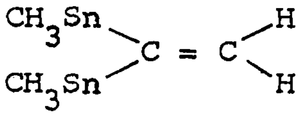
The ring A aromatic protons of the compound resonance as multiplet in the region δ7.08-7.37 of which ortho protons possibly appear at 7.11 as doublet along with very fine meta splitting pattern having coupling constant (J value) ∽7.5 Hz for each ortho coupling. The para and meta protons of the ring appear in the range δ 7.24-7.37. Due to their appearance as aggegate, individual interpretations of these have not been attempted.

In connection with the above discussion, the chemical shifts of methine and methylene protons of β-benzoyl-α-phenylethyltin trichloride may be justified in the following manner.

Methine proton in the compound has been found to become most shielded proton δ 3.77 and methylene protons δ 3.85-4.13 have been found to become somewhat deshielded due to presence of carbonyl group attached to the same methylene carbon atom from those of the compound of the type $RR'CH_2$ (R, R' = alkyl group) where δ is 1.3 (298). In general the presence of carbonyl group (i.e. compound of the type RCH_2COR') increases the δ value from the range 1.3 to 2.4 (298). Further similar saturated estertin compounds are found to possess the chemical shift for methylene protons in the range 2.35-3.33 (265). Therefore further deshielding effect in β-benzoyl-α-phenylethyltin trichloride may be attributed to the presence of phenyl substitution. Though methine proton is most shielded one yet there is also some deshielding effect is found by comparing its chemical shift with other methine protons in similar saturated aliphatic estertin compounds with δ 1.2-3.66 (265) which is possibly due to phenyl substitution to the methine carbon.

In most cases, while carrying out the high resolution ^{1}H NMR spectroscopy of the organotin compounds containing protons in the suitable position so that tin nucleus may couple with the proton, the complexity in the resulting spectrum is found to arise due to 117/119 Sn satellites (Fig. 8a). Many of these data have already been reviewed. In most cases it holds that $|{}^{3}J({}^{119}Sn{}^{1}H)| > |{}^{2}J({}^{119}Sn{}^{1}H)|$ where J value indicates the coupling constants with the corresponding protons. The figure in the prefix of J indicates the distance of tin nucleus from the particular proton with which tin nucleus couples them in terms of number of one bond-distances. In case of restricted rotations of the carbon atoms linked to tin atom in the coupling path-way $^{119}Sn-C-C-$, the relative order of magnitude of coupling constants for tin nucleus with the protons are as follows:

$$|{}^{3}J({}^{119}Sn{}^{1}H)|_{Trans} > |{}^{3}J({}^{119}Sn{}^{1}H)|_{cis} \approx |{}^{2}J({}^{119}Sn{}^{1}H)| \qquad (299)$$

In the system  , the value of $^{118}Sn{}^{1}H$ coupling shows the following values.

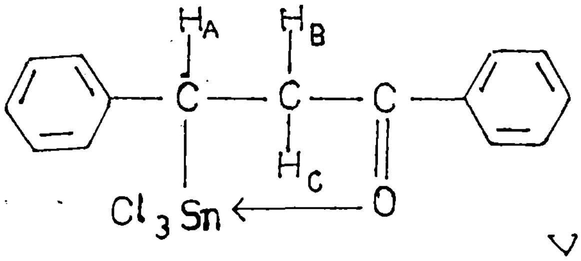
$|{}^{3}J({}^{119}Sn{}^{1}H)|_{Trans} = 208$ Hz;

$|{}^{3}J({}^{119}Sn{}^{1}H)|_{Cis} = 124$ Hz .

Though the system of present compound β-benzoyl-α-phenylethyltin trichloride is somewhat different yet there is a similarity among the said two systems.

In β-benzoyl-α-phenylethyltin trichloride there is some sort of restricted rotation for which vicinal and geminal coupling arises as indicated by 360 MHz ^{1}H NMR spectrum. Hence there should develop following types of $^{117/119}Sn^{1}H$ couplings due to $^{117/119}Sn$ nucleus with the three aliphatic protons.

Since there are three different aliphatic protons relative to $^{117/119}Sn$ nucleus, the present system may be represented as follows for the case representing the particular $^{117/119}Sn^{1}H$ interaction (VI).



VI

The ^{119}Sn nucleus couples with $^{1}H_B$ giving rise to firstly a doublet with a coupling constant (calculated by measurement from the scale) $|^{3}J(^{119}Sn^{1}H)|_{Trans} = 220$ Hz, a value which is comparable to the reference compound (208 Hz). Here in the said doublet each splitted signal again due to $^{1}H_B$ $^{1}H_C$ geminal coupling splits giving rise to doublet and hence in resultant a quartet as net splitting. But $^{1}H_C$ faces interaction with $^{1}H_A$ and hence each of the doublet gives rise to quartet. Therefore in total $^{119}Sn^{1}H_B$ interaction gives rise to octet. Similar is the case with ^{117}Sn nucleus whose splitted signals are very near by to those of signals of ^{119}Sn with close $\left|^{3}J(^{117}Sn^{1}H)\right|_{Trans}$ value.

In the same fashion the value $\left|^{3}J(^{119}Sn^{1}H)\right|_{Cis}$ = 110 Hz is determined which is also in good agreement with the reference compound (124 Hz). Here also each of the signals of doublet due to $^{119}Sn^{1}H_C$ is splitted ultimately to a quartet due $^{1}H_C$ $^{1}H_B$ interaction and $^{1}H_B$ $^{1}H_A$ interaction (since $^{1}H_B$ of $^{1}H_C$ $^{1}H_B$ interaction undergoes interaction with $^{1}H_A$) and hence a total of octet for net $^{119}Sn^{1}H_C$ interaction. $^{117}Sn^{1}H_C$ interaction gives rise to octet which is very close to octet obtained for $^{119}Sn^{1}H_C$ interaction and hence giving nearly same value for coupling constant J.

For $^{119}Sn^{1}H_A$ interaction the value $\left|^{2}J(^{119}Sn^{1}H)\right| \approx$ 110 Hz is obtained which is also comparable to reference compound [$(CH_3Sn)_2C = CH_2$]. In this case also the formation of quartet from each signal of the doublet due to $^{119}Sn^{1}H_A$ interaction and finally a total of octet due to net result of interactions (due to $^{1}H_A$$^{1}H_B$ and $^{1}H_B$$^{1}H_C$ interactions). Similarly $^{117}Sn^{1}H_A$ gives rise to two quartets for two splitted signals of the doublet and hence a octet as net splitting signals. The set of signals for $^{117}Sn^{1}H_A$ interaction is very close to $^{119}Sn^{1}H_A$ interaction and hence giving rise to nearly same value for coupling constant (J value).

Hutton et al (265) also reported similar $J(Sn\text{-}H_\alpha)$ and $J(Sn\text{-}H_\beta)$ values for several estertin compounds.

Compound	$J(Sn\text{-}H_\alpha)$	$J(Sn\text{-}H_\beta)$
$Cl_3SnCH_2CH_2COOCH_3$	102 Hz	186 Hz
$Br_3SnCH_2CH_2COOCH_3$	92 Hz	192 Hz
$Cl_3SnCH_2CH_2COOC_4H_9$	118 Hz	209 Hz
$Cl_3SnCH_2CH_2COOC_6H_5$	112 Hz	221 Hz

[All the reported values in this table are the mean of the $^{117}Sn\text{-}H$ and $^{119}Sn\text{-}H$ coupling constants].

From the ^{1}H NMR spectrum (Fig 11) at 80.13 MHz of β-acetyl-α-phenylethyltin trichloride the following observations can be made. With the present compound individual interaction of different protons can not be interpreted since here the resolution has been carried out at 80.13MHz as compared to resolution of β-benzoyl-α-phenylethyltin trichloride at 360 MHz.

However in the spectral pattern there are four well defined resolved peaks are found in the range ~ δ1.7-3.52, which may be attributed to aliphatic protons. Of these methyl protons are likely to appear at δ 1.7. The methine proton and two magnetically non equivalent methylene protons constitute a set of aliphatic protons. These three protons appear at δ 2.45, 2.7, 3.52. Since the spectrum has been recorded at 8013MHz, further comments about the individual position of these three protons in the spectrum is not possible. The integration curve for these three non equivalent protons also shows their ratio as 1:1:1 . Of course possibly methine proton appears at δ 2.45 since it is most shielded among these three.

The aromatic protons of the compound resonance as multiplet in the region δ 6.65-7.7. Due to the appearance of these protons as an aggregate, the individual interpretation of these have not been attempted.

The overall spectral pattern is satisfactory to explain the proposed molecular structure of the compound.

The presence of signals due to interactions of $^{117/119}$Sn nucleus with protons is absent in ^{1}H NMR spectrum at 80.13 MHz of β-acetyl-α-phenylethyltin trichloride and hence their interpretations are not possible as given in case of corresponding compound β-benzoyl-α-phenylethyltin trichloride where a high resolution ^{1}H NMR spectrum (at 360 MHz) has been recorded.

From the ^{1}H NMR spectrum (Fig. 13) at 80.13 MHz of β-styrylcarbonyl-α-phenylethyltin trichloride in $CDCl_3$ solution the following observations can be made. From the nature of the integration curve, it seems that possibly methylene protons appear at δ3.6, methine proton appears at δ1.8. The aromatic and olefinic protons appear in the range $\sim$ δ6.9-8.25. The integration due to olefinic protons is not clearly identifiable in presence of the aromatic protons and therefore the integration for aromatic and olefinic protons are taken together. The observed ratio for aromatic and olefinic protons : methylene protons : methine proton is approximately 12:2:1. The ratio supports the proposed molecular composition where there should be ten aromatic protons, two olefinic protons, two methylene protons and one methine proton.

The interpretations of interactions of $^{117/119}$Sn nucleus with protons in the compound β-styrylcarbonyl-α-phenylethyltin trichloride are not possible due to same reason as mentioned in case of β-acetyl-α-phenylethyltin trichloride.

The broad band decoupled ^{13}C NMR spectrum (at 90.56 MHz) of β-benzoyl-α-phenylethyltin trichloride is shown (Fig. 9) along with the proton coupled ^{13}C NMR spectrum at the top. The spectrum was recorded with $CDCl_3$ solution of the compound.

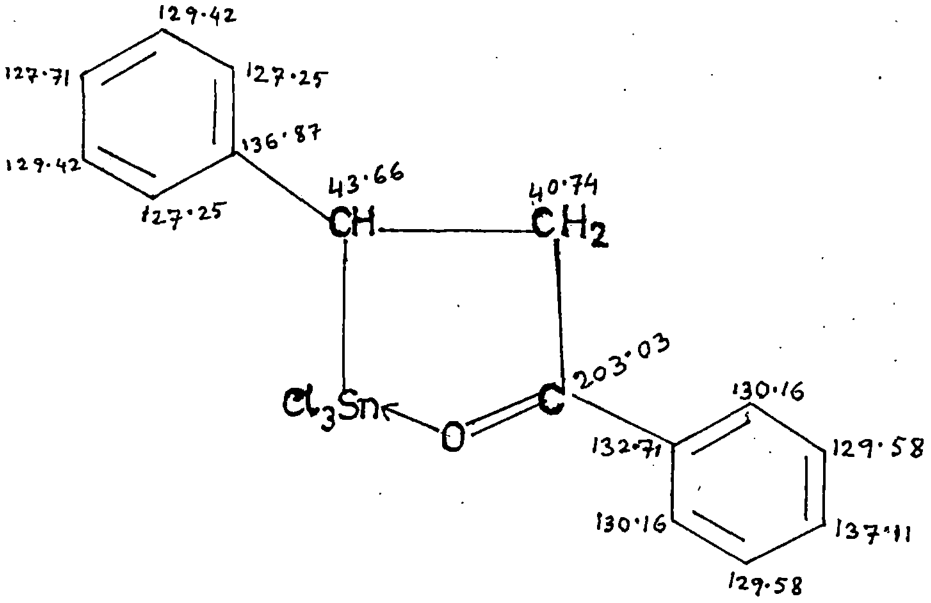
In the fully decoupled spectrum of the compound there are eleven resolved peaks which are at δ 40.74, 43.66, 127.25, 127.71, 129.42, 129.58, 130.16, 132.71, 136.87, 137.11 and 203.03. Each of the peaks at δ 127.25, 129.42, 129.58, 130.16 is integrated for two carbons and therefore accounting the total of fiteen carbons (VII). The multiplicity for each carbon have been assigned from the fully proton decoupled spectrum, which are as follows.

Singlet : at δ 132.71, 136.87, 203.03

Doublet : at δ 43.66, 127.25, 127.71, 129.42, 129.58, 130.16, 137.11

Triplet : at δ 40.74.

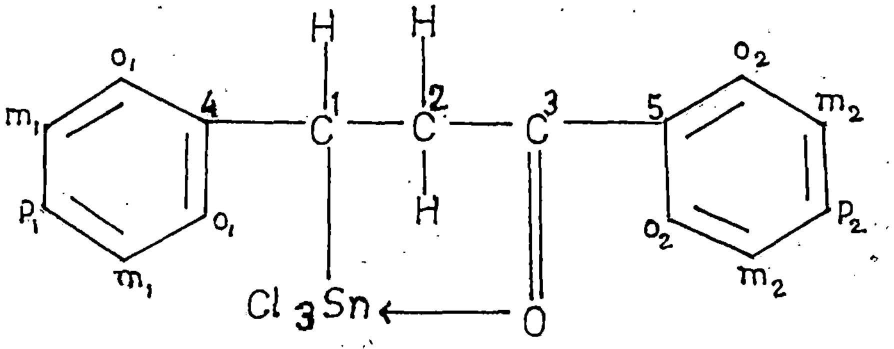
The assignment of ^{13}C chemical shifts of this compound is shown as follows. (VII)



VII

As in the case of high resolution ^{1}H NMR Spectroscopy of the organotin compounds $^{117/119}Sn$ satellites are obtained in the spectrum due to $^{117/119}Sn\,^{1}H$ interactions, during ^{13}C NMR spectroscopy of the organotin compounds also give rise to satellite peaks in the spectrum (Fig. 9) due to $^{117/119}Sn\ ^{13}C$ interactions.

In the present case i.e. with the compound β-benzoyl-α-phenylethyltin trichloride ^{13}C NMR spectrum (at 90.56 MHz) supplies the following data for $^{117/119}Sn$ ^{13}C interactions. For the ease of representation the carbon atoms of the compound are numbered (VIII).



VIII

$|^{1}J(^{119}Sn\ ^{13}C^{1})| = 800.1$ Hz; $|^{1}J(^{117}Sn\ ^{13}C^{1})| = 763.5$ Hz;

$|^{2}J(^{119}Sn^{13}C^{2})| = 27.0$ Hz; $|^{2}J(^{119}Sn^{13}C^{4})| = 93.6$ Hz;

$|^{3}J(^{119}Sn^{13}C^{3})| = 106.8$ Hz ; $|^{3}J(^{119}Sn^{13}C^{O_2})| = 68.7$ Hz;

$|^{4}J\ (^{119}Sn^{13}C^{m_2}| = 34.6$ Hz; $|^{5}J(^{119}Sn^{13}C^{p_2})| = 43.2$ Hz.

Since the long range couplings $^{n}J\ (^{119}Sn^{13}C)$ $(n \geqslant 4)$ become comparatively less important, the values of coupling constants (J values) of ^{119}Sn nucleus with the carbon atoms of the phenyl ring attached to carbonyl carbon atom are not recorded.

The proton decoupled ^{13}C NMR spectrum (Fig. 14) of the $CDCl_3$ solution of the compound (β-styryl carbonyl-α-phenylethyltin trichloride) was taken at 20.15 MHz. From the comparable position of the peaks in the spectrum of this compound with those in the spectrum of β-benzoyl-α-phenylethyltin trichloride following similarities in peak positions are observed, on the basis of which some structural interpretations of the present compound are made.

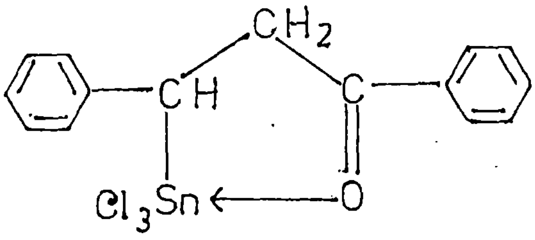
Carbonyl carbon of dibenzylideneacetone compound appears at δ201.99 compared to the compound of benzylideneacetophenone which appears at δ 203.03. The methine and methylene carbons appear at δ 43.66 and 40.74 with the β-benzoyl-α-phenylethyltin trichloride and methine and methylene carbons in the similar compound of dibenzylideneacetone, β-styryl-carbonyl α-phenylethyltin trichloride appear at δ43.39 and δ 42.76 respectively. The aromatic carbons in the said two compounds range δ127.25-137.11 and δ 127.19-137.02. Beside these, two new resolved peaks in the ^{13}C NMR spectrum of dibenzylideneacetone compound appear to which there is no corresponding peaks in the ^{13}C NMR spectrum of similar compound of benzylideneacetophenone. These new peaks are at δ152.08 and δ 121.71. These two peaks are attributed to two olefinic carbons of which olefinic carbon adjacent to carbonyl carbon is suggested to account for the position δ 152.08 and the other (which is adjacent to phenyl ring) for the position δ121.71 in the spectrum.

^{119}Sn NMR spectrum could be recorded for only β-benzoyl-α-phenylethyltin trichloride. The spectrum was recorded at 134.294 MHz with tetramethyltin as standard in a Bruker Spectrospin (360 MHz) NMR Spectrometer at Riga, U.S.S.R. The spectrum of the sample (β-benzoyl-α-phenylethyltin trichloride) was recorded in $CDCl_3$ solution.

The ^{119}Sn peak appears at δ -154.7 (Fig. 8). Appearance of ^{119}Sn peak at this position in the spectrum may indicate a penta coordinated tin atom within the molecule of the compound.

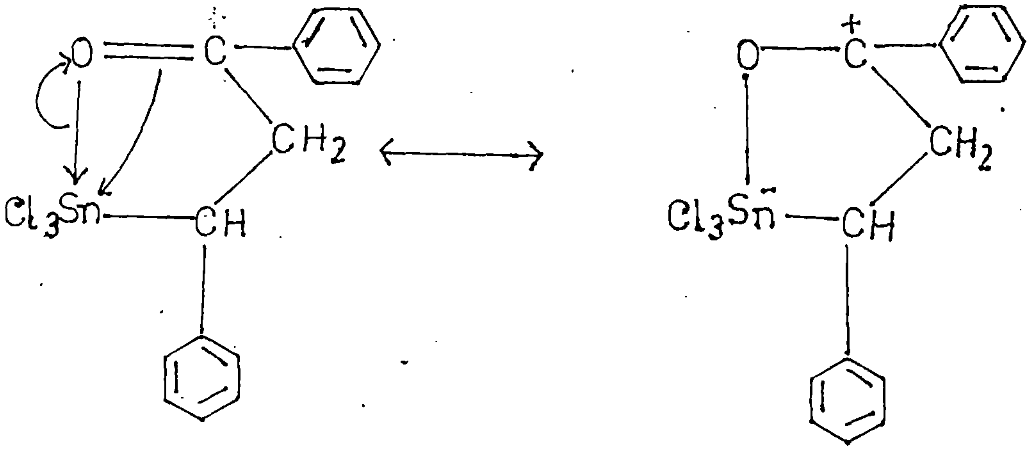
On the basis of the earlier discussions and data, an intramolecular carbonyl coordination to Sn can be suggested for β-benzolyl-α-phenylethyltin trichloride. The IR spectrum gives a strong band at ∼1605 cm^{-1} indicating the coordination of carbonyl group to tin.

The molecular structure of β-benzoyl-α-phenylethyltin trichloride may be suggested as follows (IX).



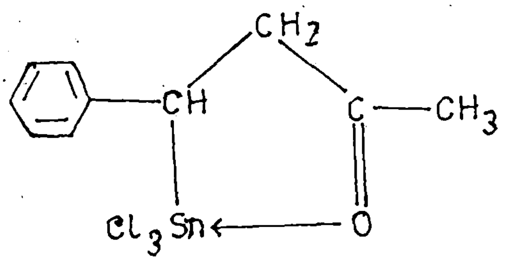
IX

In the molecule of β-benzoyl-α-phenylethyltin trichloride, similar resonating structures may exist as in the case of phenyl esters (Structure III and IV). However, with the present compound, the resonating structures are not exactly similar to those of phenyl esters. The resonance hybrid with the present organotin trihalide can be represented as follows (X).



X

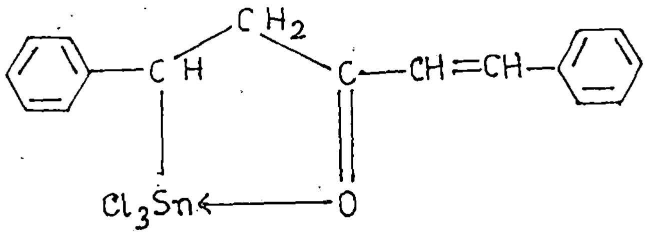
In the similar fashion, the molecular structure of β-acetyl-α-phenylethyltin trichloride may be suggested (XI).



XI

The structure of monomeric organotin trichloride (β-styryl carbonyl-α-phenylethyltin trichloride) derived from dibenzylideneacetone is also possibly similar to structure IX and structure XI having intramolecular carbonyl coordination to Sn atom as indicated by the lower carbonyl absorption frequency than usual expected value in absence of such intramolecular coordination. The presence of tin-chlorine bond is also indicated by ν(Sn-Cl) absorptions at 290 cm^{-1}, 330 cm^{-1} and 390 cm^{-1} in the far infrared spectrum. Moreover ^1H NMR spectrum of the compound indicates the presence of one methine proton, two methylene protons and twelve protons in the aromatic region (possibly ten aromatic protons and two olefinic protons) and thus accounts fifteen protons in total within the molecule. ^{13}C NMR spectrum shows clearly the presence of a carbonyl carbon atom, one methine carbon, one methylene carbon and fourteen carbon atoms in the aromatic region.

Thus considering the data of elemental analysis, and the overall pattern of IR, ^{1}H NMR and ^{13}C NMR spectra, the structure of β-styryl$\overset{\text{Carbonyl}}{\wedge}$-$\alpha$-phenylethyltin trichloride may be reasonably suggested as follows (XII).

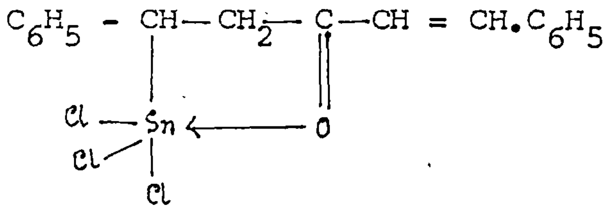


XII

As discussed before the major reaction products obtained from the reaction of Dibenzylidene acetone and $HSnCl_3$ under different conditions were a yellow compound (m.p. 155°) and a red compound (m.p. 160°). From the elemental analyses the empirical formulae $C_{51}H_{41}O_3SnCl$ and $C_{68}H_{54}O_4Sn_2Cl_2$ may be assigned. The yellow compound gave a thiocyanate corresponding to $C_{51}H_{41}O_3SnSCN$ having a melting point 75°C. Moreover, one 1.5 diphenyl carbazonate of yellow compound was isolated (m.p. 120°) corresponding to $C_{51}H_{41}O_3Sn(C_{13}H_{11}ON_4)$. The IR spectra of red, yellow chloride or yellow thiocyanate are closely similar except the thiocyanato derivative, which had a very strong band $\sim$2010 cm^{-1} for -SCN group. The ^{1}H NMR spectra of above mentioned red, yellow chloride and yellow thiocyanate were found to be nearly identical.

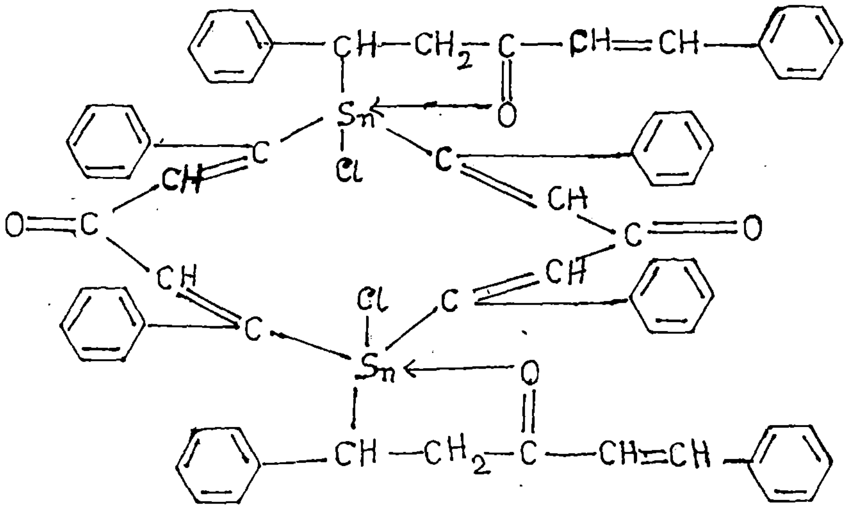
In IR spectra as indicated earlier the presence of olefinic linkage in both red and yellow compounds were obtained. Moreover there might be in molecular coordination of carbonyl group/groups to tin atom(s) for red and yellow chloride and ~~yellow~~ thiocyanate compounds.

So far we are not in a position to assign any definite structures for any of these compounds due to lack of a satisfactory explanation of ^{1}H NMR spectra obtained for these compounds. These compounds may have been formed by the elimination of hydrochloride molecules from the light yellow crystalline compound (m.p. 120°c) of the following type (XIII) ~~are~~ after reaction.



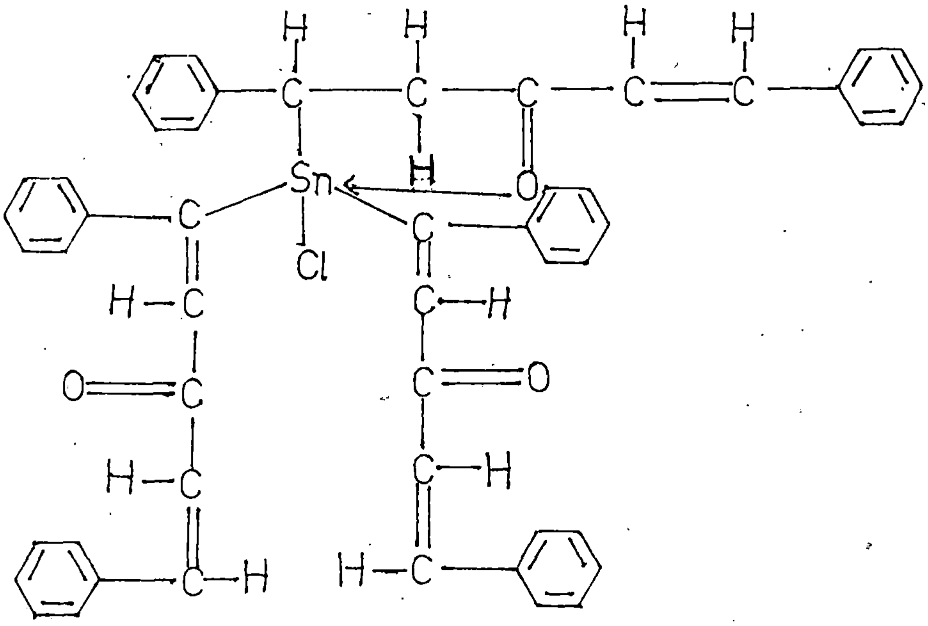
XIII

With more molecules of dibenzylideneacetone, we at best can venture to suggest the structures like the following: (XIV , XV)

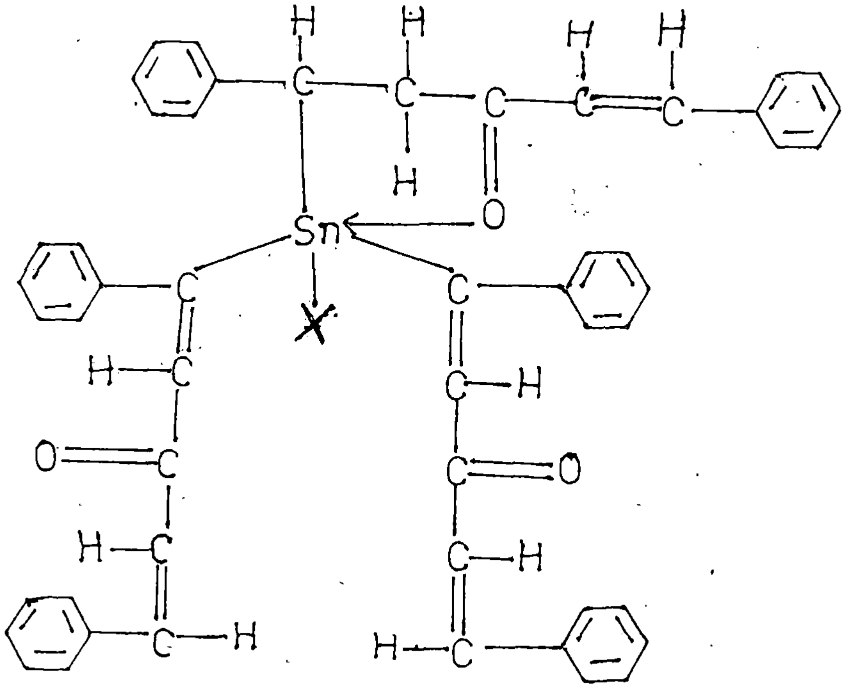


Red compound (m.p. 160°C)

XIV



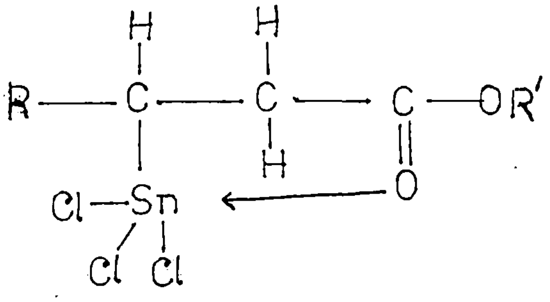
Yellow compound (m.p. 155°c)



X = SCN , HDPC

XV

Hutton et al (265) suggested two mechanisms for the formation of estertin compounds of the type as follows (XVI).



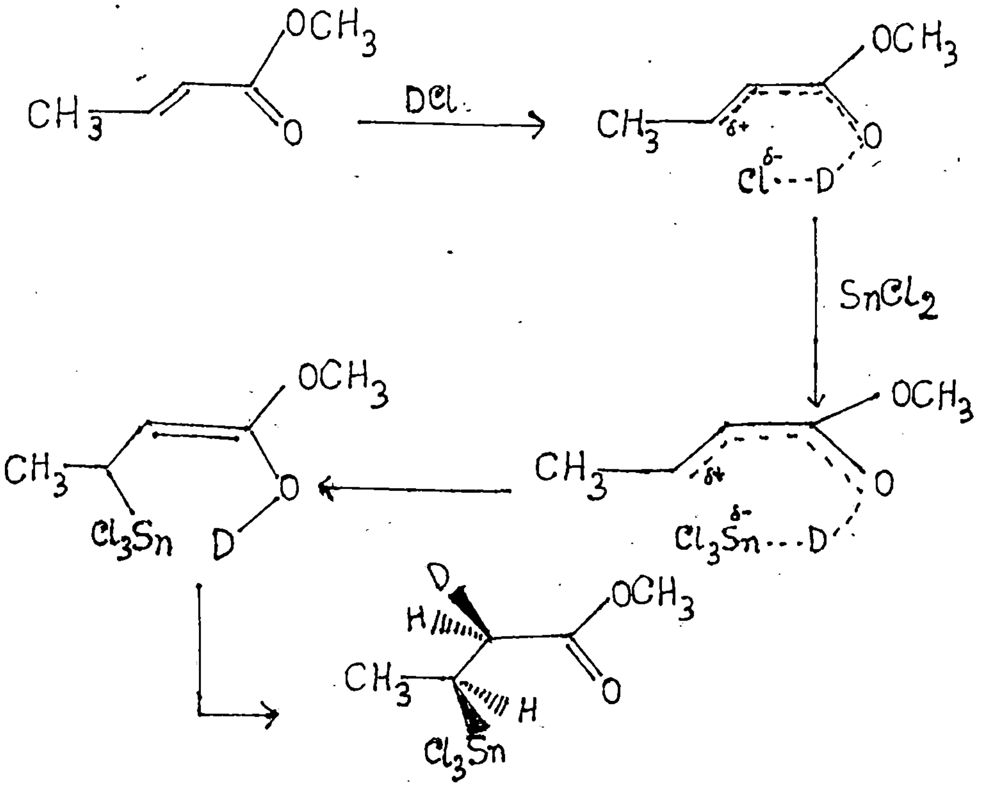
XVI

(R = H or alkyl
R' = alkyl)

(A) The primary step in the chlorostannation reaction in the <u>in situ</u> reaction conditions (in non polar and possibly in all solvents) was monomer solvation of hydrogen chloride. The solvated hydrogen chloride then reacted with stannous chloride to give

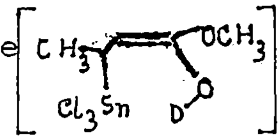
$$\text{monomer} \; : \xrightarrow{\qquad} HSnCl_3. \text{ aggregate}$$

which then collapsed by the attack of Cl_3Sn at the β-carbon atom of the ester group. The complete reaction sequence for $DSnCl_3$ and methyl crotonate was represented as follows.

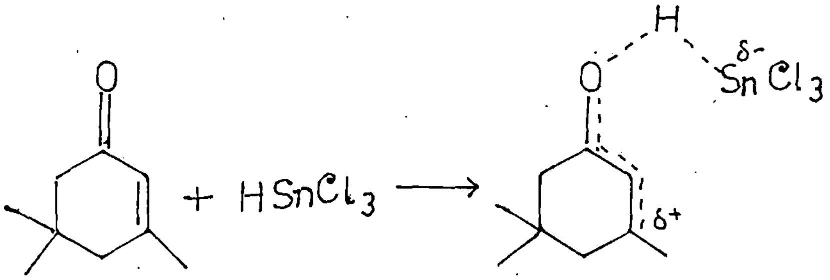


Scheme I

The above mechanism (Scheme I) represented a tin hydride addition to a $\rangle C = C \langle$ double bond with the $\overset{\delta-}{Sn}-\overset{\delta+}{H}$ polarisation of the tin-hydrogen bond. The $HSnCl_3$ provided a unique example of a tin-hydride species reacting in this fashion unlike all the previous tin hydride additions which had been either by free radical or with the $\overset{\delta+}{Sn}\text{-----}\overset{\delta-}{H}$ polarisation of the tin-hydrogen bond.

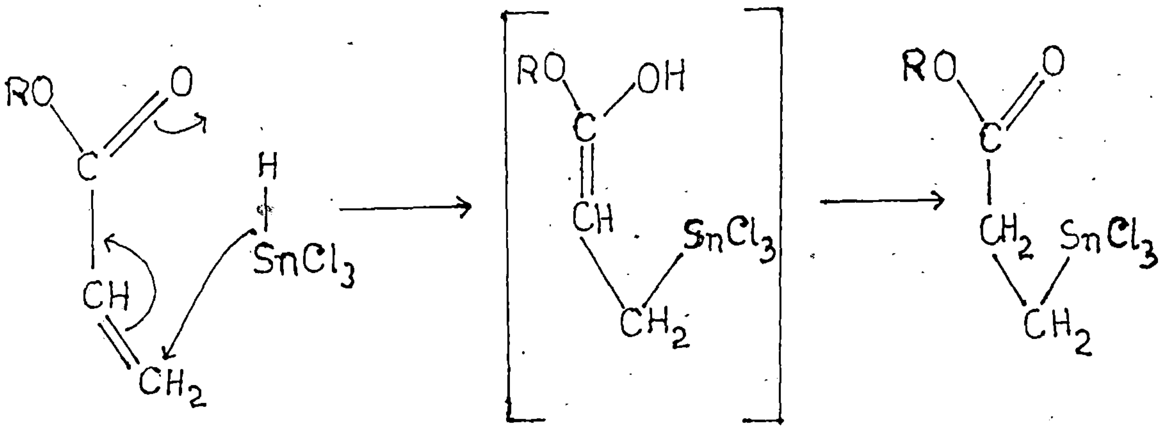
In order to achieve "Cis" addition to the double bond, ketonisation of the enol intermediate  must occur by an intra-rather than an intermolecular process. The latter process would almost certainly result in "trans" addition, by analogy with the addition of DCl to α,β-unsaturated esters, in which the final ketonisation step was catalysed by other DCl molecule. Here in this case, the deuterium transfer might be assisted by a chlorine atom of the $-SnCl_3$ group.

The inactivity of the isophorone was explained on the basis of the unfavourable geometry of the complex, since the $SnCl_3^-$ entity would be located too far from the active site as shown below.



Scheme II

(B) On the other hand a concerted mechanism was also suggested by Hutton et al as an alternative equally probable mechanism.



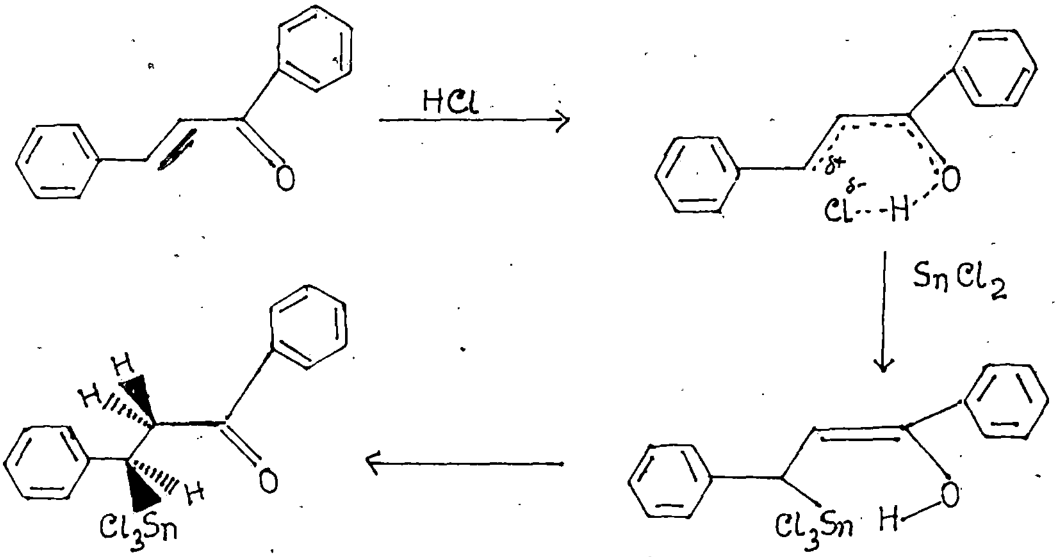
Scheme III

This mechanism also favoured against a simple four-centered mechanism since isophorone with a trans configuration, was found unreactive with regard to this chlorostannation reaction.

In the current investigation the attempt to prepare such substituted tin chlorides, was based on the use of α, β-unsaturated ketones of the form $C_6H_5CH = CHCOR$ (where R stood for $-C_6H_5$, $-CH_3$, $-CH = CHC_6H_5$).

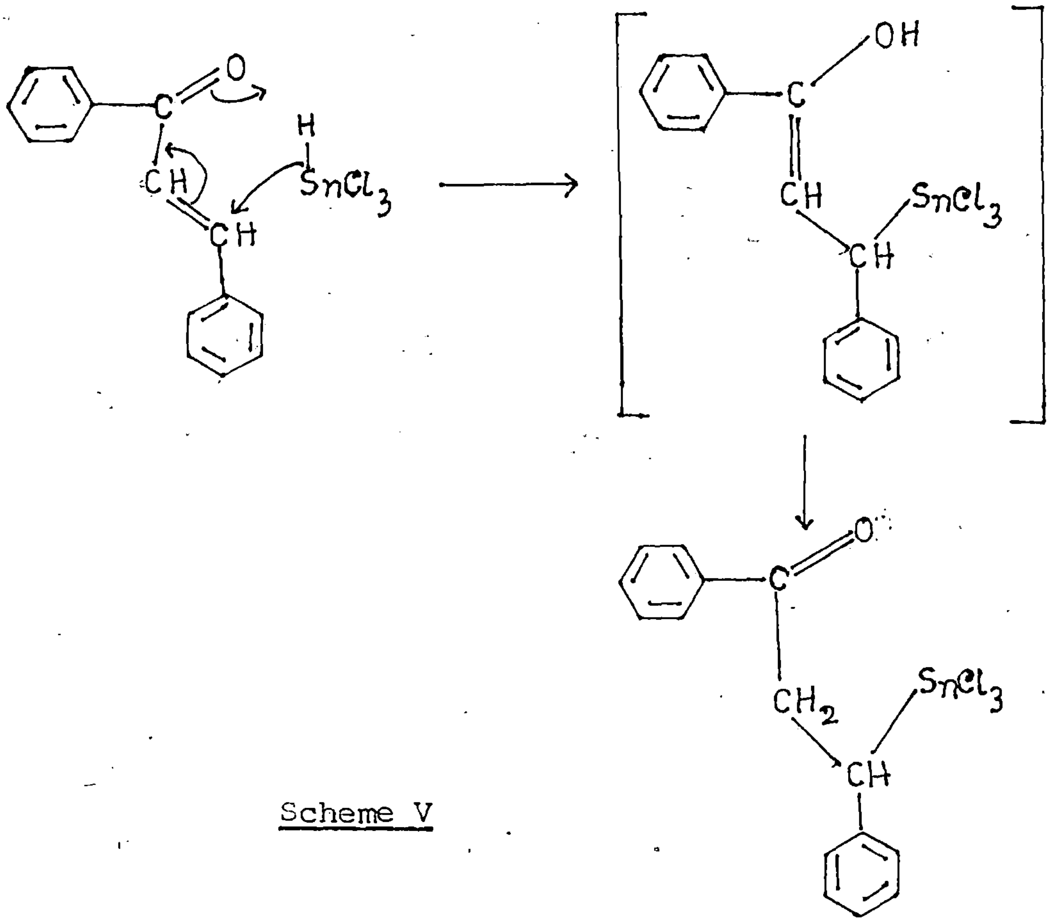
The course of the reaction between benzylideneacetophenone (chalcone), hydrogen chloride and stannous chloride may be explained as follows in the line of Hutton et al's work under the subheadings (C) and (D).

(C)



Scheme IV

(D) A concerted mechanism for the formation of β-benzoyl-α-phenylethyltin trichloride may be also suggested as shown below.

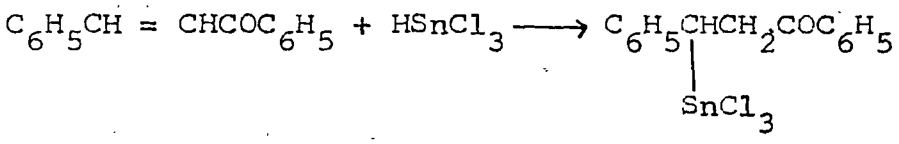


Scheme V

Apparently such a mechanism does not involve any free hydrogen chloride and hence according to this mechanism the reaction should proceed equally well in absence of excess amount of free hydrogen chloride after the formation of trichlorostannane from stannous chloride and hydrogen chloride. Practically the reaction could not be carried out after removing completely the free hydrogen chloride from the reaction mixture, but it was noticed that the course of the reaction and hence the yield of the final product at least remarkably influenced by the amount of free hydrogen chloride in the reaction mixture. Some amount of free hydrogen chloride was found very much essential for the good yield of the final compound. This necessity of excess amount of free hydrogen chloride can be explained by considering the following reaction:

$$\mathrm{HCl} + \mathrm{SnCl_2} \rightleftharpoons \mathrm{HSnCl_3}$$

Excess amount of hydrogen chloride will try always to increase the amount of trichlorostannane and hence increasing one of the reactant of the reaction is likely to increase the final product.

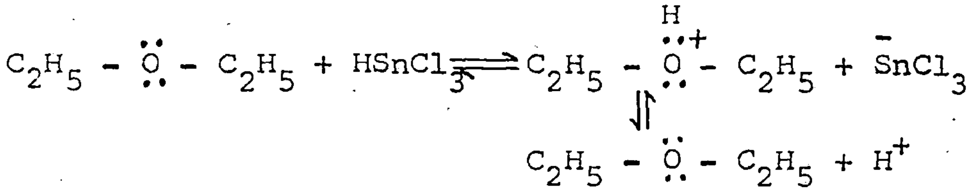


$$\mathrm{C_6H_5CH = CHCOC_6H_5} + \mathrm{HSnCl_3} \longrightarrow \mathrm{C_6H_5\underset{\displaystyle SnCl_3}{\underset{|}{C}}HCH_2COC_6H_5}$$

Beside these two mechanisms, a third ionic mechanism can be put forward to explain the formation of β-benzoyl-α-phenylethyltin trichloride. Though apparently the ionisation of $HSnCl_3$ (formed from the reaction of hydrogen chloride and stannous chloride) as

$$HSnCl_3 \rightleftharpoons H^+ + \bar{S}nCl_3$$

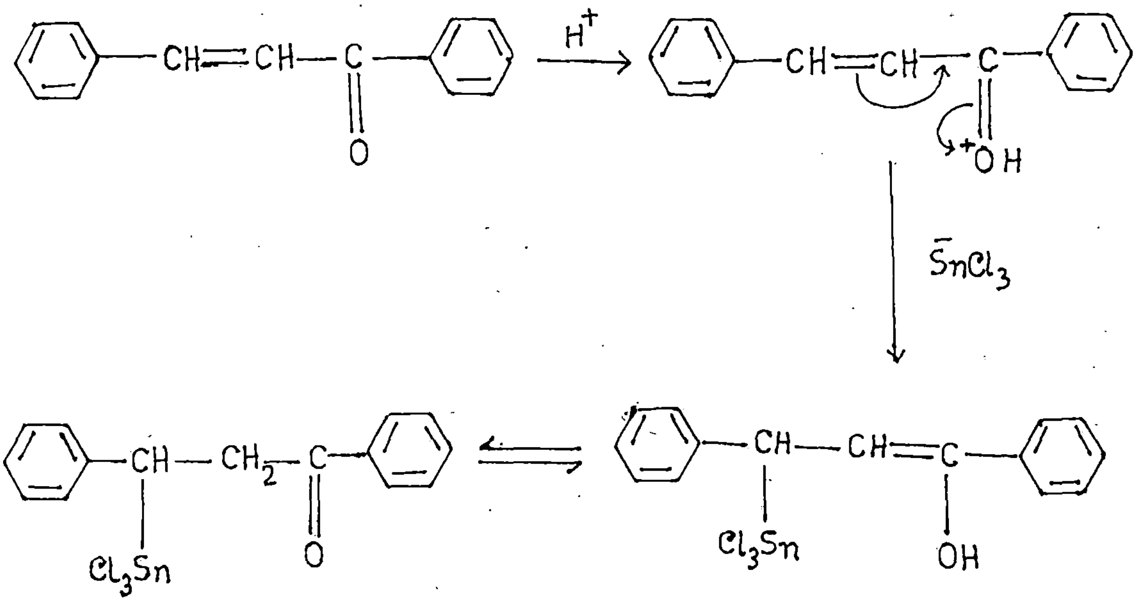
may not be probable in non polar solvent, yet at least a part of $HSnCl_3$ may suffer such ionisation in ether medium, and this is due to presence of lone pair of electrons on oxygen atom. Moreover it was found that the amount of ether in the reaction mixture altered the final yield of the products. In fact it was found that the amount of final product decreased to a remarkable extent with the decrease in amount of solvent, though the reactants still remained dissolved in the medium. Hence the participation of the ether molecule in the reaction mixture may be of significant importance. Probably ether molecule form an equilibrium with the $HSnCl_3$ molecule as follows



$$\begin{array}{l} C_2H_5 - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} - C_2H_5 + HSnCl_3 \rightleftharpoons C_2H_5 - \underset{\cdot\cdot}{\overset{\overset{H}{\cdot\cdot +}}{O}} - C_2H_5 + \bar{S}nCl_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow \\ \qquad\qquad\qquad\qquad\qquad\qquad C_2H_5 - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} - C_2H_5 + H^+ \end{array}$$

Scheme VI

The reaction mechanism for the formation of β-benzoyl-α-phenylethyltin trichloride may be indicated as follows:

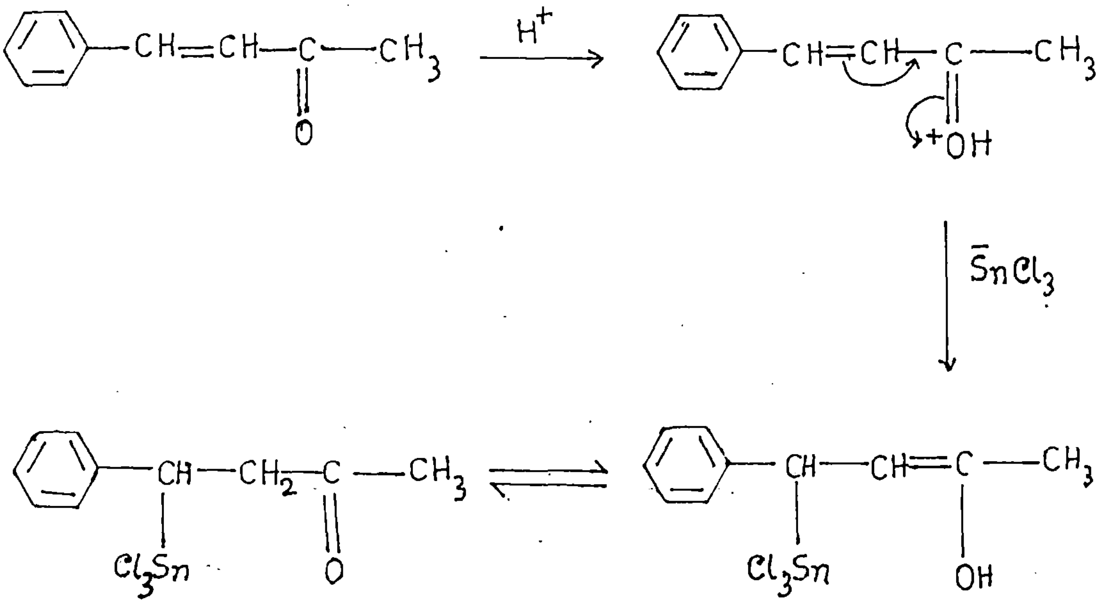


Scheme VII

This mechanism is very much similar to Michael type addition reaction of α,β-unsaturated carbonyl compounds (300).

As this reaction proceeds on, the concentrations of H^+ and $\bar{S}nCl_3$ decrease in the reaction medium due to their consumption and hence as a result further ionisation of $HSnCl_3$ is effected to form the β-benzoyl-α-phenylethyltin trichloride in quantities.

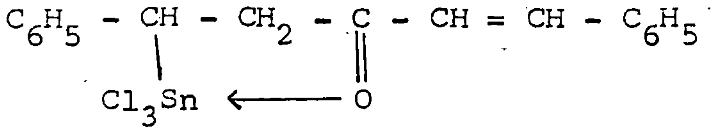
The mechanism of formation of β-acetyl-α-phenylethyltin trichloride may be similar to β-benzoyl-α-phenylethyltin trichloride as per mechanism (C)/(D) though the yield of the compound was extremely poor. However, β-acetyl-α-phenylethyltin trichloride can be obtained in reasonable yield by the reaction of trichlorostannane and benzylideneacetone. As suggested in case of chalcone, the following mechanism may also be suggested in the present case.



Scheme VIII

The reaction between dibenzylideneacetone, stannous chloride and hydrogen chloride yielded complex products. The formation of the complex products may be due to the presence of two olefinic systems in the dibenzylideneacetone molecule. It is most likely that the second trichlorostannane molecule can not add to dibenzylideneacetone molecule because of the absence of a suitable second carbonyl group.

However in one of the attempts, it was found possible to isolate a monomeric compound, e.g.



$$C_6H_5 - \underset{\overset{|}{Cl_3Sn}}{CH} - CH_2 - \underset{\overset{\|}{O}}{C} - CH = CH - C_6H_5$$

which may be formed by a mechanism as suggested in earlier cases. The major products of the reactions were an yellow product of the composition $C_{51}H_{41}O_3SnCl$ and a red product of the composition $C_{68}H_{54}O_4Sn_2Cl_2$. None of these two compounds could be characterised properly. Hence no mechanism for these is suggested here.

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