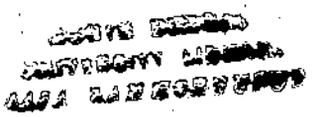
PREPARATION AND REACTIONS OF SOME ORGANOTIN COMPOUNDS : APPLICATIONS TO ORGANIC SYNTHESIS



THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (SCIENCE)
OF
NORTH BENGAL UNIVERSITY

CHAITALI DEB

DEPARTMENT OF CHEMISTRY

NORTH BENGAL UNIVERSITY

1993

Dedicated to

my parents

PREFACE

Investigations comprised this thesis entitled "PREPARATION AND REACTIONS OF SOME ORGANOTIN COMPOUNDS: APPLICATIONS TO ORGANIC SYNTHESIS", were initiated in May, 1989 in the Department of Chemistry, North Bengal University, Darjeeling-734 430, under the supervision of Dr. B. Basu, Lecturer, Department of Chemistry, N.B.U. A brief account of the objective and nature of the work has been presented in the "Summary".

The author has much pleasure in expressing her heartfelt gratitude to Dr. B. Basu, for his constant inspiration, advice and valuable guidance throughout the period of this research work.

The author wishes to express her sincere thanks to Dr. L. R. Subramanian, Universitat Tubingen, Germany and to Mr. T. Hinomoto, Jeol Ltd., Japan for recording ^{1}H- and ^{13}C-NMR spectra of most of the compounds determined here in this thesis. Thanks are due to Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Powai, Bombay for providing ^{119}Sn-NMR; RSIC, IISc., Bangalore for ^{1}H-NMR spectra. Thanks are also due to RSIC, Central Drug Research Institute, Lucknow; Mr. S. K. Sarkar, Mr. P.P.Bhattacharya, Indian Association for the Cultivation of Science, Calcutta for elemental analyses. For routine NMR works, the author

expresses her thanks to Mr.U.K.Saha, DRL, IICT Hyderabad-500 007.

The author is highly indebted to Dr.A.Majumder, Department of Chemistry for recording IR spectra. The author also takes the opportunity to record her sincere gratitude to teachers of this Department and extends her thanks to Dr.A.Adhikari and to all her friends.

The author is grateful to the University of North Bengal for financial assistance. The author also acknowledges her thanks to CSIR, New Delhi for providing a Senior Research Fellowship.

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SUMMARY

Investigations embodied in this thesis entitled 'PREPARATION AND REACTIONS OF SOME ORGANOTIN COMPOUNDS: APPLICATIONS TO ORGANIC SYNTHESIS' are primarily concerned with studies on organotin compounds in the arena of their applications in organic synthesis alongwith their effectiveness as biocides as an extension. The thesis has been divided into two parts: **PART-I** and **PART-II**. PART-I deals with the studies directed towards utilisation of triorganotin carboxylates in organic synthesis and as fungicides and comprises three sections.

SECTION-A : **Preparation and characterisation(spectral and elemental) of a series of α,β-unsaturated(olefinic and acetylenic) triorganostannyl carboxylates and their regioselective reaction with mercury(II) salts.**

In the **Introduction**, the chemistry of organotins has been briefly reviewed with special emphasis to the preparation, structure and reactivity of triorganotin carboxylates.

In order to investigate the relative reactivity of stannyl ester and C—C multiple bond towards mercury(II) salts, a series of α,β-unsaturated(olefinic and acetylenic) tri-n-butyl- and triphenyl- stannyl esters(1-13) have been prepared from their corresponding acids. The structural compositions for these esters have been assigned from their spectral (IR, UV, ^{1}H-, ^{13}C- and ^{119}Sn-NMR) and elemental analyses data. From the IR spectra, the chemical shifts

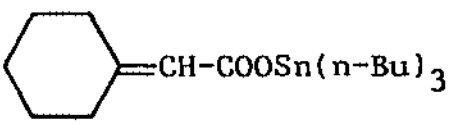
R^1-CH=CH-COOSnR_3

(1); R^1 = H, R = n-Bu (2); R^1 = Me, R = n-Bu

(3); R^1 = Me, R = Ph (4); R^1 = Ph, R = n-Bu

(5); R^1 = p-$NO_2C_6H_4$-, R=n-Bu (6); R^1 = p-$NO_2C_6H_4$-, R = Ph

(7); R^1 = CH_3CH=CH- , R=n-Bu (8); R^1 = CH_3CH=CH- , R = Ph

(9); 

(10); $CH_3C{\equiv}C$-COOSn(n-Bu)$_3$ (11); $CH_3C{\equiv}C$-COOSnPh$_3$

(12); Ph-C$\equiv$C-COOSn(n-Bu)$_3$ (13); Ph-C$\equiv$C-COOSnPh$_3$

values in ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra and the $^nJ(^{119}Sn-^{13}C)$ values (n = 1, 2, 3; the carbon atoms attached to tin), the structural features relating to coordination number of tin atom and the possible geometry of the molecule have been discussed. Although most of these esters have been assigned as possessing tetrahedral arrangement with four-coordinate tin, the triphenyltin-but-2-ynoate(11) has the spectral data compatible with having trans trigonal bipyramidal geometry and five-coordinate tin atom.

Finally, the reaction of these unsaturated stannyl esters with HgX_2 (X = Cl; OAc) has been studied in different solvents ranging from protic/aprotic polar to aprotic nonpolar. From the results, it has been revealed that the unsaturated stannyl esters undergo demetallation reactions resulting in the formation of the corresponding acids and no mercuration of the olefinic/acetylenic multiple bond has been

detected. While the alkyl esters of α,β-unsaturated acids, upon treatment with mercury(II) salts, undergo solvomercuration of C-C multiple bonds, the corresponding stannyl esters, upon similar treatment, react preferentially at the ester function keeping the olefin/acetylene unreacted. The present study, therefore, develops a useful approach for protection of C-C multiple bonds with the preferential and regioselective reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts.

SECTION-B : **Transesterification of alkyl/aryl esters to triorganostannyl esters under neutral condition and their hydrolysis into carboxylic acids using dilute acids at room temperature.**

In this section, development of a new mild and facile method for the hydrolysis of alkyl (primary, tertiary) and aromatic esters through their corresponding triorganostannyl esters has been described. As a prelude to this section, the previous methods for masking and demasking a carboxyl function have been briefly reviewed.

The present method consists of two steps. In the first step, the alkyl/aryl carboxylates are transesterified to the triorganostannyl esters under completely neutral conditions, such as (i) by azeotropic distillation of esters(14) with bis tri-n-butyl- or triphenyl- tin oxide in carbon tetrachloride or toluene or (ii) by heating their neat mixture. The corresponding triorganostannyl carboxylates(15) so formed undergo easy hydrolysis to acids(16) by treatment with dilute acids (5N HCl or glacial AcOH) at room temperature.

$$R^1COOR^2 + (R_3Sn)_2O \longrightarrow R^1\text{-}COOSnR_3 + R_3OR^2$$

(14) (15)

$$\downarrow HX$$

$$R^1\text{-}COOH + R_3SnOX$$

(16)

R^1=alkyl (primary, tertiary), aryl, α,β-unsaturated functions,
R^2=alkyl, phenyl and benzyl groups,
R= n-butyl, phenyl groups,
X=Cl, OAc.

In all the cases, facile formation of stannyl esters and their facile hydrolysis have been observed in overall excellent yields.

SECTION-C : **Toxicity (fungucidal and phyto-) of a series of α,β-unsaturated triorganostannyl carboxylates against some phytopathogenic fungi.**

As a prelude to this section, a concise account of applications and biological effects of triorganotin carboxylates has been outlined. As an extension, the present study comprises the fungicidal- and phyto- toxicity *in vitro* of a series of α,β-unsaturated triorganotin carboxylates against two fungi, *Alterneria solani* and *Piricularia oryzae* and the results have been discussed. The compounds screened here have been prepared in connection with studies described in **SECTION-A.** The ED_{95} values (fungicidal effectiveness) for each compounds at different times (24 hr., 48hr. and 72 hr.) have been obtained from the % of growth inhibition of the fungi at different concentrations. From the results, all the compounds tested are found to be active against *A. solani* and *P. oryzae*. Tri-n-butylstannyl crotonate

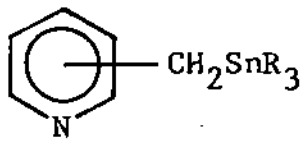
(2) and tri-n-butylstannyl p-nitro cinnamate(5) have exhibited highest fungitoxicity against A. solani. In contrast, triphenylstannyl but-2-ynoate(11) is the most toxic against P. oryzae after 24 hours incubation though its corresponding tri-n-butylstannyl ester(10) is more toxic after 48 hours and 72 hours of incubation. The compound(9), tri-n-butylstannyl cyclohexylidene acetate inhibits the growth of fungi(P. oryzae) within a range of average activity. With regard to phytotoxicity, most of these esters exhibit little or no toxicity against the germination of rice seed.

[The present study (**SECTION-A**) on the selectivity of mercury(II) salts in reactions with α,β-unsaturated(olefinic) stannyl esters has been published in J. **ORGANOMET. CHEM.** and a reprint has been attached. The extension of this work with acetylenic and triphenyltin esters alongwith detail spectral findings has been submitted to J. **ORGANOMET. CHEM.** The works described in **SECTION-B** have been published in **IND. J. CHEM.(B)** and a reprint has been attached. A part of this work has been presented in the **27th. Annual Convention of Chemists (1990).** A part of the experimental findings presented in **SECTION-C** has been submitted to **SYNTH. REACT. INORG. MET. -ORG. CHEM.**]

PART-II : **Preparation of Picolyltrialkylstannanes and on the mechanism involving ambident nucleophilicity of picolyl anion.**

This part of the thesis describes studies with unsymmetrical tetraorganotin compounds of the type R^1SnR_3, where R^1 stands for a C_5H_5N-CH_2 (2-,4-), picolyl group, and R stands for alkyl group. In the **Introduction**, these systems have been compared with allyl-(18) and benzyl-(19) trialkyl-

stannanes and their methods of preparation and reactions are briefly discussed. During the present work, several attempts



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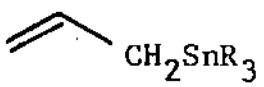

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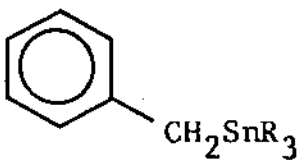


(19)

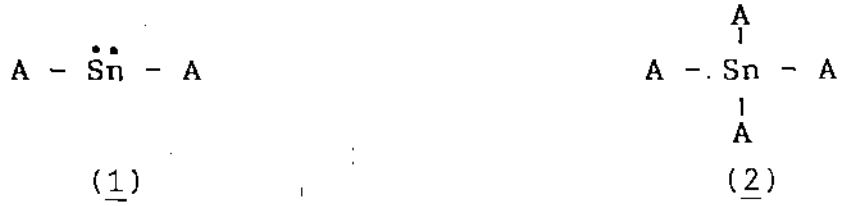
R = Me or R = n-Bu

have been made to prepare the compounds(17) through the generation of picolyl anion. Based on chemical/spectral evidence, involvement of ambident nucleophilicity of the picolyl anion has been suggested. The competition between N-stannylation versus C-stannylation has been considered in terms of role of solvents. A poor yield of the picolyltri-alkyl stannane(17) has been realised during the present study. Further works to improve the yields are being undertaken in this laboratory for substantiating the suggested mechanism and for studying their proposed reactions.

PART -- I SECTION - A

Preparation and characterisation (spectral and elemental) of a series of α,β-unsaturated (olefinic and acetylenic) triorganostannyl carboxylates and their regioselective reaction with mercury(II) salts.

Covalences of two and four would them be expected for these elements in neutral molecules. The two covalent state of tin, i.e., Sn(II) and Sn(IV) may be represented as in structure(1) and (2) respectively, where A is any covalently bound atom or group. These two states are not at all analogous



(1) (2)

chemically. Because of sp^3 hybridisation, the organometallic compounds of Group IV A are relatively stable and possess relatively low chemical reactivity. The marked increase in stability of R_4Sn compounds over R_2Sn types demonstrates the effect of increased hybridisation. Thus, the organic chemistry of tin is essentially restricted to the +4 oxidation state[2].

A bond between M-C, where M is carbon, there is possibility of forming double bond ($p\pi$-$p\pi$). When M substitutes other element of this group such as silicon, germanium, tin or lead, there is enough evidence that the d orbitals of these elements are used for bonding ($d\pi$-$p\pi$). A simple example illustrates this phenomenon. With the four acids of the type p-$R_3M.C_6H_4.COOH$, where M represents carbon, silicon germanium or tin, carbon is the most electronegative of the four elements and should enhance the acid strength to

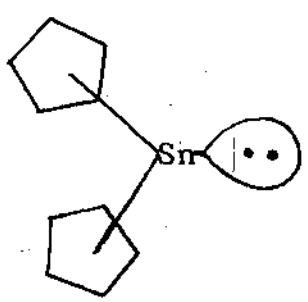
the greatest extent. Actually the carbon compound shows the lowest acid strength, indicating that $d\pi$-$p\pi$ bonding is operative in the other three compound[3].

Because of the considerable difference in electronegativity when M is shifted from carbon to silicon and other elements of this group, the polarity of the M-C bond increases. The increment is more as the M is descended in the group and the bond becomes more sensitive to attack by polar reagents[4]. In other words, the metal—carbon bond strengths decrease and the bond distances increase going down the group, resulting in progressively decreasing thermal stability.

Organotin compounds are defined as those that contain at least one Sn — C bond, the carbon atom being part of an organic group. The first reports of the existence of "Organic bodies of tin", as they were then known, appeared in 1852[5,6]. One was by Carl Lowig[5], the other by Edward Frankland[6]. The search to isolate a series of dialkyltin(R_2Sn) compounds in the second half of the 19th century was destined to be unsuccessful could only be established by experiment, and in the course of experimental studies of this point, there were a number of erroneous reports[7,8]. The isolation of diethyltin and diphenyltin are now known to be polymers of tin(IV), that is, $(Et_2Sn)_n$ and $(Ph_2Sn)_2$[9].

The search for organotin(II) species did, however, lead to an improvement in the indirect method of preparing tetraethyltin. In 1879, Frankland[10] studied the reaction between stannous chloride and diethylzinc, hoping by analogy with results obtained by Buckton[11] simply to displace the chlorides with ethyl groups. The product, however, was not diethyltin, Et_2Sn, but Et_4Sn. As a route to Et_4Sn, this reaction proved superior to Buckton's original method[11], which used $SnCl_4$. This new reaction remained the method of choice for preparing tetraalkyltins until the early years of the 20th century, when Pope and Peachey[12] first made use of the action of a Grignard reagent on stannic chloride. The early history of organotin chemistry has been recently reviewed by N. W. Nicholson[13].

However, organotin(II) species are known either where attached to bulky ligands[9,14] or where the organic substituent is cyclopentadiene[15], e.g., as in (3). Chambers and

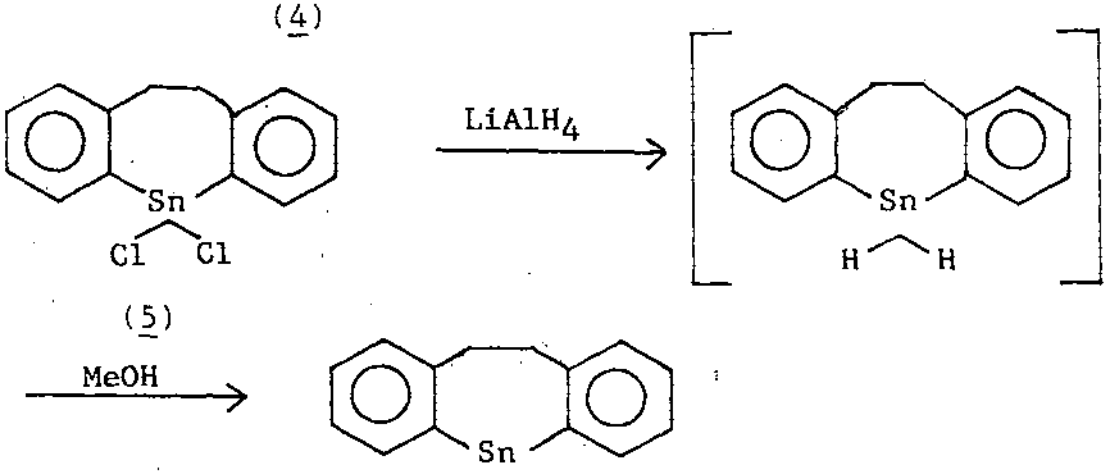


(3)

Scherer[16] prepared diphenyltin in the monomolecular form by warming diphenyltin dihydride(4) at room temperature. This reaction was also used to prepare 10, 11 dihydrodibenzo[b,f] stannoepin(6) from the corresponding tin dichloride(5) by reduction with $LiAlH_4$[17].

$$(C_6H_5)_2SnH_2 \longrightarrow (C_6H_5)_2Sn + H_2$$

(4)



(5)

(6)

The first review of organotin compounds was achieved in 1937 by Drause and Van Grosse[18]. Later the field of organotin chemistry was reviewed by Gilman et al. in 1960[4], with comprehensive tables of the compounds which were then known. In 1967, Richard Weiss[19] published his review of different class of organotin compounds with their properties and references. Afterwords, several monographs by J.J.Zuckerman(Ed)[20], by Newmann[9] and by Poller[21], and a multi-author work edited by A. K Sawyer[22] were published in 1970 and Davies and Smith in 1980[23a] and 1982[23b].

A volume of Houben-Weyl deals particularly with preparative method[24], and recent volumes of Gmelin have covered several classes of organotin derivatives[25]. Structural aspects of this class of compounds have been reviewed[26] and a comprehensive bibliography of X-ray diffraction studies is available from the International Tin Research Institute[27]. The use of organotin compounds in organic synthesis was reviewed by Pereyre in 1976[28].

Because of diverse applications in industry and in basic research, the chemistry of organotin compounds has gained considerable importance[23b,29]. Many interesting, versatile aspects of inorganic and organic tin chemistry have been unravelled by using the powerful array of physical techniques. Investigations can be performed by the general techniques such as UV[21], IR[21,30] ^{1}H-NMR[21,31], ^{13}C-NMR[32], Mass spectroscopy[33] and also by the specialised techniques of ^{119}m Sn Mossbauer Spectroscopy[21,23b] and ^{119}Sn NMR[23b,34] spectrometry. These two techniques provide complementary information on the structure of organotin molecule in the solid state and in solution. During the present work, application of these spectroscopic investigations(except ^{119}mSn Mossbauer Spectroscopy) have been carried out on several α,β -unsaturated tin carboxylates and other organotin compounds.

The ascension of organotin compounds into the domain of synthetic organic chemistry has been dramatically documented over the past decades[35-39]. In their central role

as reagents for the construction of C-C bond, they have demonstrated remarkable virtuasity in the myriad of reaction pathway available. Among these several stand out for their generality and utility such as 1) tin-lithium exchange[40], 2) transtion metal-catalysed coupling[41], and radical reaction[9,42]. Various aspects of electrophilicity of these organotin compounds, their stereoselection with respect to enantio-, diastereo- and regioselectivity have become the important and vital features for using these organotin compounds as reagents in synthetic organic chemistry[39].

While many different organotin derivatives engage in these processes, the allyl and vinyltins enjoy widespread applications due presumably to their enhanced reactivity and latent functionality (Our studies related to benzyltins have been presented in the **Part-II** of this dissertation). However, apart from these unsymmetrical tetraorganotins of the type $R'SnR_3$, organotin esters of organic carboxylic acids comprise one of the most important class of compounds in the ever expanding field of organotin chemistry.

Since a major part of the present work, embodied in **Part-I, (SECTION-A, B & C)**, included studies with several organotin carboxylates, earlier studies on this type of organotin compounds may be briefly reviewed with varying degree of details in respect of preparative modes, Structural chemistry, biological activities and their uses in synthetic

organic chemistry. The biocidal activities are discussed in the **SECTION-C** of this **Part-I** in connection with our studies[43] on fungicidal activities, phytotoxicity of several previously known and newly synthesised α,β - unsaturated tin esters.

I.A-2: Organotin Carboxylates :

The compounds containing -OCOR' groups bonded to tin are defined as organotin esters which may be either monomeric or polymeric and of three general types viz. $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$, where R and R' may be same or different groups. Tin tetracarboxylates, $Sn(OCOR')_4$, are not organotin compounds in the strict sense of the term, that organotin compounds consist of at least one tin-carbon bond.

I.A-2.1: Preparative Methods :

Among the preparative methods of these organotin esters, the most common and important being reaction between organotin oxides (or hydroxides) and organic carboxylic acids or anhydrides (equations 1-3)[44].

$$R_3Sn\text{-}O\text{-}SnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O \quad .....(1)$$

$$R_3Sn\text{-}O\text{-}SnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR' \quad .....(2)$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \quad \ldots\ldots (3)$$

Esterifications are usually achieved by azeotropic dehydration of the reactants in boiling benzene or toluene, using a Dean-Stark seperator. Alternatively, the reactants are heated in neat mixture until the evolution of water ceased, e.g., (equation 4)[45].

$$(Bu_3Sn)_2O + 2\text{-}o\text{-}HO\text{-}C_6H_4\text{-}COOH \xrightarrow[\text{Neat mixture}]{100\text{-}110^\circ C} 2\text{-}o\text{-}OH\text{-}C_6H_4COOSnBu_3 + H_2O \quad \ldots\ldots (4)$$

Another general method involves the reaction of organotin halides with metal salts of carboxylic acids[46] or organotin sulfides with silver salts of carboxylic acids[47] (equation 5).

$$R_{4-n}SnX_n + mM(O_2CR')_q \longrightarrow R_{4-n}Sn(O_2CR')_n + mMX_q \quad \ldots\ldots (5)$$

X = halogen or sulfer, and

M = Na, K, Ag, Pb or Tl.

Organotin carboxylates are prepared by direct reaction of tetraorganotins with metal salts of carboxylic acids[48] as well as the cleavage of one or more organic groups from tetraorganotins by carboxylic acids[48,49] (equation 6).

In the acidolysis reaction (equation 6), vinyl groups are cleaved more readily than saturated alkyl groups, but less readily than phenyl[4], successive groups are lost with increasing difficulty. Tetraallyltin is more reactive than tetravinyltin[50]. Tetramethyltin is found to react with mercury(I) acetate in methanol at room temperature to form trimethyltin acetate (equation 7)[51].

$$R_4Sn + n\ R'COOH \longrightarrow R_{4-n}Sn(OCOR')_n + n\ RH \quad \ldots(6)$$

$$2Me_4Sn + Hg_2(OCOCH_3)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_2H_6 \quad \ldots(7)$$

Another method includes the reaction between organotin hydride and carboxylic acid with evolution of hydrogen, as shown in equations (8, 9)[52].

$$Bu_2SnH_2 + 2\ MeCOOH \xrightarrow[Et_2O]{4.5h} Bu_2Sn(OCOMe)_2 + 2H_2 \quad \ldots(8)$$

$$Ph_3SnH + EtCOOH \xrightarrow[60°C\ /3h]{Et_2O} Ph_3SnOCOEt + H_2 \quad \ldots(9)$$

Muettertin et al.[53] showed that organotin halocarboxylates, $R_2Sn(X)OCOR'$, may be prepared conveniently by heating together, in an inert solvent, equimolar proportion of a dihalide and dicarboxylates (equation 10).

$$Bu_2SnBr_2 + Bu_2Sn(OCOMe)_2 \longrightarrow 2\ Bu_2Sn(Br)OCOMe \quad ....(10)$$

Finally, during the present study, we developed a method by which alkyl or aryl esters (carboxyl group attached to primary or tertiary carbon atom) may be transesterified to triorganotin carboxylates (equation 11)[54].

$$R^1\text{-}COOR^2 + (R_3Sn)_2O \longrightarrow R^1\text{-}COOSnR_3 + R^2OSnR_3 \quad ...(11)$$

The details of this procedure have been described in Part-I, SECTION-B of this dissertation.

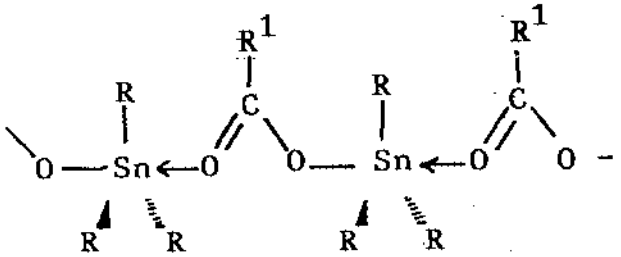
Several other methods are known, but including the methods described in equations (8-10) are not used extensively from preparative point of view.

I.A-2.2: Structure and Reactivity :

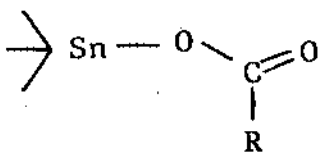
The structure of the organotin carboxylates have been determined by spectroscopy in solution phase as well as in solid phase and by crystallography in solid phase. IR and NMR spectroscopy have been extensively used to investigate structure of organotin esters.

The organotin carboxylates are known to exist in polymeric associated form, as in (7a) in the solid phase. This

chain polymer, involving bridging carboxylate groups and planar or near-planar R_3Sn moieties, has been demonstrated crystallographically for $Me_3SnOCOMe$[55], $Me_3SnOCOCF_3$[55], $Me_3SnOCHO$[56], $Bz_3SnOCOMe$[57] and $(CH_2{=}CH)_3SnOCOCH_3$[58]. Sterically



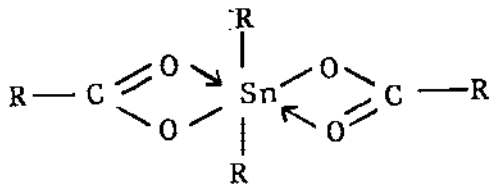
In the solid state (7a)



In dilute solution (7b)

hindered groups, however, prevent this association e.g., Alcock et al.[59] showed that $Cy_3SnOCOMe$ is present as monomer with the tin atom occupying a distorted tetrahedral geometry.

Okawara et al.[60] and several other workers[60c] investigated the structural aspects of triorganotin carboxylates by infrared and far-infrared spectroscopy in the solid state and in solution phase. They came up with the conclusion that on dilution of the associated triorganotin carboxylates in organic solvents usually produces oligomeric and finally monomeric species containing tetrahedral tin atom and free ester carbonyl functionality (7a & 7b)[60,61]. Dialkyltin dicarboxylates were suggested to be monomeric with hexacoordinate tin(8)[62].



(8)

From proton magnetic resonance data on organotin carboxylates, attempts have been made to correlate tin-proton coupling constants with the structures of these compounds and it is now generally accepted that the values of $J(^{119}Sn\text{-}C\text{-}H)$ increase with increasing percent s-character of the Sn-C bond[63]. However, carbon-13 spectroscopy has certain advantages over proton spectroscopy in the elucidation of structure of organotin esters[64]. For example; (i) the differences in the coupling constant $^{1}J(C\text{-}Sn)$ are much greater than those in $^{2}J(H\text{-}Sn)$; (ii) since the carbon of the alkyl or aryl group is directly bonded to tin, the variations in $^{1}J(C\text{-}Sn)$ more accurately reflect rehybridisation at the tin atom than do those in $^{2}J(H\text{-}Sn)$; (iii) for alkyl groups like propyl, butyl etc., it is possible to measure $^{1}J(C\text{-}Sn)$ accurately where $^{2}J(H\text{-}Sn)$ can not be measured under normal conditions; (iv) for such long-chain alkyl groups the identity of the compound and within limits, its purity can be established without doubt.

Of the ten naturally occuring isotopes of tin, only ^{119}Sn(abundance 8.58%), ^{117}Sn(abundance 7.57%) and ^{115}Sn (abundance 0.34%) have a nuclear spin $I=\frac{1}{2}$ and are, therefore,

amenable to study by NMR spectroscopy. In practice, the isotope of choice is usually ^{119}Sn, due to its higher abundance and its greater sensitivity to NMR detection.

Early measurements of ^{119}Sn chemical shifts were carried out by the heteronuclear double resonance technique[65], more recently, the advent of pulsed Fourier Transform (FT) technique enabled high quality ^{119}Sn NMR spectra[34]. The ^{119}Sn chemical shifts values alongwith the $^{n}J(^{119}Sn-^{13}C)$ data have been used to describe the structure of organotin compounds, the coordination number of tin etc. In the recent years, solid phase NMR spectroscopic data have been used to assign structure and coordination number of tin of several organotin esters[66-69].

Since a vast literature on the structure of organotin carboxylates were covered in the review written by Davies et al.[23b] and on ^{119}Sn-NMR spectroscopy by P. J. Smith & A. P. Tupciauskas[34a] and by B. Wrackmeyer[34b], it seemed reasonable to discuss the literature observations (including the recent works) only pertaining to our present work, wherever necessary.

With regard to reactivity of Sn-C bond, the electronegativity of C and Sn are 2.5 and 1.8 (in the Pauling scale) respectively indicating highly covalence in nature. However,

Sn-C bond can readily participate in ionic reactions through polarisation, where the carbon acts as a nucleophile and the tin atom acts as an electrophilic centre. On the other hand, the bonds between tin and heteroatoms (Sn-X, where X=N, O, F, Cl, Br etc.) are thermodynamically quite stable, but are chemically highly labile and readily participate in various substitution reactions. The large size of tin atom (covalent radius 1.4A°), the greater polarisability of the Sn-X bond relative to that of C-X bond and the possible participation of the tin 3d orbitals appear to be the major factors responsible for the greater ease of substitution reaction at tin than at carbon[35]. In view of this, several workers have utilised organotin compounds in modern organic synthesis. The synthetic efforts directed towards the utilisation of organotin carboxylates are presented briefly in the next few pages.

The thermal decarboxylation of triorganotin esters[30] was utilised in the preparation of unsymmetrical tetraorganotin compounds of the type $R'SnR_3$, where the R—Sn bond formation was taken place. Trialkyltin formate, however, led to the formation of trialkyltin hydride with the formation of Sn-H bond (equation 12)[71].

$$H\text{-}COOSnR_3 \xrightarrow[(R = Pr,\ Bu)]{100\text{-}170^\circ C} R_3Sn\text{-}H + CO_2 \quad \ldots\ldots \quad (12)$$

$$R_3SnO\text{-}CO\text{-}C{\equiv}C\text{-}CO\text{-}O\text{-}SnR_3 \xrightarrow[(R=Et,\ Pr,\ Bu)]{\sim 160^\circ C} R_3Sn\text{-}C{\equiv}C\text{-}SnR_3 + 2CO_2 \quad [72]$$

$$Ph\text{-}C{\equiv}C\text{-}CO\text{-}OSnBu_3 \xrightarrow{\sim 60^\circ C} Ph\text{-}C{\equiv}C\text{-}SnBu_3 \quad [71]$$

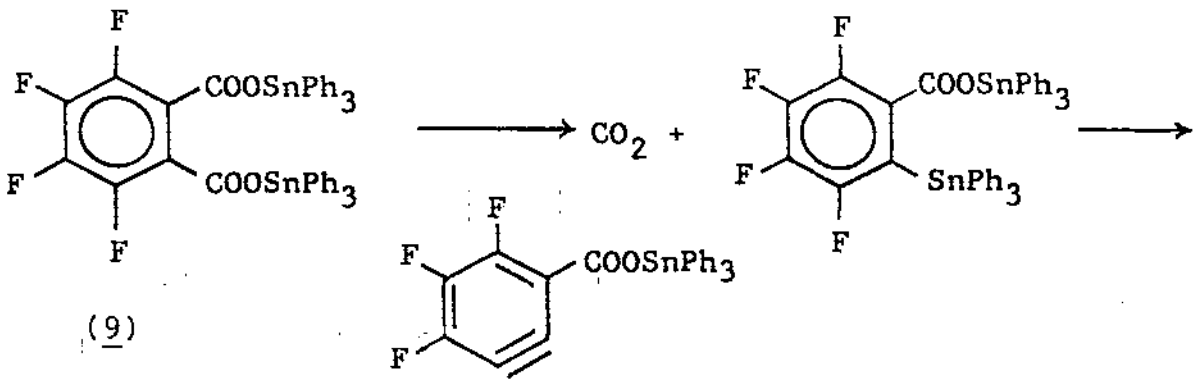
van der Kerk and Luijten[73] showed that organotin compounds containing a cyanomethyl group attached to the tin atom could be prepared by heating trialkyltin or triphenyltin cyanoacetates. e.g.,

$$NC\text{-}CH_2\text{-}CO_2SnPh_3 \xrightarrow[\text{vacuum}]{140^\circ C/\text{under}} \underset{49\%}{NC\text{-}CH_2\text{-}SnPh_3}$$

In 1977, Deacon and Farquharson[74] prepared several polyfluorophenyl stannanes utilising this thermal decarboxylation in boiling pyridine. They also reported that thermal decomposi-

$$RCOOSnPh_3 \xrightarrow{Py/\text{boiling}} R\text{-}SnPh_3 + CO_2$$
$$(R = C_6F_5,\ p\text{-}MeO.C_6F_4,\ p\text{-}EtOC_6F_4 \text{ or } o\text{-}HC_6F_4)$$

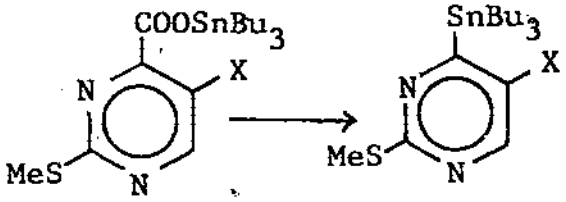
tion of bis(triphenyltin) tetrafluorophthalate(9) gave an insoluble high melting solid, identified as Ph_3SnF by IR spectroscopy[75]. They proposed a possible reaction path comprising hemidecarboxylation[76] followed by elimination of the fluorine ortho to the bulky triphenyltin substituent[77]. However, the aryne(10) was not isolated or characterised[74].



(9)

(10)

Recently, K. Undheim and his collaborators[78] reported that the decarboxylation can be catalysed by Pd(II) complex and thereby getting better yield, e.g., thermal decarboxylation of the 2-methylthio derivatives(11) and (12) in refluxing anisole gave the 4-stannylated products in only 30-40% yield. Free-radical conditions, AIBN and illumination did not significantly affect the yield. Metal catalysis did influence the reaction; Pd(II) complexes were best. Use of bis (acetonitrile) and bis(triphenylphosphine) palladium(II) dichloride increased the yield of 4-stannylated product up to 70% after refluxing in anisole for 4-6 hours.



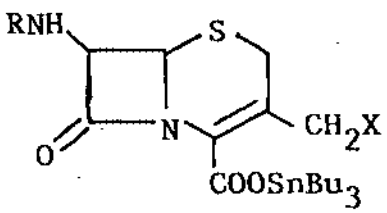
(11) X = Cl

(12) X = Br

Reaction condition	Yield
(i) 190-225°C, neat at 10mm Hg/3hr.	30-40%
(ii) $(MeCN)_2PdCl_2$/ PhOMe/ 4-6hr.	70%

Tris(triphenylphosphine) rhodium(I) chloride, however, which is a decarbonylation catalyst, had only a slight effect on the decarboxylation reaction ; yield 50%.

As a masking group of organic carboxyl function, triorganostannyl(-SnR_3) moiety has certain advantages over alkyl group (discussed in SECTION-B, p.106). Conversion of 7-amino cephalosphoranic acids to their tributylstannyl esters(13)., by treatment with bis(tributyltin) oxide in refluxing benzene increased the solubility of these acids in the reaction medium, and at the end of a reaction sequence involving the ester(13), the free acid was reprecipitated by hydrolysis.

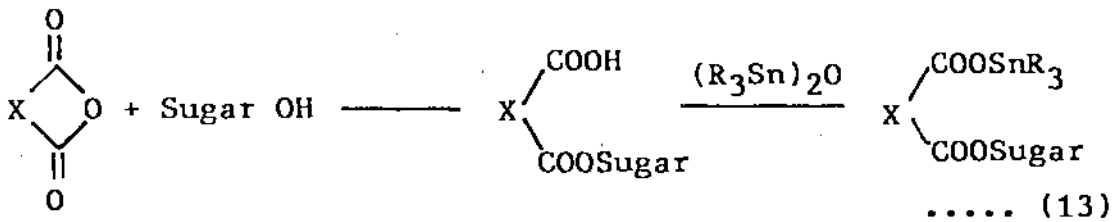


R = R^1CO or H

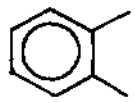
X = $MeCO_2$, N_3 or H

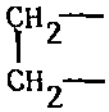
(13)

In a recent study, Poller et al.[79] reported that direct phthalation and succinylation of sugars gave mono esters (14, 15) which were converted to stannyl sugar esters (16, 17) having enhanced biocidal properties (equation 13).

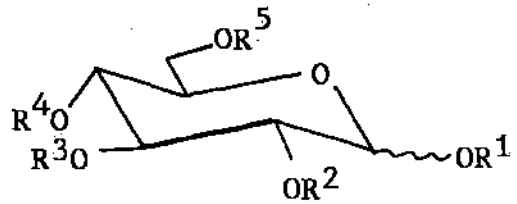


..... (13)

X =  (14), Monoester (16), Diester

X =  (15), Monoester (17), Diester

In compounds (18-22), they demonstrated that a tributyltin function can have a dual role, first to activate sugar hydroxyl groups towards phthalation and second to confer high biocidal activity on the product.



(18) $R^1 = R^4 = R^5 = Bu_3Sn$, $R^2 = R^3 = H$;

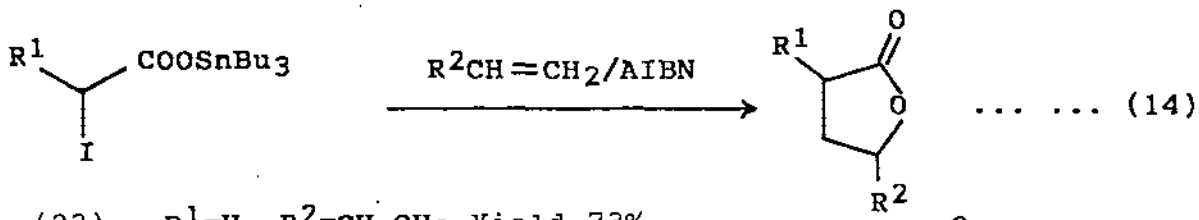
(19) $R^1 = R^5 = O\text{-}COC_6H_4COOSnBu_3$, $R^2 = R^3 = R^4 = H$;

(20) $R^1 = R^5 = O\text{-}COC_6H_4COOMe$, $R^2 = R^3 = R^4 = Ac$;

(21) $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = O\text{-}COC_6H_4COOSnBu_3$

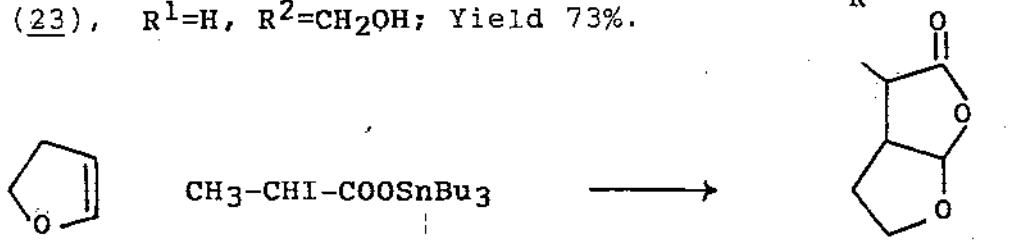
(22) $R^1 = R^2 = R^3 = R^4 = Ac$, $R^5 = O\text{-}COC_6H_4COOMe$;

Lactones are important functionality incorporated in many natural products. Electron-rich alkenes are found to react with α-iodo triorganotin esters in the presence of radical initiator to produce γ-lactone as depicted in equation (14). AIBN was found to be more effective and convenient than any other initiation procedure[80].



... ... (14)

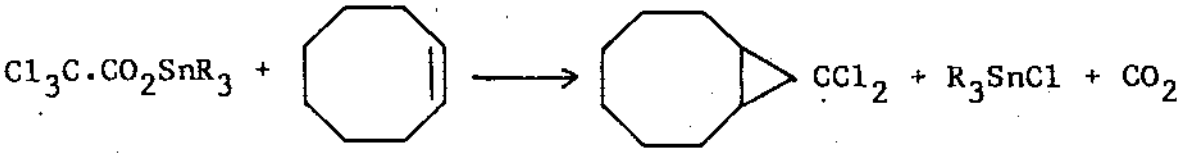
(23), R^1=H, R^2=CH_2OH; Yield 73%.



(72%) (24)

According to authors, the process probably involved first the generation of a radical which then added to the alkene before cyclisation, with concomitant elimination of the tributylstannyl radical. Regardless of the mechanism, this reaction proved to be of high synthetic value. α-Bromo esters, however, gave lower yield of the lactone.

The organotin esters of haloacetic acid are known to produce carbenes. Seyferth and his associates[81] observed that organotin esters of trichloroacetic acid, when heated, were able to transfer dichloro carbene being reacted with unsaturated substrates (equation 15).



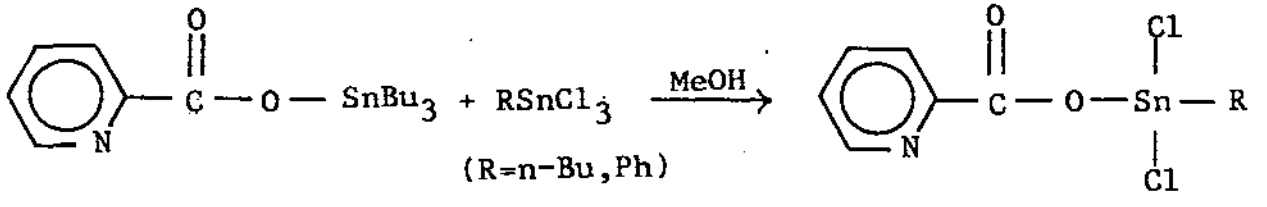
... ... (15)

Although it was not clear, the reaction might involve either R_3SnCl_3 as intermediate or decarboxylation and carbene transfer simultaneously in a concerted manner.

Mono-[82], di-[60c] and tri-[83] organotin carboxylates are known to undergo exchange reactions with other organotin compounds to yield mixed carboxylates derivatives (equations 16, 17).

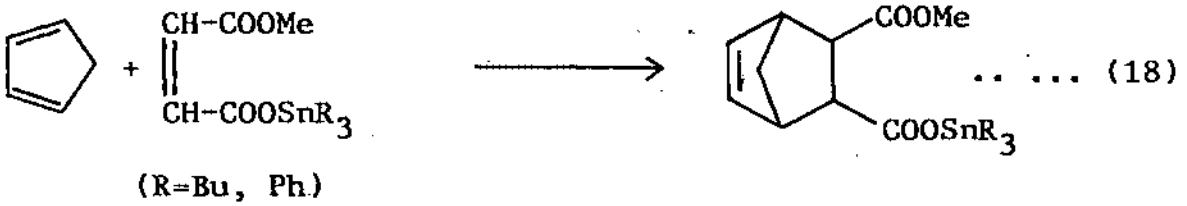
$$R_2Sn(OCOR^1)_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR^1)X \quad \ldots\ldots (16)$$

(X=halogen, OR, H etc.)

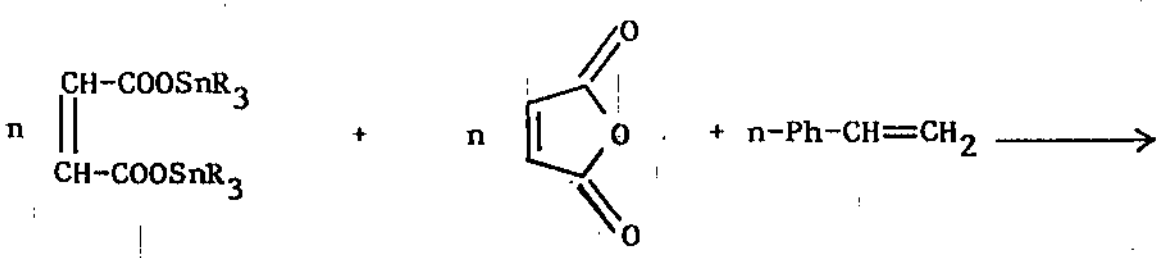


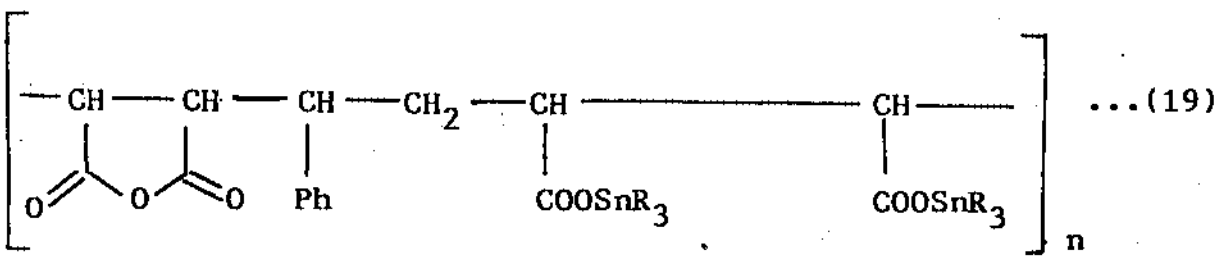
+ Bu_3SnCl ... .. (17)

Poller et al.[84] showed that the unsaturated organotin esters are capable of participating in Diels-Alder reaction as dienophile. For example, organotin alkyl maleates reacted with cyclopentadiene (equation 18). In some cases the tin esters were copolymerised to form polymers with pendant trialkylstannyl groups (equation 19).[85]



.. ... (18)





...(19)

The polymerisation reactions were achieved by the use of heat or free radical initiator and the resulting organotin polymers (where R=Bu or Ph) have important commercial outlets

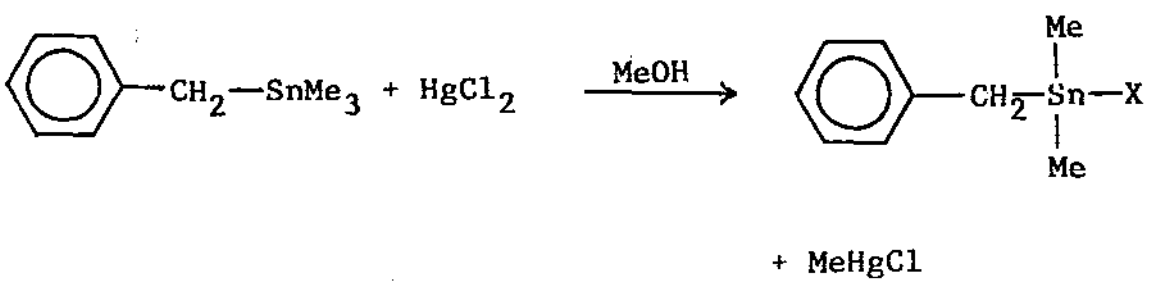
in biocidal paints[86] for protecting ship's hulls. Recently, Babu et al.[87] described the copolymerisation of functional and alkyl methacrylates with tributyltin methacrylates and showed that the presence of functional units in the copolymers can be utilised to selectively cross-link the polymers so that the rate of release of tin moiety can be controlled which is believed to have played a role in biocidic properties.

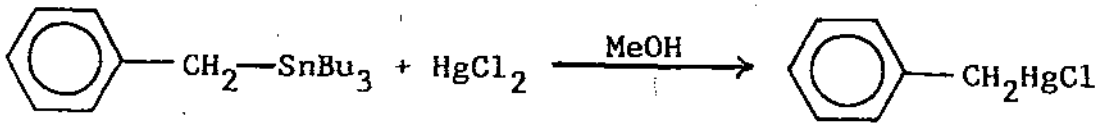
I.A-3: Present work: Background, Objective, Results and discussion

From the synthetic efforts directed towards the utilisation of organotin carboxylates delineated in the preceding pages, it is evident that apart from the broad spectrum of industrial applications of organotin esters[20,23b,29], such as, organo chemicals (fungicidal, antifeedants), antifouling biocides (in plants), disinfectants, PVC stabiliser, homogenous catalysts, anthelmintics etc., there are potentialities remain in the use of them in synthetic organic chemistry. The application of organotin carboxylates in modern organic synthesis continues to grow at an impressive rate because the tin esters are easily accessible in pure form, fairly stable, storable without special caution and they exhibit wide range of reactivity. Nevertheless, organotin carboxylates, in particular the triorganotin carboxylates are hydrolytically more

stable than triorganosilyl esters[35].

The action of electrophiles on the alkyltin compounds was studied in some detail. The relative reactivity of simple alkyl or aryl tins towards electrophilic reagents, like iodine, bromine and mercury(II) salts, was ascertained in the studies of Abraham et al.[88-90] and of several other workers[91-93]. In 1980, Abraham and his coworker[88] reported the sequence of reactivity of R-Sn bond in $R\text{-}SnR_3$ towards mercury(II) salts in methanol: Ph(1.4×10^5) > Me(430) > $PhCH_2$(11) > Et(1) > n-Pr(0.19) > n-Bu(0.17). The reactivity of benzyl group was found to be ten times more than that of the higher n-alkyl groups. In contrast, the methyl group was observed to be substituted from tin atom ca. forty times as rapidly as the benzyl group. Therefore, it was concluded that for benzyltrimethyltin, the methyl group should preferentially be removed at ca. one hundred twenty times (taking into account a statistical factor) faster the rate of benzyl group.





+ Bu_3SnCl

We were interested to compare this action of electrophilic reagent, mercury(II) salts on triorganotin ester, $R'SnR_3$, where the tin atom is bonded to hetero atom ($-O-\overset{\overset{O}{\|}}{C}-R''=R'$). In this area, Roy and Ghosh[94,95] from this department carried out a search during 1977-1978. They reported that triorganotin carboxylates upon treatment with mercury(II) salts resulted in the formation of polymeric tin-containing products alongwith the formation of corresponding acids, alkyltin halides, organomercuric halides etc. They described[95] this reaction as demetallation reaction and proposed the probable pathways, based on chemical evidence.

A)

1. $nR'COOSnR_3 + nHgX_2 \longrightarrow nR'COOSnR_2X + nRHgX$
2. $nR'COOSnR_2X + nR'COOSnR_3 \longrightarrow n(R'COO)_2SnR_2 + nR_3SnX$
3. $n(R'COO)_2SnR_2 + nHgX_2 \longrightarrow n(R'COO)_2SnRX + nRHgX$
4. $n(R'COO)_2SnRX + 2nHOH \longrightarrow [R'COOSnR(OH)_2] + nHX + nR'COOH$

$$R'COOSnR_3 + HgX_2 + H_2O \longrightarrow \frac{1}{2n}[R'COOSnR(OH)_2]_n + \tfrac{1}{2}R_3SnX + RHgX + \tfrac{1}{2}HX + \tfrac{1}{2}R'COOH$$

(Where (i) R=Ph ; R'=H ; X=Cl, (ii) R=Ph ; R'=H, CH_3, CH_2CH_3 ; X=Br, I and (iii) R=Pr, Bu ; R'=CH_3 ; X=Cl).

However, when R=Ph ; R'=CH_3, CH_2CH_3 and X=Cl, the reactions take the following course after the 3rd step of the above sequence (A):

B)

4. $n(R'COO)_2SnRX + nR'COOSnR_3 \longrightarrow n(R'COO)_3SnR + nR_3SnX$
5. $n(R'COO)_3SnR + nHgX_2 \longrightarrow n(R'COO)_3SnX + nRHgX$
6. $n(R'COO)_3Snx + 4nHOH \longrightarrow [Sn(OH)_4]_n + nHX + 3nR'COOH$

The overall reaction, therefore, is

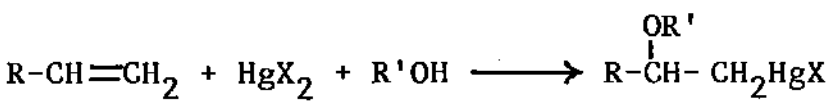
$$R'COOSnR_3 + HgX_2 + \frac{4}{3}H_2O \longrightarrow \frac{1}{3n}[Sn(OH)_4]_n + \frac{2}{3}R_3SnX + RHgX + \frac{1}{3}HX + R'COOH$$

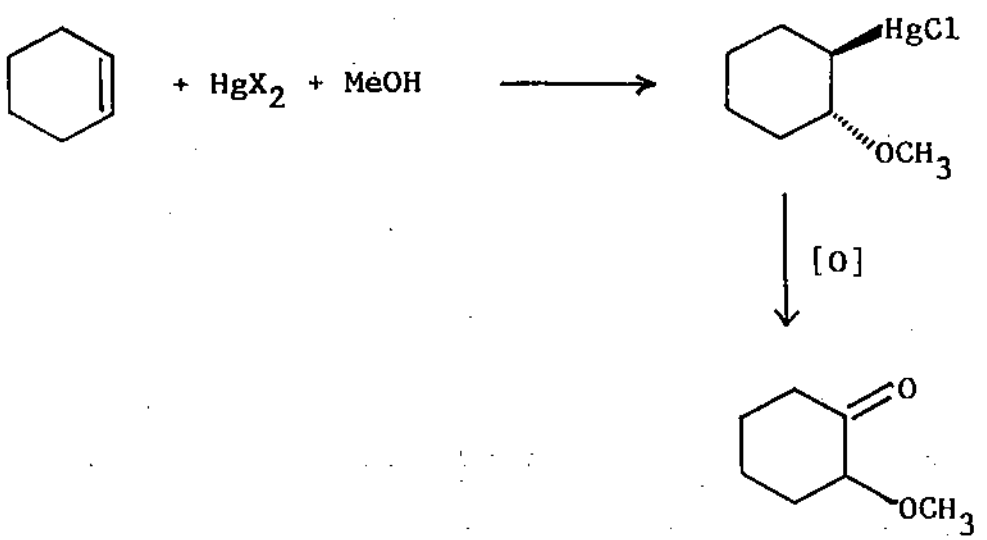
Roy and Ghosh[95] reasoned that the preference for the hydrolysis of substituted organotin esters(4th step in A) or substituted tin ester(6th step in B) could be attributed to the difference in acid strength of the carboxylic acids of the corresponding organotin carboxylates. Thus the more acidic formic acid ester underwent ready hydrolysis after the 3rd step(A) producing the tin polymer. On the other hand, triphenyltin acetate and propionate reacted with mercury(II) chloride to form the intermediates $(R'COO)_2SnPhCl$ [R'=CH_3, Et] that preceded the hydrolysis and underwent further

substitution to form the acid finally in the 6th step(B).

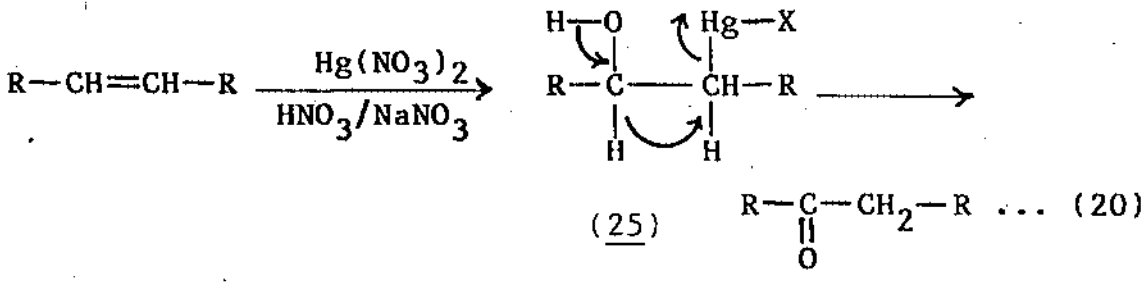
At this point, it occurred to us that the reaction of an unsaturated tin carboxylates with mercury(II) salts could be interesting since the unsaturated function is also capable of reacting with mercuric salts. There might be a competition between the unsaturation and tin ester function present in the same molecule to react with mercuric salts.

The reaction of an alkene with mercury(II) salt in presence of a solvent is commonly known as solvomercuration[96]. The resulting organomercurials have found many applications in organic synthesis[97,98]. For exmaple ;





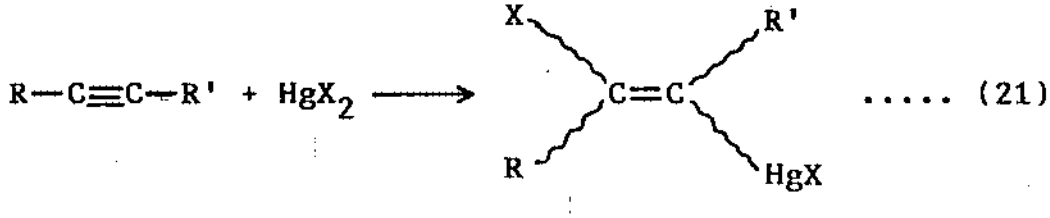
Sometimes solvomercuration of an alkene resulted in the formation of β-hydroxymercurial(25) which could be involved in solvolytic rearrangement producing ketones[99] (equation 20).



(25) $R-\overset{\overset{O}{\|}}{C}-CH_2-R$ ... (20)

In neutral or acidic media, terminal and internal alkynes often added to mercury salts to afford vinyl mercurials (equation 21).

Alkynes reported to add mercuric halides include acetylene[100], propyne[101], cyclooctyne[102], vinyl acetylene[101,103], alkynyl ethers[104], propergylic alcohols[105,106] and halides[105,107]. Mercuric acetate[108] and



..... (21)

X=F, Cl, OAc, SCN

thiocyanide[109] also added to a variety of internal alkyl or aryl acetylenes to generate vinyl mercurials. Several α,β -unsaturated ketones[110], acids[111,112] and esters[111,113,114] are known to undergo mercuration with Hg(II) salts. As for example, solvomercuration of α,β -unsaturated alkyl ester was utilised in the preparation of dl-serine[115].

$$CH_2{=}CHCO_2CH_3 \xrightarrow[CH_3OH]{Hg(OAc)_2} CH_3OCH_2\overset{CH}{\underset{}{}}(HgOAc)CO_2CH_3 \xrightarrow{KBr}$$

$$CH_3OCH_2CH(HgBr)CO_2CH_3 \xrightarrow{Br_2} CH_3OCH_2CHBrCO_2CH_3 \xrightarrow[H_2SO_4]{NaOH}$$

$$CH_3OCH_2CHBrCO_2H \xrightarrow{NH_3} CH_3OCH_2CH(NH_2)CO_2H \xrightarrow{HBr}$$

$$HOCH_2CH(NH_3Br)CO_2H \xrightarrow{NH_3} HOCH_2CH(NH_2)CO_2H$$

α,β -unsaturated acetylenic ester also undergoes solvomercuration, the organomercurial being treated with bromine to afford α,α-dibromo-β-keto ester[116].

$$R-C\equiv C-COOR' \xrightarrow[ii)\ Br_2]{i)\ Hg(OAc)_2} R-\overset{O}{\overset{\|}{C}}-\overset{Br}{\underset{Br}{\overset{|}{\underset{|}{C}}}}-COOR'$$

Recently, R. C. Larock had reviewed[98] in detail this mercuration reaction to prepare organomercurials and their uses in organic synthesis.

It, therefore, seemed appropriate to investigate the reaction of α,β-unsaturated stannyl esters with various mercuric salts with a view to figure out the nature of reactivity of both of these two functions (unsaturation and tin carboxylate group) towards mercury(II) salts.

I.A-3.1: Preparation and characterisation of α,β-unsaturated triorganostannyl carboxylates and their reactivity towards Hg(II) salts

The present study dealt with the preparation, characterisation(by spectroscopy, elemental analysis) of a series of unsaturated (both olefinic and acetylenic) tri-n-butyltin carboxylates and triphenyltin carboxylates and their reaction behaviour towards mercury(II) salts (HgX_2 ; X=Cl, OAc) under different reaction conditions.

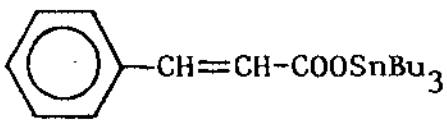
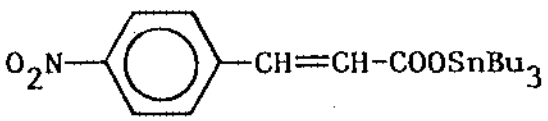
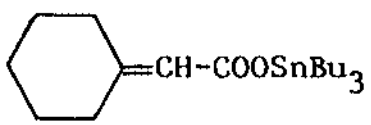
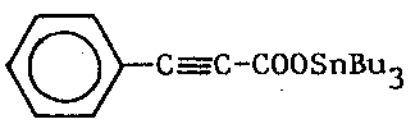
The unsaturated tin carboxylates(26-30 & 32, 33), (TABLE-I) were prepared in the usual procedure[21] from their corresponding acids with bis tri-n-butyltin oxide in refluxing benzene using a Dean-Stark water seperator. The cyclohexylidene acetic acid, however, afforded the corresponding tri-n-butyltin ester(31) while mixing the reagents at room temperature. Similarly, the triphenyltin carboxylates

(34-38) were prepared in the same procedure by using bis(triphenyltin) oxide. The esters were purified either by column chromatography or by crystallisation directly and obtained in good to excellent yield (see Experimental). They were characterised by spectral and elemental analyses data.

Infrared spectral data for organotin carboxylates are useful in comparing solid and solution state structures. The carbonyl group stretching frequency in the series of alkyl ester derivatives generally shifts to higher values with respect to free carboxylic acid carbonyl group. A lowering of ν(CO) would be expected if the carbonyl oxygen is involved in coordination. The influence of conjugated unsaturation would be effective equally both in non-coordinated or coordinated carbonyl function. Moreover, the asymmetric carboxyl stretch, $\nu_{asym}(CO_2)$ is most sensitive to structural changes in the carboxylate group coordination[117] and in addition the $\nu_{sym}(CO_2)$ frequencies are also considered.

The detailed infrared spectral studies of these organotin carboxylates(26-38) were not carried out since the present investigation was mainly aimed to study their nature of reaction toward electrophilic reagents, such as mercury(II) salts. However, the IR spectra of these tin carboxylates(26-38) were recroded in nujol and important observed frequencies were given in TABLE-I.

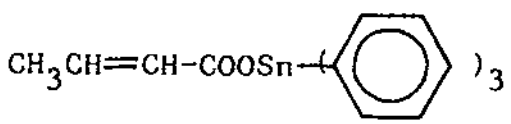
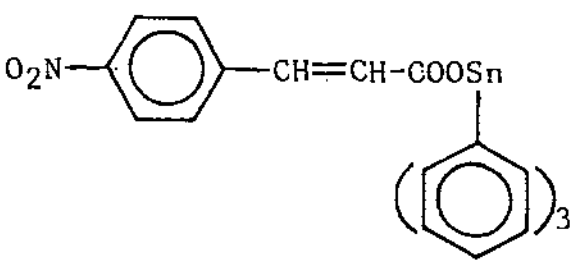
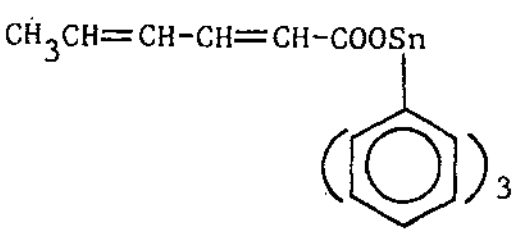
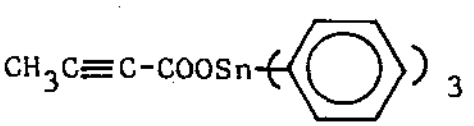
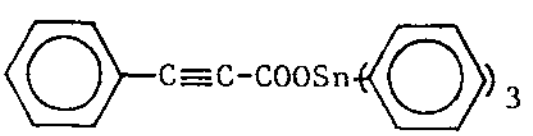
TABLE-I

No.	Triorganotin Carboxylates	IR spectral data	
		$\nu_{asym}(CO_2)$/C=C/ aromatic ring (in cm^{-1})	$\nu_{sym}(CO_2)$ (in cm^{-1})
(26)	$CH_2{=}CH\text{-}COOSnBu_3$	1645, 1655	1530, 1550
(27)	$CH_3CH{=}CH\text{-}COOSnBu_3$	1655	1535, 1555
(28)		1640	1540, 1555, 1580
(29)		1635	1550, 1563, 1595
(30)	$CH_3CH{=}CH\text{-}CH{=}CH\text{-}COOSnBu_3$	1600, 1625	1500
(31)		1625	1548, 1567
(32)	$CH_3C{\equiv}C\text{-}COOSnBu_3$	1560, 2250(C≡C)	1540
(33)		1560, [2125, 2310 (C≡C)]	1505

Contd...

Contd....

TABLE-I

No.	Triorganotin Carboxylates	IR spectral data	
		$\nu_{asym}(CO_2)$/C=C/ aromatic ring (in cm^{-1})	$\nu_{sym}(CO_2)$ (in cm^{-1})
(34)		1650	1515, 1545, 1570
(35)		1610, 1640	1590
(36)		1610, 1635	1575
(37)		1565, 2250(C≡C)	1510
(38)		1570 2220(C≡C)	1515

Assignments of bands associated with $\nu_{asym}(CO_2)$ mode of these compounds(26-38) were ambiguous owing to the presence of stretching vibration of both C-C double bond and the aromatic ring in the same region of the spectrum.

For compounds(26,27 & 34), the $\nu(CO_2)$ in nujol appeared at the regions 1650-1655cm^{-1} and 1530-1545cm^{-1}, while for tri-n-butyl cyclohexylidene acetate(31), the $\nu(CO_2)$ displayed at 1625, 1567 and 1548 cm^{-1}. The higher range could be attributable to $\nu_{asym}(CO_2)$ and the lower range was due to $\nu_{sym}(CO_2)$.Tri-n-butyltin cinnamate(28), p-nitro cinnamate(29) and sorbate(30) showed infrared absorptions at the regions 1625-1640cm^{-1} and 1500-1563 cm^{-1}, a lower range of frequency than that in stannyl acrylate(26) and crotonates(27 and 34). This could be explained probably on the basis of more conjugation available through the phenyl ring or the C-C double bond (in sorbate ester). The corresponding triphenyltin esters of p-nitro cinnamic(35) and sorbic(36) acids showed $\nu_{asym}(CO_2)$ at 1575-1590 cm^{-1}. An additional band appeared at 1610 cm^{-1}, in each compound, (35) and (36), could be assigned for phenyl ring or the C-C double bond.

Sorbic acid, for example, the $\nu_{asym}(CO_2)$ for acid was reported[118a] at 1690 cm^{-1}, its ethyl ester at 1710cm^{-1} and its tri-n-butyltin(30) and triphenyltin(36) ester displayed corresponding bands at the region 1600-1635 cm^{-1}. Similarly, $\nu_{asym}(CO_2)$ for p-nitro cinnamic acid was observed[118b] at 1690cm^{-1} while its tri-n-butyltin ester(29)

showed band at 1635 cm^{-1} and the corresponding triphenyl p-nitro cinnamate(35) gave $\nu_{asym}(CO_2)$ at 1640, 1610 cm^{-1} indicating a lowering of frequency than the acid. However, in 1988, Sharma et al.[69] reported that $\nu_{asym}(CO_2)$ for tri-n-butyl p-methoxy cinnamate was observed at 1585 cm^{-1}, in the solid state and suggested bridging bidentate nature for the carboxylate group[119,120]. This band had shifted to 1625 cm^{-1} in solution state, indicating cleavage of weak intramolecular bridges on dissolution. On the other hand, the triphenyltin p-methoxy cinnamate showed $\nu_{asym}(CO_2)$ frequency at 1620 cm^{-1}, both in solid and solution phase and they assigned that this was associated with a unidentate carboxylate group.

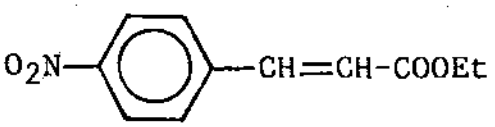
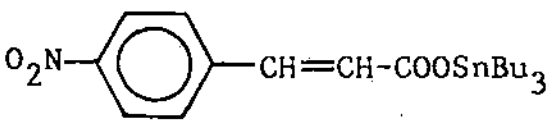
The α,β-unsaturated tin carboxylates, included in the present studies, displayed the $\nu_{asym}(CO_2)$ frequency at the region 1625-1655 cm^{-1}, in nujol. As compared to the observations of Sharma et al.[69] for triorganostannyl α,β-unsaturated (olefinic) carboxylates, it could be suggested the tri-n-butyltin esters(26-31 , 34-36) were probably associated with unidentate carboxylate group.

Since, we extended our investigation to α,β-unsaturated acetylenic tin carboxylates, the infrared spectra for the compounds (32, 33, 37 and 38) were also recorded in nujol mull and summarised in **TABLE-I.** The infrared absorption bands for C—C triple bond were found as expected[121], at the region

2220-2250 cm^{-1} for the esters (32, 37 and 38). However, compound(33) exhibited the C≡C band at 2310 cm^{-1}, 2125 cm^{-1}. The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands were observed at the regions 1560-1570 cm^{-1} and 1505-1540 cm^{-1} respectively. Compared to α,β-unsaturated(olefinic) tin carboxylates, a bridging bidentate nature for the carboxylate group could be suggested. However, their infrared absorption in solution phase could provide more information regarding structure, which were not performed.

The proton and carbon-13 NMR chemical shifts values for these organotin esters(26-38) were assigned by comparison with the related compounds[63,64,69,122,123]. A comparative observation of a few proton chemical shifts, in particular the α- and β- olefinic hydrogens, between the stannyl and alkyl esters revealed no appreciable shifting. As for example, α- and β- protons for ethyl sorbate appeared[124] at δ 5.65 and δ 7.20 respectively, whereas those in tributyltin sorbate(30) resonanced at δ 5.79 and δ 7.15. Similarly, for ethyl crotonate the α- and β-protons appeared[125] at δ 5.82(d) and δ 7.00(m) respectively while the corresponding tri-n-tutyltin ester(27) exhibited doublet (with small allylic coupling) for α-H at 5.84 and multiplets for β-H at δ 6.84. In case of ethyl p-nitro cinnamate, the α- and β- protons displayed[125] at δ 6.60 and δ 7.73 respectively whereas, for the tri-n-butylstannyl p-nitro cinnamate(29), the α- and β-

protons appeared at δ 6.58 and δ 7.59.

Compound	α-H δ-ppm	β-H δ-ppm
$CH_3CH{=}CH{-}CH{=}CH{-}COOEt$	5.65	7.20
$CH_3CH{=}CH{-}CH{=}CH{-}COOSnBu_3$	5.79	7.15
$CH_3{-}CH{=}CH{-}COOEt$	5.82	7.00
$CH_3{-}CH{=}CH{-}COOSnBu_3$	5.84	6.84
	6.60	7.73
	6.58	7.59

For the studies of tin-proton coupling constant values it was suggested[63,126] that the J values are a measure of the percentage of s-character in the tin-carbon bond. However, as described earlier(p.13), the $^{n}J(^{119}Sn{-}^{13}C)$ values provide more accurate informations on the hybridisation of tin-carbon bond than the J values of ^{119}Sn-C-H bond.

For n-butyltin esters, the butyl protons appeared as follows : C_1, and C_3, protons in the range of δ 1.04-1.48 as a multiplets, the protons attached to C_2, displayed in the region of δ 1.48-1.74 as a multiplet and C_1, protons exhibited triplet in the range of δ 0.83-0.92. The chemical shifts for protons attached to carbons C_1,-C_4, were shown in TABLE-II The proton chemical shifts for the butyl protons were found to be consistent with the literature data[31,69].The other proton chemical shifts were given in the experimental section of this Part-I, SECTION-A.

For triphenyltin esters of crotonic(34), p-nitro cinnamic(35), sorbic(36), but-2-ynoic(37) and phenylpropynoic (38) acids, the aromatic protons appeared as multiplets and therefore, the individual aromatic proton chemical shifts could be assigned.

Carbon-13 magnetic resonance spectra of these organotin esters(26-38) were recorded and analysed during this study. The carbonyl carbon appeared in the range δ173.85-170.87 for the tin esters(26-30 & 34-36) whereas the corresponding carbon for compound(31) appeared at δ 177.50. In the series of acetylenic tin esters(32, 33, 37 & 38), the carbonyl carbon displayed in the range of δ 156.75-159.77, lower range than the olefinic compounds. This might be attributable to the presence of triple bond which made the

TABLE-II

Compound No.	$H-C_1$, & $H-C_3$, (as multiplet) δ ppm	$H-C_2$, (as multiplet) δ ppm	$H-C_3$, (as triplet) δ ppm
(26)	1.18-1.43	1.49-1.62	0.84(J=7.21 Hz)
(27)	1.20-1.39	1.54-1.74	0.85(J=7.25 Hz)
(28)	1.27-1.42	1.58-1.71	0.92(J=7.22 Hz)
(29)	1.15-1.48	1.57-1.71	0.90(J=7.23 Hz)
(30)	1.10-1.44	1.53-1.72	0.88(J=7.22 Hz)
(31)	1.04-1.41	1.48-1.66	0.83(J=7.22 Hz)
(32)	1.09-1.40	1.49-1.68	0.84(J=7.19 Hz)
(33)	1.20-1.46	1.58-1.70	0.91(J=7.21 Hz)

upfield shifting. The n-butyltin carbons($C_{1'}$-$C_{4'}$) were given in **TABLE-III** and the carbons of the aromatic ring(C_i-C_o-C_m-C_p) attached to tin atom were summarised in **TABLE-IV.**

As described previously, ^{13}C-[127,128] and ^{119}Sn-NMR had been used by several workers in the recent years to examine coordination geometry of the tin atom in some tri-n-butyltin compounds[64,69,122,129]. In 1984, Lycka and his associates[122] made an extensive investigation on ^{13}C- and ^{119}Sn-NMR spectra of a set of tri-n-butyltin(IV) compounds and their complexes in coordinating and non-coordinating solvents. They found that the chemical shifts $\delta(^{13}C)$ and $\delta(^{119}Sn)$ and the coupling constants $^{1}J(^{119}Sn-^{13}C)$ depend significantly on the coordination number of the tin atom and on the geometry of its coordination sphere. For compounds $n\text{-}Bu_3SnX$ as neat liquids and $CDCl_3$ solution the $^{1}J(^{119}Sn-^{13}C)$ values were obtained in the range of 326.7-386.7 Hz and they suggested that this range are typical of sp^3-sp^3 character of Sn-C bond in non-planar Bu_3Sn grouping. The tri-n-butyltin esters(26-33) included here showed $^{1}J(^{119}Sn-^{13}C)$ values in the range of 351.21-379.39 Hz. This was in good agreement with literature[122] values and thus suggested unidented tetrahedron structure for the n-butyl esters. Also the chemical shifts $\delta[^{13}C(1') - C(4')]$ in all the compounds were found(**TABLE-III**) within the ranges of tri-n-butyltin(IV) carboxylates reported[64,69,122,129] earlier. Again, the

TABLE-III

Compound No	C_1,	C_2,	C_3,	C_4,	$^1J(^{119}Sn-^{13}C)$	$^3J(^{119}Sn-^{13}C)$	^{119}Sn
	δ in ppm				in Hz	in Hz	δ ppm
(26)	16.46	27.64	27.00	13.60	351.84	64.66	-
(27)	16.41	27.67	27.02	13.62	356.12	64.91	-
(28)	16.57	27.72	27.09	13.68	353.66	65.41	-
(29)	16.65	27.82	27.03	13.63	379.39	64.53	+120.258
(30)	16.46	27.68	27.02	13.61	351.21	64.40	+106.576
(31)	16.41	27.83	27.00	13.62	355.42	64.03	+108.213 +100.281
(32)	16.81	27.69	27.02	13.56	353.98	65.66	+131.811
(33)	16.96	27.75	27.06	13.61	351.71	65.91	-

$^{3}J(^{119}Sn-^{13}C)$ coupling constant values were observed to be in the range of 64.03-65.91 Hz and compatible with published values. From the ^{13}C-NMR spectra available to us, we could not calculate the coupling constant values $^{n}J(^{119}Sn-^{13}C)$ when n=2,4. Furthermore, since we had to depend on the external sources for magnetic resonance spectra, the variation of chemical shift values with respect to concentration and various coordinating solvents could not be undertaken during this study.

However, a comparative table (TABLE-V) comprising of similar class of tri-n-butyltin carboxylates may be given here for corroborating our assigned structures.

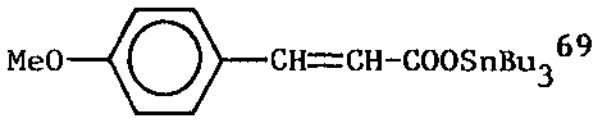
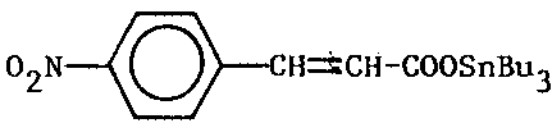
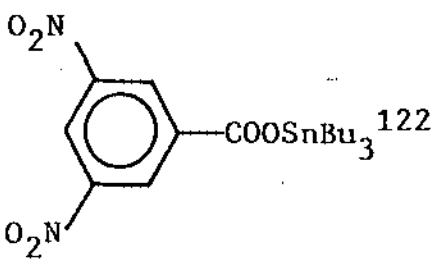
The chemical shifts $\delta(^{119}Sn)$ for a few tributyltin esters(29), (30) and (31) in $CDCl_3$ solution were found in the range δ 100.281 to 120.258 ppm, indicating tetrahedral arrangement[122] with four coordinate tin. However, the compound(31) showed two $\delta(^{119}Sn)$ values at 108.213 and 100.281 ppm.

The important ^{13}C- and ^{119}Sn-NMR spectral data for triphenyltin esters(34-38) were compiled in TABLE-IV. The chemical shifts $\delta(^{13}C)$ of the carbon atoms in the ipso-positions of the phenyl groups varied over a range of §137.58 - 142.64. It was observed by Lycka et al.[123] that the

TABLE-IV

Compound No.	C_i	C_o	C_m	C_p	$^2J(^{119}Sn-^{13}C)$	$^3J(^{119}Sn-^{13}C)$	In ppm
	δ in ppm				in Hz	in Hz	$\delta_{(^{119}sn)}$
(34)	138.59	136.92	128.89	130.07	48.11	63.40	-182.664
(35)	138.04	136.93	129.06	130.37	48.30	63.65	-103.37
(36)	138.69	136.94	128.89	130.06	48.18	63.21	-160.846
(37)	142.64	136.08	128.34	128.96	45.66	74.28	-250.807
(38)	137.58	136.95	129.08	130.45	48.18	68.87	-

TABLE-V

Tri-n-butyltin Carboxylates	Solvent	C_1, C_2, C_3, C_4, δ in ppm				$n_J(^{119}Sn-^{13}C)$(Hz) n=1	n=2	n=3	^{119}Sn δ in ppm
	$CDCl_3$	27.56	27.73	26.88	13.45	-	-	-	+104.7
	$CDCl_3$	16.65	27.82	27.03	13.63	379.39	-	64.53	+120.258
	$CDCl_3$	16.57	27.39	26.61	13.11	351.6	22.0	66.0	+140.0

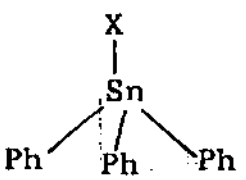
δ -values for the carbon at ipso-position shifted downfield for the five coordinate tin compounds from those for four coordinate tin compounds. It thus seemed probable that the Sn-C(phenyl) bond becomes more polar with increasing coordination of tin atom. Triphenyltin but-2-ynoate(37) showed the ipso-carbons at δ 142.64, downfield than the ipso-carbons at δ 137.58-138.69 and by comparison it was expected that compound(37) might possess penta-coordinate tin atom being coordinated with D_6-DMSO.

The value of coupling constant, reflecting spin-spin coupling of neighbouring atoms joined by a simple bond, depends mainly on the magnitude of the Fermi-contant term. In the case when none of the participating bonding atoms have a lone electron pair, the ^1J values are directly proportional to the s-character of their hybrid orbitals[130]. Therefore, the triphenyltin(IV) compounds (sp^2 hybrid carbon orbital) have higher ^1J values than analogous trialkyltin (sp^3 hybrid orbital) compounds. For the same reason and in accordance with Bent's rule[131] in all the compounds with a Ph_3Sn-halogen bond the $^1J(^{119}Sn-^{13}C)$ values decrease in the order Cl>Br>I. The proportion of s-character in the tin hybrid orbitals provides a satisfactory explanation of the obtained $^1J(^{119}Sn-^{13}C)$ values of the triphenyltin(IV) compounds of the suggested structural types.

Unfortunately, from our ^{13}C-NMR spectra of the

compounds(34-38) we could not be able to calculate the $^{1}J(^{119}Sn-^{13}C)$ values. However, $^{n}J(^{119}Sn-^{13}C)$; n=2, 3 values were calculated and found compitable with Lycka's[123] observations.

According to Lycka et al.[123], for a group of compounds of similar compositions, the $\delta(^{119}Sn)$ chemical shifts seemed to depend mainly on the total electron density on the central tin atom. The Ph_3SnX compounds having the values $\delta(^{119}Sn)$ shifted downfield in the range of -40 to -120 ppm compared with that of Ph_4Sn (^{119}Sn δ=-128.1) should have four-coordinate tin and tetrahedral arrangement of phenyl and X substituents [structural type (39)].



(Four-coordinate tin)
Tetrahedron

(39)

Although precise interpretation of the chemical shifts $\delta(^{119}Sn)$ of these tin carboxylates(34-38) studied here was difficult, in the case of triphenyltin p-nitro cinnamate (35), the p-nitro group being strongly electron withdrawing, reduced electron density on the central tin atom. Thus, the $\delta(^{119}Sn)$ value obtained for the tin cinnamate(35) at δ -103.37 came well within the range (-40 to 120 ppm)

observed by Lycka and his collaborators[123]. Keeping conformity with Lycka's observations it might be tentatively assumed that the possible structural arrangement for compound(35) would be tetrahedral with four-coordinate tin.

The ^{119}Sn chemical shifts for compounds triphenyltin crotonate(34) and triphenyltin butynoate(37) were exhibited at δ -182.664 and δ -250.807 ppm respectively. On the basis of the values of chemical shifts $\delta(^{119}Sn)$ and the coupling constants $^{1}J(^{119}Sn-^{13}C)$, Lycka et al.[123] concluded that the possible structural arrangements for compounds(Ph_3SnX) with (^{119}Sn) values (δ -180 to -200) and (δ -200 to -260) were characterised by having cis and trans trigonal bipyramidal geometry respectively with five-coordinate tin atom in both cases.

It was difficult to conclude the structural arrangement for compound(34) by only checking $\delta(^{119}Sn)$ value and moreover it was appeared at δ -182.664, merginally within the range of cis trigonal bipyramidal geometry(δ -180 to 200). However, as suggested earlier from the $\delta(^{13}C)$ value of the ipso-carbon (appeared downfield) for compound(37), the $\delta(^{119}Sn)$ value at -250.807 ppm also corroborated that the triphenyltin but-2-ynoate(37) should possess five coordinate tin atom and having trans trigonal bipyramidal geometry. However, for making a conclusion about the geometry and coordination number of tin atom of these α,β-unsaturated tin

carboxylates, a more detailed NMR investigation was necessary. Because of the lack of these instruments facility in this department we could not be able to undertake such measurements.

Having prepared the unsaturated triorganostannyl carboxylates(26-28), we turned our attention to investigate the reaction behaviour of these esters with mercuric chloride or mercuric acetate in different solvents. The nature of solvents employed in the present study included protic polar (methanol) aprotic polar(acetonitrile) and aprotic non-polar (benzene). Initially we attempted this reaction with a few α,β -unsaturated(olefinic) tri-n-butyltin esters(26, 27, 28, 29, 30 and 31). Among these esters the double bond was either unsubstituted(26), or β-monosubstituted(27), (28), or β-monosubstituted with extended conjugation through another olefinic C—C bond(30) or β,β-disubstituted olefinic and cyclic compound(31), (TABLE-I).

In all the cases, treatment with mercuric chloride in different solvents at different temperature afforded with the formation of butylmercuric chloride(BuHgCl) and the corresponding unsaturated acids alongwith other products as mentioned previously(p.25-26). The formation of BuHgCl and the carboxylic acid were beleived to take place by demetallation of the C-Sn bond with the eventual hydrolysis

of the resulting substituted intermediates. However, the C—C double bond was found to be unreacted from mercuration.

Treatment of these unsaturated tin carboxylates(26-31) with mercuric acetate also afforded with the formation of BuHgCl and the corresponding unsaturated acids alongwith other products and again, mercuration of the C—C double bond was not observed. The formation of BuHgCl in the case of mercuric acetate was probably occurred during washing of the reaction mixture with brine(aqueous NaCl solution).

Thus, it was found that the ester function underwent demetallation preferentially over the mercuration of C—C double bond when α,β-unsaturated stannyl esters were treated with mercuric chloride or mercuric acetate. Since C—C double bonds are quite reactive towards mercury(II) salts, as depicted earlier (p.27-29), we considered that this reaction might portend certain potentials in organic synthesis.

The C—C triple bonds are also reactive towards mercury(II) salts and therefore we extended our studies to examine the reaction of acetylenic unsaturated tin esters with mercuric salts.

The acetylenic compounds(32, 33) were treated with mercury (II) chlorides and mercury(II) acetates in different solvents. Similar observations were found by isolating the

corresponding acetylenic unsaturated acids and BuHgCl. However, in the case of tri-n-butylstannyl but-2-ynoate(32), immediately after the treatment of mercury(II) acetate in methanol, large amount of solid was appeared. The solid was filtered off after the reaction time (TABLE-VI) was over and the filtrate was concentrated and worked-up to furnish the but-2-ynoic acid in only 26% yield.

It was stated[95] that these demetallation reactions of triorganotin carboxylates with Hg(II) salts depend on the nature of the organic groups bonded to tin. We chose to observe the effect of phenyl group attached to tin atom. Accordingly, similar reactions were attended with both olefinic triphenyltin esters(34, 35, 36) and acetylenic triphenyltin esters(37, 38) and the results were summarised in **TABLE-VI.** Though, Roy and Ghosh[95] obtained some contrasting behaviour of mercuric acetate towards triphenyltin esters, we observed almost comparable results both by using mercuric acetate and mercuric chloride.

In terms of yield of the acids it seemed that two factors could be of importance, besides the role of solvents. Firstly, Abraham et al.[88] observed that in the electrophilic substitution at the carbon centre bonded to tin atom, the aryl-tin bond underwent cleavage more rapidly than the cleavage of alkyl-tin bond when treated with mercury(II)

TABLE-VI

Compound	HgX_2	Solvent	Time/Temp.	Yield(%) of BuHgCl or PhHgCl	Yield (%) of acid
(26)	X=Cl	MeOH	48h/r.t.	89	42
	X=Cl	CH_3CN	6h/reflux	86	40
	X=OAc	MeOH	48h/r.t.	84	30
	X=OAc	CH_3CN	6h/reflux	82	42
(27)	X=Cl	MeOH	48h/r.t.	40	45
	X=Cl	PhH	4h/reflux	88	43
	X=OAc	CH_3CN	4h/reflux	96	47
	X=OAc	PhH	4h/reflux	84	48
(28)	X=Cl	MeOH	48h/r.t.	96	45
	X=Cl	CH_3CN	6h/reflux	94	48
	X=OAc	MeOH	48h/r.t.	85	46
	X=OAc	CH_3CN	6h/reflux	90	49
(29)	X=Cl	PhH	4h/reflux	72	30
	X=OAc	MeOH	48h/r.t.	70	32
(30)	X=OAc	MeOH	48h/r.t.	71	50
	X=Cl	PhH	4h/reflux	76	43
	X=Cl	CH_3CN	6h/reflux	92	59

Contd...

Contd...

TABLE-VI

Compound	HgX_2	Solvent	Time/Temp.	Yield(%) of BuHgCl or PhHgCl	Yield (%) of acid
(31)	X=OAc	MeOH	48h/r.t.	73	48
	X=Cl	PhH	4h/reflux	78	44
(32)	X=Cl	CH_3CN	4h/reflux	55	28
	X=OAc	MeOH	48h/r.t.	50	26
(33)	X=OAc	MeOH	48h/r.t.	86	46
(34)	X=Cl	CH_3CN	4h/reflux	80	42
	X=OAc	MeOH	48h/r.t.	78	40
(35)	X=Cl	CH_3CN	4h/reflux	92	60
	X=OAc	MeOH	48h/r.t.	85	48
(36)	X=Cl	CH_3CN	4h/reflux	92	59
	X=OAc	MeOH	48h/r.t.	78	40
(37)	X=Cl	CH_3CN	5min/reflux	98	62
(38)	X=Cl	PhH	1h/reflux	90	58

salts. Similar observations were noticed by Roy and Ghosh[94,95] in the case of triorganotin carboxylates. However, Roy and Ghosh [95] suggested that the ultimate hydrolysis of the resulting substituted intermediates (reaction pathway, p.25-26) would be governed by the polarity of the Sn-O bond of the organotin carboxylates. The more polar bond, or in turn the more acid strength of the corresponding acid, contraction of the 'd' orbital of the tin atom should be more pronounced. This could enhance the probability of the attack of a nucleophile, e.g., water, at the tin atom resulting in carboxylate hydrolysis. They came up with this conclusion from their finding among the triphenyltin esters of formate, acetate and propionate. The triphenyltin formate, the corresponding acid being more acidic, reacted with $HgCl_2$ to produce the intermediate[$(HCOO)_2SnPHX$] and the latter was attacked by water and hydrolysed to form acid and polymeric tin compound. On the other hand, $CH_3COOSnPh_3$ and $CH_3CH_2COOSnPh_3$ produced the corresponding acids in better yield through the intermediate[$(R'COO)_3SnX$; ($R'=CH_3$, Et)] alongwith tin hydroxide and other compounds.

From our observations with phenyltin and n-butyltin carboxylate it seemed difficult to make any generalisation in respect of yields of the acids. On some occasion, such as triphenyltin p-nitro cinnamate(35), underwent demetallation upon treatment with Hg(II) salts furnishing the

corresponding acids in much better yield than tri-n-butyltin ester(29). This was in conformity with Abraham's observation[88] that the phenyl substituents attached to tin undergo electrophilic substitution faster than alkyl groups attached to tin. Similar observations were found in the case of acetylenic compounds. For example, the tri-n-butyltin but-2-ynoate(32) furnished the acid in 26-28% yield while its triphenyltin ester(37) gave 62% acid in much less time when treated with Hg(II) salts under identical conditions. On the other hand, the stannyl sorbates did not produce any remarkable reactivity difference between its n-butyl (30) and phenyl(36) esters. The formation of organomercuric chloride (BuHgCl or PhHgCl) was evident from the reaction sequence, reported by Roy et al.[95](p.25-26).

In respect of role of solvents used here, it may be pointed out that although methanol required a lower temperature to bring about the reaction, use of aprotic polar solvent, such as acetonitrile, afforded the acid in better yield in less reaction time in many cases (**TABLE-VI**).

I,A-3.2: Conclusion :

The present approach therefore revealed that while the alkyl esters of α,β-unsaturated(olefinic/acetylenic) acids, upon treatment with mercury(II) salts, undergo solvo -

mercuration of C—C double/triple bond, the corresponding stannyl esters, upon similar treatment, react preferentially and regioselectively at the ester function keeping the olefinic bond unreacted. Thus by using the stannyl esters we were able to protect the C—C double/triple bond and thereby providing a useful approach for preferential and regioselective reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts[136,137]. The result was the formation of the corresponding acids and alkyl mercuric halides and thus this reaction also provided a mild and neutral condition for hydrolysis of alkyl/aryl esters since these tin esters could be prepared from these alkyl/aryl esters[54] (SECTION-B of this dissertation).

Finally, it may be assumed that the phenyl group attached to the tin atom and the acidity of the carboxylic acid in aprotic polar solvent might govern the overall reaction pathway leading to higher yield of the carboxylic acid.

I.A-4: Experimental

Note : The compounds described are all racemates. Melting points were taken in an open capillary in sulfuric acid bath. M.p.s. and b.p.s. are not corrected. IR spectra were recorded on Pye Unicam SP 3-300S and on Perkin-Elmer model PE 298 spectrophotometer in nujol mull (unless otherwise stated). For recording UV spectra a Shimadzu UV-240 spectrophotometer was used. ^{1}H-NMR spectra were taken at 60 MHz on a Varian T-60A or Varian EM-360 and at 250 MHz on a Bruker's spectrometer. ^{13}C-NMR spectra were measured at 62.896 MHz on a Bruker's spectrometer. ^{119}Sn-NMR were obtained on a VXR-300S equipped with multinuclear probe and operating at 111.862 MHz. The chemical shifts in NMR spectra were determined relative to internal Tetramethylsilane for ^{1}H- and ^{13}C- and to external tetramethylstannane for ^{119}Sn-NMR respectively. In the ^{1}H- and ^{13}C- NMR spectra, $C_{1'}$-$C_{4'}$ correspond to the n-butyl group attached to tin and C_i, C_o, C_m, C_p correspond to the phenyl ring attached to tin. Tin was estimated gravimetically as SnO_2. column chromatography were performed on silica gel (60-120 mesh) or neutral alumina (Brockman grade I). Extracts were dried over anhydrous Na_2SO_4. Light petroleum refers to the fraction of b.p. 60-80°C. Ether refers to diethylether. Product purities were routinely checked by TLC using silica gel IB-F (Baker-flex), made by J. T. Baker Inc., Phillipsburg, N. J.

Solvents and commercial reagents were purified and dried by conventional methods before use. Bis (triphenyltin) oxide used here was prepared by the reaction of triphenyltin chloride with 50% excess of sodium hydroxide, as described by McLean et al. [K. A. Elegbede and R. McLean, J. Organomet. Chem., 20, 387 (1955)].

In IR spectra, the abbreviations s, m, w stood for strong, medium and weak bands. In NMR spectra, s, d, t, m, br., were used for singlet, doublet, triplet, multiplet and broad peaks respectively. The chemical shifts(δ) values were expressed in ppm.

Preparation of a few acids used here following the literature procedures.

1) Hexa-2,4-dienoic acid (Sorbic acid) :

In a 100 ml round bottom flask fitted with reflux condenser, crotonaldehyde (10g, 0.1426 mole), malonic acid (15g, 0.1441 mole) and 15 ml dry pyridine (b.p. 113-115°C) were taken. The reaction mixture was heated on a water bath for 3 hours. At the end of that period the vigorous evolution of carbon dioxide was ceased. After cooling, the reaction mixture was acidified by adding dropwise cold dilute sulfuric acid with caution and gentle shaking in an ice-cold condition. Yellow coloured crystalline solid was started to separate immediately from the mother liquor. For the completion of crystallisation it was kept overnight in the refrigerator. Next day, the solid was separated by filtration and washed with ice-cold water. After drying, it was recrystallised from benzene to afford pure sorbic acid (4.8g, 30%), m.p. 132-133°C(lit.[121] m.p. 134°). IR: ν_{max} 1690 cm^{-1}.

2) p-nitro cinnamic acid :

A mixture of 4.2g (0.0277 mole) of p-nitro benzaldehyde (m.p. 105-108°C), 2.9g (0.0279 mole) of malonic

acid (m.p. 135-137°C) and 3 ml dry pyridine (b.p. 113-115°C) were taken in a 50 ml round bottom flask attached to a reflux condenser. A few drops of piperidine was added to the reaction mixture, red colour appeared. Then it was heated over water bath and within 10-15 minutes the reaction mixture became solidified, warming was continued for the next 2 hours. After cooling to room temperature it was acidified by dropwise addition of dilute sulfuric acid in the ice-cold condition. Solids were allowed to settle down by keeping it in refrigerator for 4 hours. Yellow crystals were separated out by filtration and the crystals were washed with ice-cold water and dried in open air. Recrystallisation from benzene afforded pale yellow crystal of p-nitro cinnamic acid (4.8 g, 90%), m.p. 289° (dec.)[lit[132] 289° (dec.) IR: ν_{max} 1635, 1690cm^{-1}.

3) But-2-ynoic acid:

a) 3-Methylpyrazole-5-one :

To a magnetically stirred solution of ethyl acetoacetate(25g, 0.1921 mole) in absolute ethanol (15.3 ml) was added dropwise slowly 99% hydrazine hydrate (9.66 g, 0.5 mole). Exothermic reaction was ensured and the temperature of the reaction mixture was maintained at 60°C. After the addition was complete, the mixture was stirred for another hour at room temperature. It was then cooled in an ice-bath

to complete the crystallisation. Colourless, needle shaped crystalline 3-Methylpyrazole-5-one was filtered off and dried in open air, (16.9 g, 90%), m.p. 220-221°C (phase changed at 195°C), (lit.[121] m.p. 222°C).

b) 4,4-Dibromo-3-methylpyrazole-5-one :

A solution of the aforementioned crude 3-methylpyrazole-5-one (16g, 0.1631 mole) in 64 ml of glacial was taken in a 250 ml round bottom flask and stirred magnetically 26 g (0.1631 mole) of bromine in 16 ml of glacial acetic acid was added dropwise via pressure equiliser to the stirred solution. On completion of that addition, 40 ml of water and 26 g (0.1631 mole) of bromine in 16 ml glacial acetic acid were added to the reaction mixture. Clear solution was obtained at the end of second lot addition of bromine. The reaction mixture was permited to stand overnight at room temperature. Crystals of dibromo pyrazolone was separated out on addition of water. The product was filtered under water suction and washed with distilled water until the washings were neutral. The air-dried product (30, 79g, 78%) had m.p. 128-130° (lit.[121] m.p. 130-132°) and was used directly for the next step.

c) But-2-ynoic acid :

In a 1L round bottom flask, a solution of sodium hydroxide in 440 ml of water was prepared and stirred magnetically in an ice-bath until the temperature of the solution reached 0-5°C. 30g (0.1239 mole) of 4,4-Dibromo-3-methylpyrazole-5-one was added portionwise over a period of 10 minutes. The bromoketone was dissolved to give an orange-red solution which evolve nitrogen gas; the temperature of the solution during the addition showed only a slight tendency to rise. The reaction mixture was stirred for 1 hour at 0-5°C and then at room temperature for 1 hour. The solution was cooled and acidified with concentrated hydrochoric acid. Then it was extracted with diethyl ether (3 x 75 ml) and the combined ethereal layer was washed with brine and dried (Na_2SO_4). Evaporation of the solvent afforded a residue which was kept in a vacuum desiccator. After 3 days crude orange crystals of but-2-ynoic acid were appeared. Then the crystals were extracted with boiling light petroleum successively and the solution was concentrated to furnish yellow crystalline acid. Recrystallisation from benzene furnished but-2-ynoic acid (5.2 g, 50%), m.p. 72-73° (lit.[121] m.p. 75-76°C). IR : ν_{max} 1690, 2240, 2950 cm^{-1}.

4. Cyclohexylidene acetic acid :

a) Preparation of Ethyl cyclohexylidene cyano acetate :

A mixture of cyclohexanone (8.65 g, 0.0884 mole) and ethyl cyanoacetate (10g, 0.0884 mole) was dissolved in benzene (50 ml) and a few drops of piperidine were added to it. The mixture was refluxed for 2 hours using a Dean-Stark water separator. The solution was cooled and acidified with 3(N) dilute hydrochloric acid to maintain the pH as neutral. The organic part was washed with aqueous sodium bicarbonate solution carefully and then washed with brine and dried over anhydrous Na_2SO_4. Solvents were distilled off to afford an oily brown residue which was distilled under reduced pressure and collected the condensation product, ethyl cyclohexylidene cyano acetate at 117-121°/2mm Hg(15.35 g, 90%). IR(Neat): ν_{max} 1598(s, C=C), 1710(s,C=C-COOEt), 2220(s, C=C-CN)cm^{-1}.

b) Hydrolysis of Ethyl cyclohexylidene cyano acetate :

The foregoing ethyl cyclohexylidene cyano acetate (10g, 0.0518 mole) was treated with glycollic potassium hydroxide solution (prepared from 12g KOH in minimum volume of water and then added 120 ml of ethylene glycol) and refluxed for 5 hours. After cooling to room temperature the reaction mixture was poured into crushed ice and extracted with ether (3 x, 50ml) to eliminate any neutral unreacted part. The aquous layer was separated and acidified with ice-

cold dilute hydrochloric acid (3N). The acid was extracted with ether (2 x 50 ml) after saturation with sodium chloride and combined etherial layer was washed with brine and dried (Na_2SO_4). Evaporation of the solvent afforded the dark red acid (5.6 g, 71%).

c) Cyclohexylidene acetic acid :

The aforementioned crude dicarboxylic acid (3.0 g, 0.0197 mole) was taken in a sublimation tube and heated at 180° for minutes in a sublimation chamber. The desired acid was sublimed at 140-150°C/6-5 mm Hg(1.93 g, 70%), IR : ν_{max} 1685 cm^{-1}.

5. Phenylpropynoic acid :

a) 2,3-Dibromo-3-phenylpropanoate :

To a solution of ethyl cinnamate (42g, 0.2496 mole) (prepared from cinnamic acid) in carbon tetrachloride (25 ml) in 1l r.b. flask was added bromine (40g, 12.5 ml, 0.25 mole) at 0°C (ice-bath) during 30 minutes. The bromine was found to disappear rapidly at first, but more slowly towards the end of the reaction. The reaction mixture was allowed to stand for 1 hour and then poured into a large evaporatory dish so that the excess of bromine and carbon tetrachloride were evaporated. The crude ethyl 2,3-Dibromo-3-phenylpropanoate

remained as a solid cake, which was dried by pressing between large filter papers. The crude product (70g, 83%), m.p. 65-69°C (lit.[121] m.p. 66-71°C) was directly used for the next step.

The crude dibromo ester (80g, 0.2357 mole) was added to an ethanolic solution of KOH (prepared from 61g KOH in 285 ml of rectified spirit by heating). An initial exothermic reaction was set in, subsided after a short while, and then heated under gentle reflux for 6 hours on a steam-bath. The contents were poured into a large beaker, cooled and neutralise by adding concentrated hydrochloric acid with stirring until neutral to litmus. After cooling at 0°C, the precipitated solids were filtered off at the pump and washed with a little chilled alcohol. The solid compound(A) was set aside. The filtrate was transfered into the original flask and the liquid was distilled out until the temperature of the vapour reached 95°C. The residue was combined with the solid obtained earlier(A) dissolved in 200 ml of water and 200 g of crushed ice and cooled in an ice-bath. To this was added 20% sulfuric acid slowly until the solution became strongly acid to congo red. Allowed to stand for 20 minutes when the dark-coloured crude phenylpropynoic acid was separated out and filtered off, washed with three 10 ml portions of 2% sulfuric acid. The solid acid was dissolved in 150 ml of 5% sodium carbonate solution, 3 g of decolourising charcoal was added,

and heated on a water bath for 30 minutes with occasional shaking. The charcoal was eliminated by filtering off. Then the filtrate was cooled in ice-bath and 50 g of crushed ice was added to it. 20% sulfuric acid was added slowly to mechanically stirred solution until acid to congo red. After 30 minutes, the precipitate was filtered off by suction and washed with 10 ml of ice-cold 2% sulfuric acid, then with a little water and dried in the air. The yield of phenylpropynoic acid was 45% (15 g), m.p. 132-133°C (lit.[121] m.p. 134-135°C).

I.A-4.1: Preparation of α,β-Unsaturated Stannyl Carboxylates (26 - 38)

Tri-n-butylstannyl acrylate (26)

This ester was prepared from its methyl ester by transesterification method[54]. A mixture of freshly distilled methyl acrylate (1 g, 0.0116 mole) and bis tri-n-butyltin oxide (6.92g, 0.0116 mole) was gently refluxed in neat for 2 hours with very gentle heating at 60°C. It was then cooled to room temperature and colourless crystalline solid appeared which was purified by silica-gel column chromatography. Elution with 25% benzene-light petroleum afforded fine

crystals of tri-n-butylstannyl acrylate(26), (3.85g, 92%), m.p. 69-70°C(lit.[133] m.p. 69-70°C).

UV(EtOH): λ_{max} 215(ε 834).

IR: ν_{max} 1530(s), 1550(s), 1645(m), 1655(m)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.84(t, J= 7.21 Hz, 9H, C_4,), 1.18-1.43(m, 12H, C_1, & C_3,), 1.49-1.62(m, 6H, C_2,), 5.65(dd, J=2.29 & 9.80 Hz, 1H, C3), 6.07(dd, J=9.80 & 17.24 Hz, 1H, C2), 6.22 (dd, J=2.29 & 17.24 Hz, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.60(C_4,), 16.46(C_1,), 27.00(C_3,), 27.64 (C_3,), 129.18(C2), 130.35(C3), 171.36(C1).

% Analysis for $C_{15}H_{30}SnO_2$:

Found :	C	49.60	H	8.27	Sn	32.90
Calcd.:	C	49.89	H	8.37	Sn	32.87

General Procedure - I :

A solution of unsaturated acid (20 m mole) and bis tri-n-butyltin oxide (10 m mole) in dry benzene(30 ml) was heated under reflux for 3 hours with azeotropic removal of water using a Dean - Stark trap. The volatiles were removed under vacuo and the residue was purified as described below:

Tri-n-butylstannyl crotonate (27) :

A mixture of crotonic acid (1.5g, 0.0174 mole) and

bis tri-n-butyltin oxide (5.19g, 0.0087 mole) was refluxed in benzene (30 ml) following the general procedure I. The residue was crystallised twice from light petroleum to furnish(27) as colourless needles, 5.62g (86%), m.p. 81°C (lit.[134] m.p. 84°C).

UV (EtOH) : λ_{max} 224(ε=1, 618).

IR : ν_{max} 1535(s), 1555(s), 1655(s) cm^{-1}.

^{1}H-NMR ($CDCl_3$) : δ 0.85(t, J=7.25 Hz, 9H, C_4,), 1.20-1.39(m, 12H, C_1, & C_3,), 1.54-1.74(m, 6H, C_2,), 1.81(d, J=1.70, small allylic coupling, and 6.90 Hz, 3H, C4), 5.84(d, J=1.7 Hz, small allylic coupling, and 15.40 Hz, 1H, C2), 6.84(m, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.62(C_4,), 16.41(C_1,), 17.75(C4), 27.02 (C_3,), 27.67(C_2,), 124.30(C2), 143.22(C3), 171.81(C1).

% Analysis for $C_{16}H_{32}SnO_2$:

Found :	C	51.12	H	8.46	Sn	31.50
Calcd.:	C	51.23	H	8.59	Sn	31.64

Tri-n-butylstannyl cinnamate (28) :

The reaction was carried out with 2g(0.0134 mole) of cinnamic acid and 4.02g(0.0067 mole)of bis tri-n-butyltin oxide in refluxing benzene (20 ml) following the general procedure I. The residue was purified by silica-gel column

chromatography. Elution with 25% benzene-ligh petroleum afforded colourless needles or the desired compound(28), (5.31g, 90%), m.p. 71°C (lit.[134] m.p. 69-70°C).

UV(EtOH): λ_{max}215(ϵ=5,250), 270(ϵ=6,700).

IR : ν_{max} 1540(s), 1555(s), 1580(m), 1640(s)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.92(t, J=7.22 Hz, 9H, C_4,), 1.27-1.42(m, 12H, C_1, & C_3,), 1.58-1.71(m, 6H, C_2,), 6.49(d, J=15.94 Hz, 1H, C2), 7.33-7.39(m, 3H, Aromatic), 7.47-7.52(m, 2H, Aromatic), 7.61(d, J=15.94 Hz, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.68(C_4,), 16.57(C_1,), 27.09(C_3,), 27.72 (C_2,), 120.06(C6 & C8), 127.93 & 128.77(C4 & C2), 129.72(C5 & C9), 135.04(C7), 143.84(C3), 172.12(C1).

% Analysis for $C_{21}H_{34}SnO_2$:

Found :	C	57.45	H	7.68	Sn	27.23
Calcd.:	C	57.69	H	7.84	Sn	27.14

Tri-n-butylstannyl p-nitro cinnamate(29)

It was prepared from 3g(0.0155 mole) of p-nitro cinnamic acid and 4.6g(0.0077 mole) of bis tri-n-butyltin oxide dissolved in 25 ml benzene following the general Procedure I. Residue was crystallised twice from

light petroleum afforded yellow coloured crystals of tri-n-butylstannyl p-nitro cinnamate(29), (6.29g, 84%), m.p. 76°C.
UV(EtOH) : λ_{max} 232(ϵ=41,622), 305(ϵ=78,709).
IR : ν_{max} 1550(s), 1563(s), 1595(s), 1635(m)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.90(t,J=7.23 Hz, 9H, C_4,), 1.15-1.48(m, 12H, C_1, & C_3,), 1.57-1.71(m, 6H, C_2,), 6.58(d, J=15.99 Hz, 1H, C2), 7.59(d, J=15.99 Hz, 1H, C3), 7.63(dd, J=1.8 & 8.80 Hz, 2H, C5 & C9), 8.20(dd, J=1.8 & 8.80 Hz, 2H, C6 & C8).

^{13}C-NMR($CDCl_3$): δ 13.63(C_4,), 16.65(C_1,), 27.03(C_3,); 27.82(C_2,), 124.06(C6 & C8), 124.76(C2), 128.40(C5 & C9), 140.61(C4), 141.40(C3), 148.17(C7), 170.87(C1).

^{119}Sn-NMR($CDCl_3$): δ +120.258

% Analysis for $C_{21}H_{33}NSnO_4$:

Found :	C	52.43	H	6.73	N	2.81	Sn	24.73
Calcd. :	C	52.31	H	6.89	N	2.90	Sn	24.61

Tri-n-butylstannyl sorbate (30) :

A mixture of 2g(0.0178 mole) of sorbic acid and 5.31g(0.0089 mole) of bis tri-n-butyltin oxide was refluxed in 30 ml benzene following the general procedure I. The

residue was purified by recrystallisation from light petroleum to furnish colourless, neddle-shaped crystals of the desired compound(30) (6.08g, 85%), m.p. 84-85°C.

UV(EtOH): λ_{max} 252(ϵ=28,559).

IR: ν_{max} 1500(s), 1600(s), 1625(m)cm^{-1}

^{1}H-NMR($CDCl_3$): δ 0.88(t, J=7.22 Hz, 9H, C_4,), 1.10-1.44(m, 12H, C_1, & C_3,), 1.53-1.72(m, 6H, C_2,), 1.80(d, J=6.14 Hz, 3H, C6), 5.79(d, J=15.22 Hz, 1H, C2), 5.96-6.21(m, 2H, C5 & C4), 7.15(dd, J= 13.76 & 15.22 Hz, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.61(C_4,), 16.46(C_1,), 18.51(C6), 27.02 (C_3,), 27.68(C_2,), 120.87(C2), 130.10(C4), 137.58(C5), 144.19(C3), 172.46(C1).

^{119}Sn-NMR($CDCl_3$): δ +106.576

% Analysis for $C_{18}H_{34}SnO_2$:

Found :	C	54.05	H	8.73	Sn	29.73
Calcd. :	C	53.89	H	8.54	Sn	29.59

Tri-n-butylstannyl but-2-ynoate (32) :

A mixture of but-2-ynoic acid (1.5g, 0.0178 mole) and bis-tri-n-butyltin oxide (5.31g, 0.0089 mole) was refluxed in 30 ml benzene following the general procedure I.

Volatiles were removed and an oily mass was obtained. On scratching it was solidified. Solids were dissolved in minimum volume of light petroleum. Evaporation of solvent afforded the colourless crystal of(32), (5.19g, 78%), m.p. 65-66°C.

UV($CHCl_3$): λ_{max} 240(ϵ=182).

IR: ν_{max} 1540(s), 1560(s), 2250(s) cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.84(t, J=7.19 Hz, 9H, C_4,), 1.09-1.40(m, 12H, C_1, & C_3,), 1.49-1.68(m, 6H, C_2,), 1.88(s, 3H, C4).

^{13}C-NMR($CDCl_3$): δ 3.75(C4), 13.56(C_4,), 16.81(C_1,), 27.02(C_3,), 27.69(C_2,), 73.84(C2), 82.79(C3), 158.54(C1).

^{119}Sn-NMR($CDCl_3$): δ +131.811

% Analysis for $C_{16}H_{30}SnO_2$:

Found :	C	51.72	H	8.23	Sn	31.60
Calcd.:	C	51.50	H	8.10	Sn	31.81

Tri-n-butylstannyl phenylpropynoate (33)

A solution of 2.5g (0.017 mole) phenylpropynoic acid and 5.10g(0.0085 mole) of bis tri-n-butyltin oxide was heated under reflux in 30 ml benzene following the general

procedure I. Solvents were removed and an oily mass was obtained. The residue was dissolved in minimum amount of light petroleum and kept in refrigerator. After few days crystals were appeared which was separated out by filtration and washed with little amount of chilled light petroleum to furnish colourless crystals of (33), (4.24g, 57%) m.p. 56-57°C (lit.[135] m.p. 57-58°C).

UV($CHCl_3$): λ_{max} 252(ϵ=12,448), 264(ϵ=10,968).

IR: ν_{max} 1505(s), 1560(m), 2125(w), 2310(w)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.91(t, J=7.21 Hz, 9H, $C_{4'}$), 1.20-1.46(m, 12H, $C_{1'}$ & $C_{3'}$), 1.58-1.70(m, 6H, $C_{2'}$), 7.32-7.38(m, C6, C7 & C8), 7.55(d, J=6.72 Hz, 2H, C5 & C9).

^{13}C-NMR($CDCl_3$): δ 13.61($C_{4'}$), 16.96($C_{1'}$), 27.06($C_{3'}$), 27.75($C_{2'}$), 82.26(C2), 83.93(C3), 120.66(C6), 128.39(C4), 129.91(C5), 132.82(C7), 158.74(C1).

% Analysis for $C_{21}H_{32}SnO_2$:

Found :	C	57.81	H	7.63	Sn	27.01
Calcd.:	C	57.96	H	7.41	Sn	27.27

Tri-n-butylstannyl cyclohexylidene acetate (31) :

The reaction was carried out by mixing 1.5g(0.0107

mole) cyclohexylidene acetic acid and 3.19g(0.0053 mole) bis tri-n-butyltin oxide in neat. An immediate exothermic reaction was ensured. Crystals were appeared from the clear reaction mixture at room temperature and within a few minutes the whole reaction mixture became solidified. The residue was crystallised from light petroleum afforded needle shaped colourless crystals of tri-n-butylstannyl cyclohexylidene acetate (31), (3.67g, 80%), m.p. 80°C.

UV(EtOH): λ_{max} 225(ϵ=943).

IR: ν_{max} 1548(s), 1567(s), 1625(m) cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.83(t, J=7.22 Hz, 9H, $C_{4'}$), 1.04-1.41(m, 16H, Cyclohexenyl, $C_{1'}$ & $C_{3'}$), 1.48-1.66(m, 6H, $C_{2'}$), 1.94 (br. s, 4H, Cyclohexenyl), 2.87(br. s, 2H, C4), 5.47(s, 1H, C2).

^{13}C-NMR($CDCl_3$): δ 13.62($C_{4'}$), 16.41($C_{1'}$), 22.12(C6), 22.84 (C7), 25.30(C5), 27.00($C_{3'}$), 27.83($C_{2'}$), 28.38(C8), 44.30 (C4), 124.55(C2), 132.49(C3), 177.50(C1).

^{119}Sn-NMR($CDCl_3$): δ +108.213 and +100.281

% Analysis for $C_{20}H_{38}SnO_2$:

Found :	C	55.73	H	9.07	Sn	27.71
Calcd.:	C	55.97	H	8.92	Sn	27.65

General Procedure - II

To a solution of unsaturated acid(20 mmole) in either dry benzene or toluene (30 ml), bis triphenyltin oxide(10 mmole) was added. A slightly milky white solution was obtained which was turned into a clear solution after reflux for 4 hours azeotropically with a Dean-Stark water separator. After cooling to room temperature a small amount of powdery solid was precipitated which was removed by filtration. Volatiles were distilled out, the residue was dried in vacuo and purified as described below:

Triphenylstannyl Crotonate (34)

1.5g(0.0174 mole) of crotonic acid and 6.23g (0.0087 mole) of bis triphenyltin oxide were dissolved in 30 ml toluene and refluxed following the general procedure II. The residue was crystallised twice from chloroform-benzene mixture afforded colourless solids of (34), (6.06g, 80%), m.p.141-142°C.

UV($CHCl_3$): λ_{max} 241(ϵ=1,182).

IR: ν_{max} 1515(s), 1545(s), 1570(m), 1650(s)cm^{-1}.

^{1}H-NMR($CDCl_3$) δ 1.87(d, J=1.7 & 6.9 Hz, 3H, C4), 5.97(d, J=1.70 Hz, small allylic coupling, & 14.0 Hz, 1H, C2), 7.06 (m, 1H, C3), 7.37-7.50(m, 9H, Aromatic), 7.62-7.89(m, 6H, Aromatic).

^{13}C-NMR($CDCl_3$): δ 18.02(C4), 122.75(C2), 128.89(C_m), 130.07(C_p), 136.92(C_o), 138.59(C_i), 145.86(C_3), 173.07(C1).

^{119}Sn-NMR($CDCl_3$): δ -182.664

% Analysis for $C_{22}H_{20}SnO_2$:

Found :	C	60.59	H	4.47	Sn	27.19
Calcd.:	C	60.73	H	4.63	Sn	27.28

Triphenylstannyl p-nitro cinnamate (35)

A mixture of 2.5g(0.0129 mole) of p-nitro cinnamic acid and 4.63g(0.0064 mole) of bis triphenyltin oxide was heated under reflux in benzene following the general procedure II. The residue was recrystallised from acetone-petroleum mixture provided shining yellow crystals of (35), (6.17g, 88%), m.p. 178-179°C.

UV(EtOH): λ_{max} 222(ϵ=24,191), 305(ϵ=24,558).

IR: ν_{max} 1590(s), 1610(m), 1640(w) cm^{-1}.

^1H-NMR($CDCl_3$): δ 6.68(d, J=16.2 Hz, 1H,, C2), 7.37-7.54(m, 9H, Aromatic), 7.63(dd, J=1.80 & 8.80 Hz, 2H, C5 & C9), 7.75(d, J=16.2 Hz, 1H, C3), 7.78-7.83(m, 6H, Aromatic), 8.21 (dd, J=1.8 & 8.80 Hz, 2H, C6 & C8).

^{13}C-NMR($CDCl_3$): δ 123.15(C6 & C8), 124.15(C2), 128.59(C5 & C9), 129.06(C_3,), 130.37(C_4,), 136.93(C_2,), 138.04(C_1,), 140.96(C4), 142.38(C3), 148.40(C7), 171.99(C1).

^{119}Sn-NMR($CDCl_3$): δ -103.37

% Analysis for $C_{21}H_{33}NO_4Sn$:

Found :	C	52.45	H	6.64	N	2.83	Sn	24.57
Calcd.:	C	52.31	H	6.89	N	2.90	Sn	24.61

Triphenylstannyl sorbate (36)

2g (0.0178 mole) of sorbic acid and 6.38g(0.0089 mole) of bis-triphenyltin oxide were dissolved in 30 ml benzene and the solution was refluxed following the general procedure II. An oily residue was obtained after the removal of volatiles in vacuo,which on scratching for a long time was solidified. The solids were dissolved in acetone,after complete evaporation of solvent afforded crystalline off white product (36), (6.13g, 79%), m.p. 96-98°C.
UV(EtOH): λ_{max} 220(ε=88,615), 254(ε=91,076).
IR: ν_{max} 1575(w), 1610(m), 1635(w)cm^{-1}.

^1H-NMR($CDCl_3$): δ 1.73(d, J=5.84 Hz, 3H, C6), 5.80(d, J=15.56 Hz, 1H, C2), 5.94-6.16(m, 2H, C4 & C5), 7.13-7.40(m, 10H, C3

& Aromatic), 7.53-7.80(m, 6H, Aromatic).

^{13}C-NMR($CDCl_3$): δ 18.68(C6), 119.02(C2), 128.89(C_m), 130.06 (C4 & C_p), 136.94(C_o), 138.69(C_i), 139.07(C5), 146.27(c3), 173.85(C1).

% Analysis for $C_{24}H_{22}SnO_2$:

Found :	C	62.43	H	4.73	Sn	25.98
Calcd.:	C	62.51	H	4.81	Sn	25.74

Triphenylstannyl but-2-ynoate (37)

A solution of 1.5g(0.0178 mole) of but - 2- ynoic acid and 6.36g, (0.0089 mole) of bis triphenyltin oxide in 30 ml benzene was refluxed following the general procedure II. The residue was purified by crystallisation. Recrystallisation from acetone-light petroleum mixture provided colourless crystalline solids of (37), (5.87g, 76%,), m.p. 192-193°C.

UV($CHCl_3$): λ_{max} 240(ϵ=912), 258(ϵ=825).
IR: ν_{max} 1510(s), 1565(m), 2250(s)cm^{-1}.

^{1}H-NMR(D_6-DMSO):δ1.80(s, 3H, C4), 7.41-7.49(m, 9H, C_m, C_p), 7.63-7.91(m, 6H, C_o).

^{13}C-NMR(D_6-DMSO):δ 2.89(C4),76.77(C2), 79.33(C3), 128.34(C_m), 128.96(C_p), 136.08(C_o), 142.64(C_i), 156.75(C1).

^{119}Sn-NMR(D_6-DMSO):δ-250.807

% Analysis for $C_{22}H_{18}SnO_2$:

Found :	C	61.15	H	4.20	Sn	27.55
Calcd.:	C	61.01	H	4.19	Sn	27.41

Triphenylstannyl phenylpropynoate (38)

A solution of phenylpropynoic acid (2.5g, 0.0171 mole) and bis triphenyltin oxide (6.13g, 0.0085 mole) in benzene was refluxed following the general procedure II. The crude residue was recrystallised from chloroform-benzene mixture to furnish colourless needles of (38) (7.51g, 90%), m.p. 118-120°C(lit.[135] # m.p. 175-176°C).

UV($CHCl_3$): λ_{max} 258(ϵ=13,000).

IR: ν_{max} 1515(s), 1570(m), 2220(m) cm^{-1}.

^{1}H-NMR($CDCl_3$):δ 7.30-7.55((m, 14H, C5, C6, C7, C8, C9 & C_m, C_p), 7.61.7.88(m, 6H, C_o).

^{13}C-NMR($CDCl_3$): δ 81.49(C2), 86.21(C3), 120.30(C6), 128.49 (C4), 129.08(C_m), 130.27(C5), 130.45(C_p), 132.94(C7),

136.95(C_o), 137.58(C_i), 159.77(C1).

% Analysis for $C_{27}H_{20}SnO_2$:

Found :	C	65.69	H	4.12	Sn	23.62
Calcd.:	C	65.49	H	4.07	Sn	23.97

Although the melting point of compound(38) did not match with the literature value, the spectral and elemental data suggested our assigned structure to be correct.

I.A-4.2 : Reaction of α,β-unsaturated stannyl carboxylates with Hg(II) salts (X = Cl, OAc)

General Procedure

To a solution of α,β-unsaturated stannyl carboxylates (2 mmole) in a solvent(10 ml) were added mercury(II) salts (2 mmole) (HgX_2; X = Cl, OAc) and the mixture was either stirred at room temperature (in case of methanol) or heated under gentle reflux (in the case of benzene or acetonitrile) for several hours noted in TABLE-VI. A small amount of white solid was precipitated during the reaction which was filtered off. [In the case of tri-n-butyl stannyl but-2-ynoate(32), a large amount of gelatinous

precipitate appeared when its solution in MeOH was treated with mercuric acetate at room temperature. After 48 hours the deposites were filtered off]. The filtrate was diluted with ether and the organic layer was washed with aqueous sodium chloride and dried over anhydrous Na_2SO_4.Evaporation of the solvents afforded a solid residue which was crystallised from light petroleum to furnish shining flakes of BuHgCl(from tri-n-butylstannyl esters) or white leaflets of PhHgCl(from triphenylstannyl esters). BuHgCl and PhHgCl were characerised by physical/spectral data and their yields(%) were recorded in **TABLE-VI.**

Characterisation of BuHgCl :

m.p. 128°C (lit.[138] 127-130°C).

^{1}H-NMR($CDCl_3$): δ 0.95(t, 3H, J=7.29 Hz), 1.34-1.48(m, 2H), 1.67-1.78(m, 2H), 2.1(t, 2H, J=7.13 Hz).

^{13}C-NMR($CDCl_3$), ppm for APT spectra a(+) indicates 0 or 2 attached protons and a(-) indicates 1 or 3 attached protons) δ 13.47(-), 27.81(+), 30.09(+), 33.06(+).

% Analysis for C_4H_9HgCl (sublimed at 90-110°C/1 mm Hg and recrystallised from benzene-light petroleum).

Found :	C	16.08	H	3.17
Calcd.:	C	16.38	H	3.07

Characterisation of PhHgCl:

M.p.249-250°C (dec.) (lit.[139] m.p. 251°C), m.m.p. 248-249°C.

The mother liquor from the crystallisation was then diluted with ether and the acid was extracted with saturated aqueous sodium carbonate. The aqueous phase was separated and acidified with dilute hydrochloric acid(3N) under ice cold condition. The liberated acid was extracted with ether (3 x 25 ml) after saturating the aqueous part with sodium chloride. The combined ethereal layer was dried over anhydrous Na_2SO_4. The volatiles were removed and the residue was dried under vacuo. Recrystallisation from benzene-light petroleum afforded the acids, yield(%) of acids was recorded in the **TABLE-VI.** All the acids were characterised by physical and spectral data and found identical with the reported values.

^{1}H-NMR spectra of

$CH_2{=}CH{-}COOSn(\overset{1'}{C}H_2{-}\overset{2'}{C}H_2{-}\overset{3'}{C}H_2{-}\overset{4'}{C}H_3)_3$

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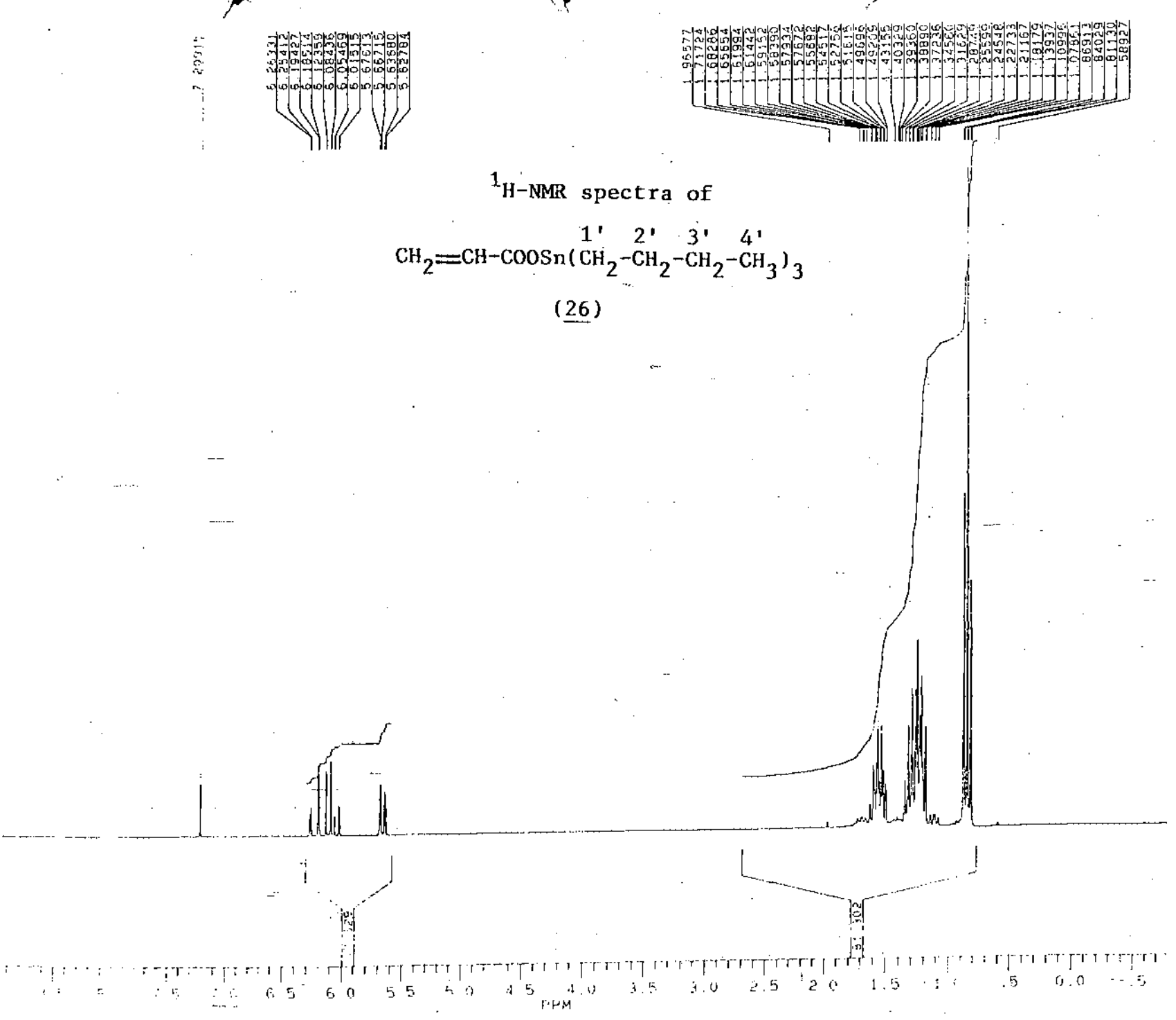


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^{13}C-NMR spectra of

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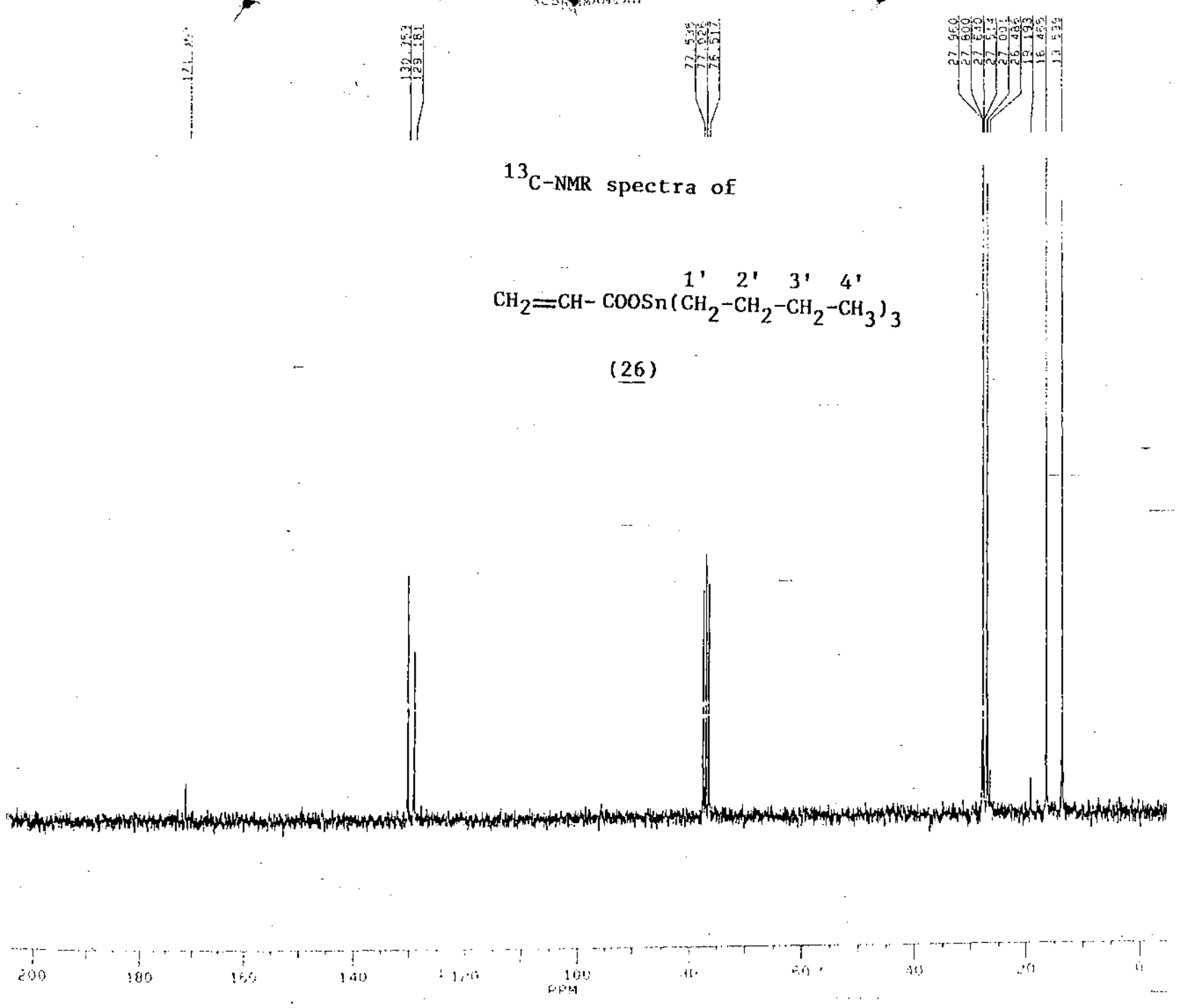
(26)



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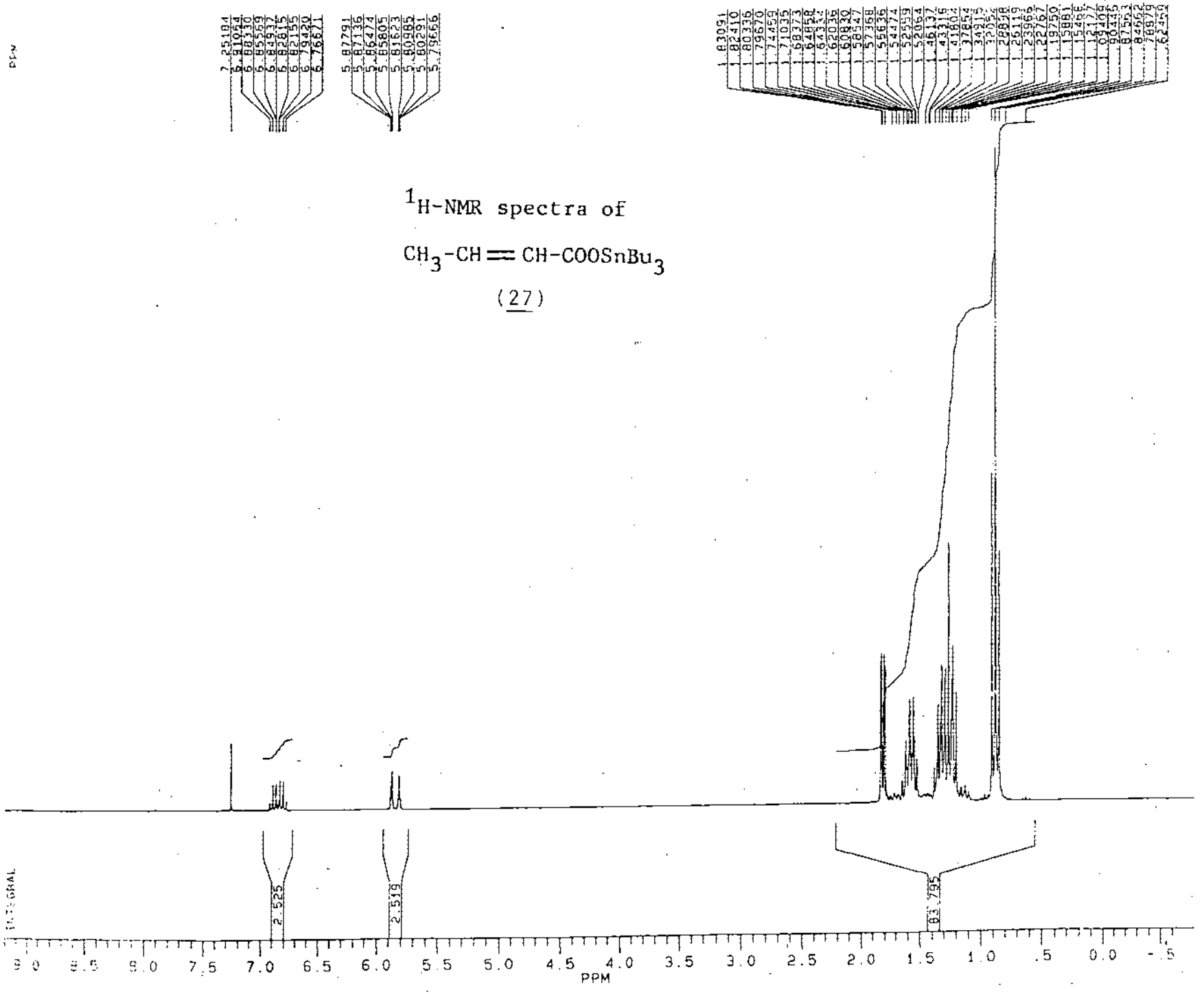
SUBRAMANIAN

^{1}H-NMR spectra of

$CH_3-CH=CH-COOSnBu_3$

(27)



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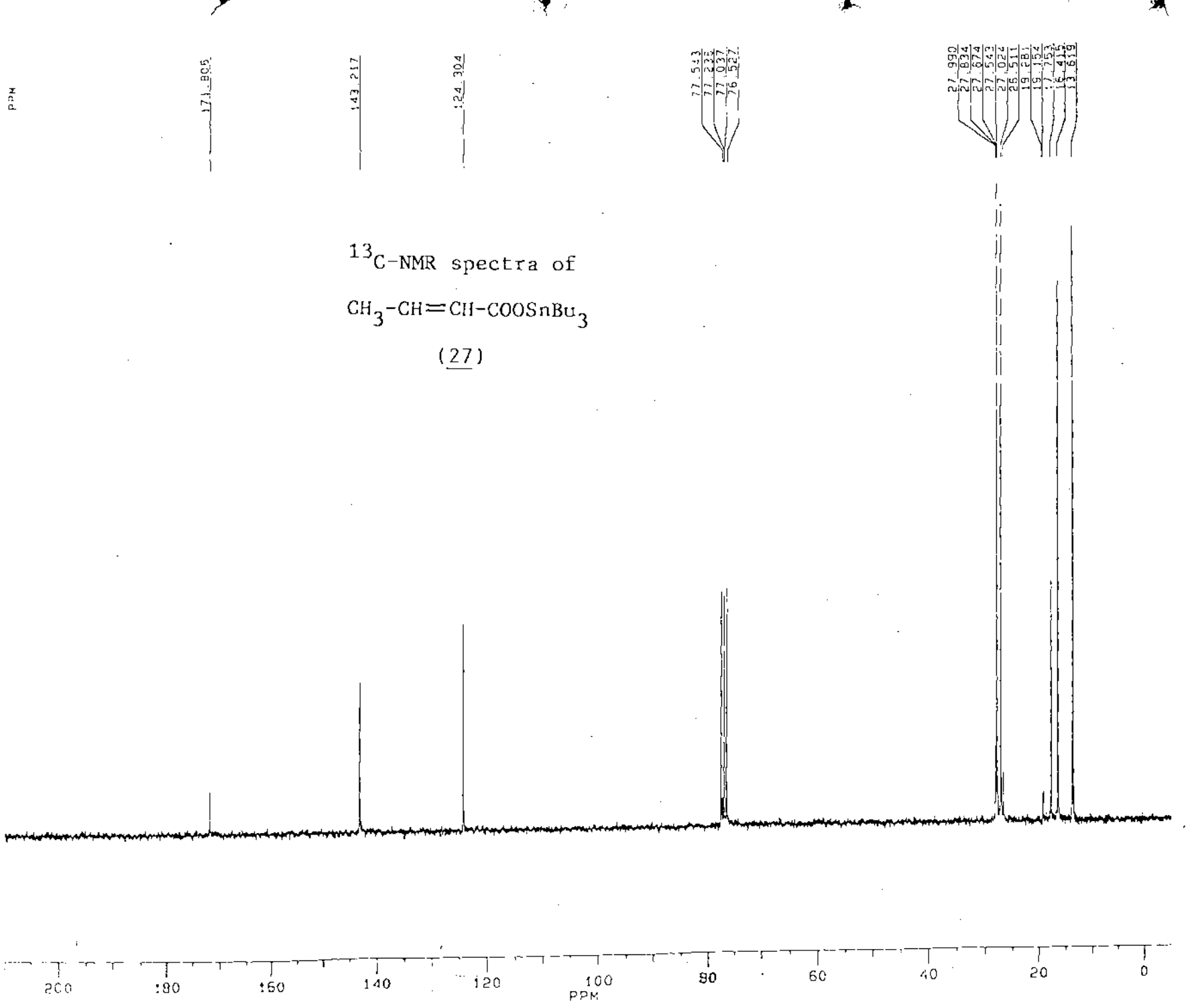

^{13}C-NMR spectra of

CH_3-CH=CH-COOSnBu_3

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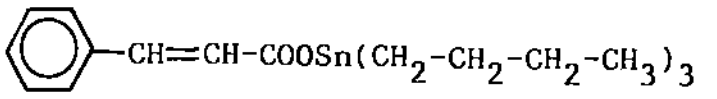

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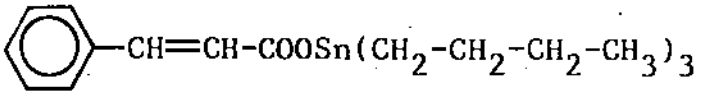

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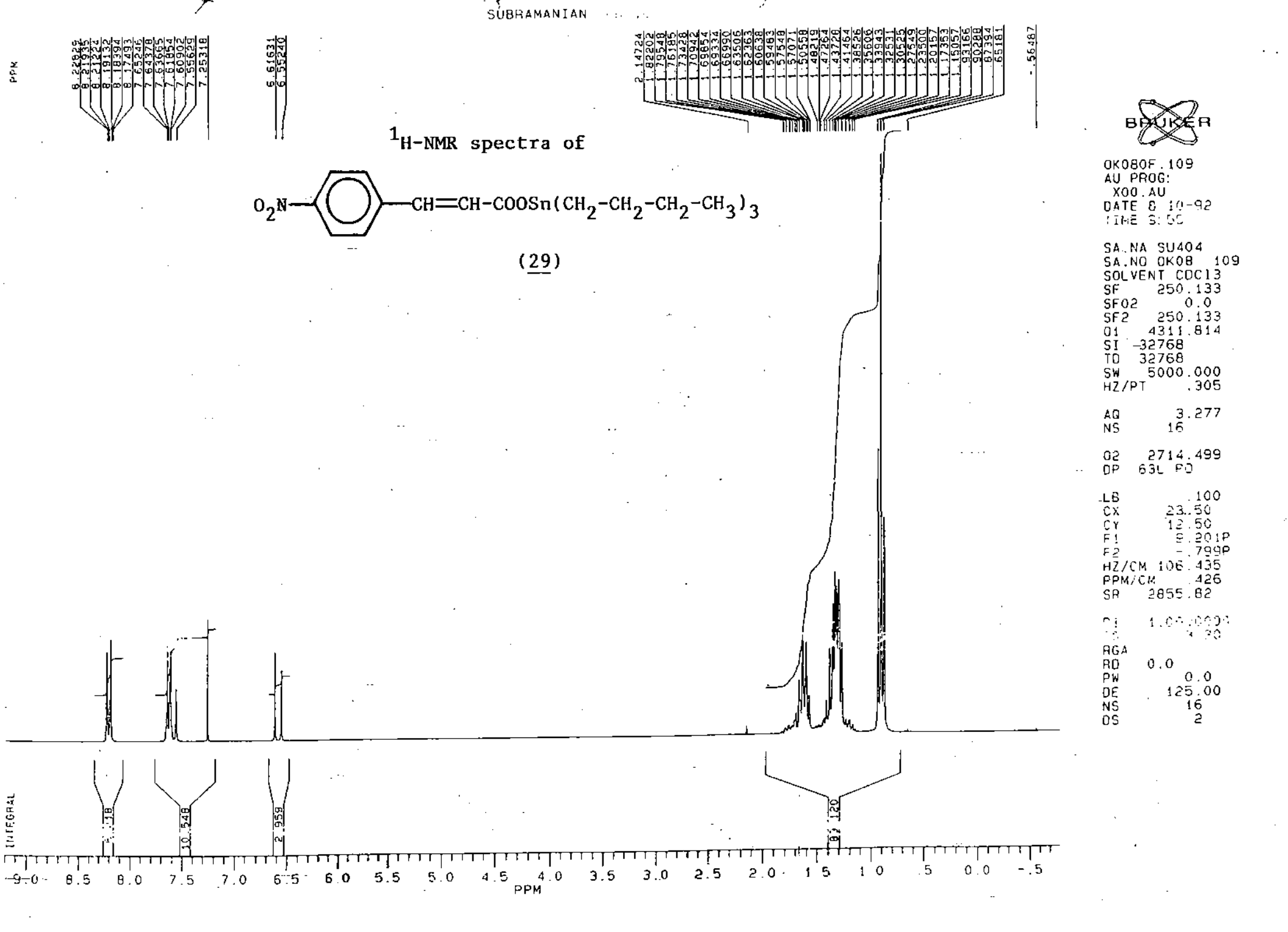

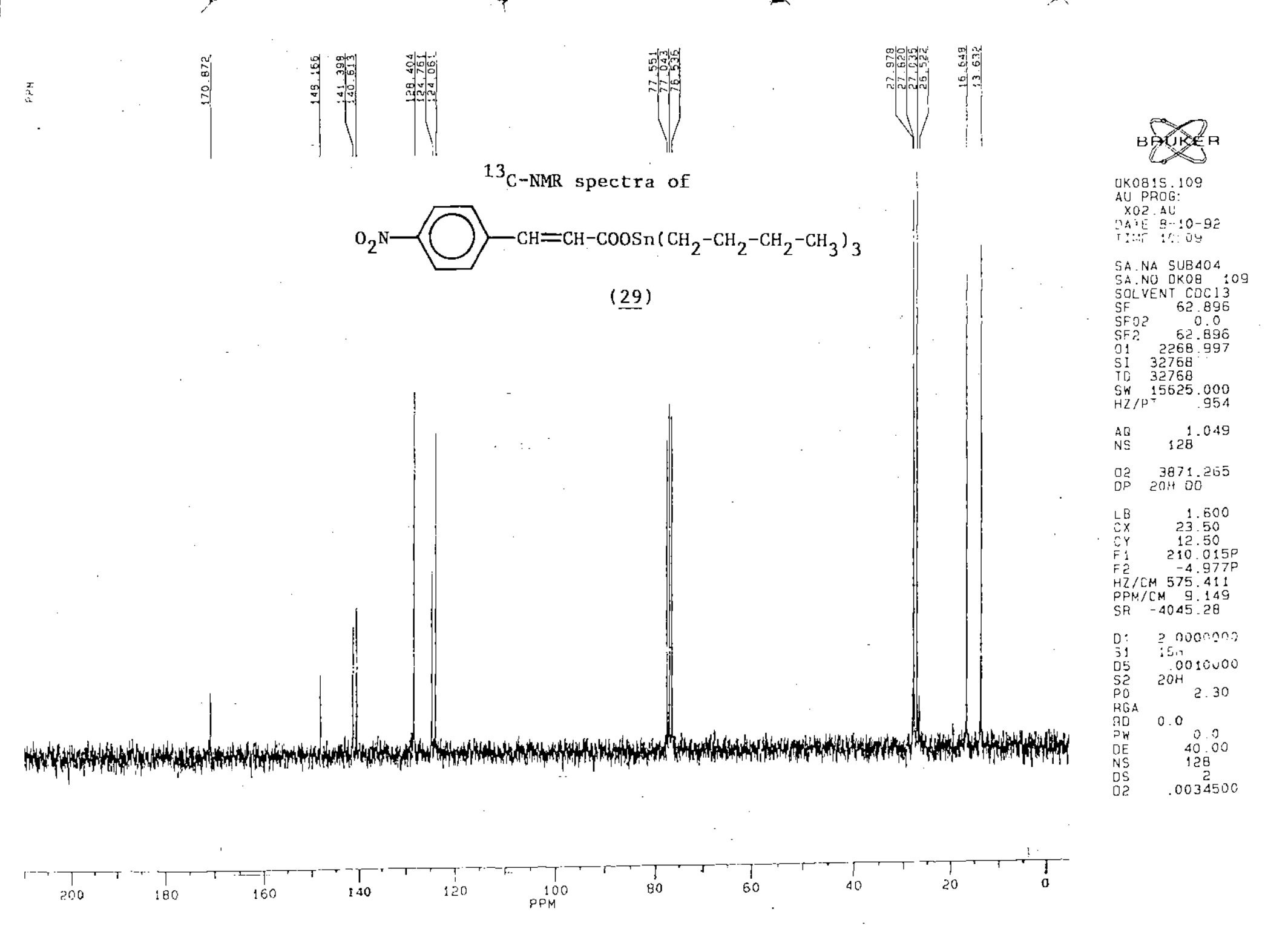

^{13}C-NMR spectra of

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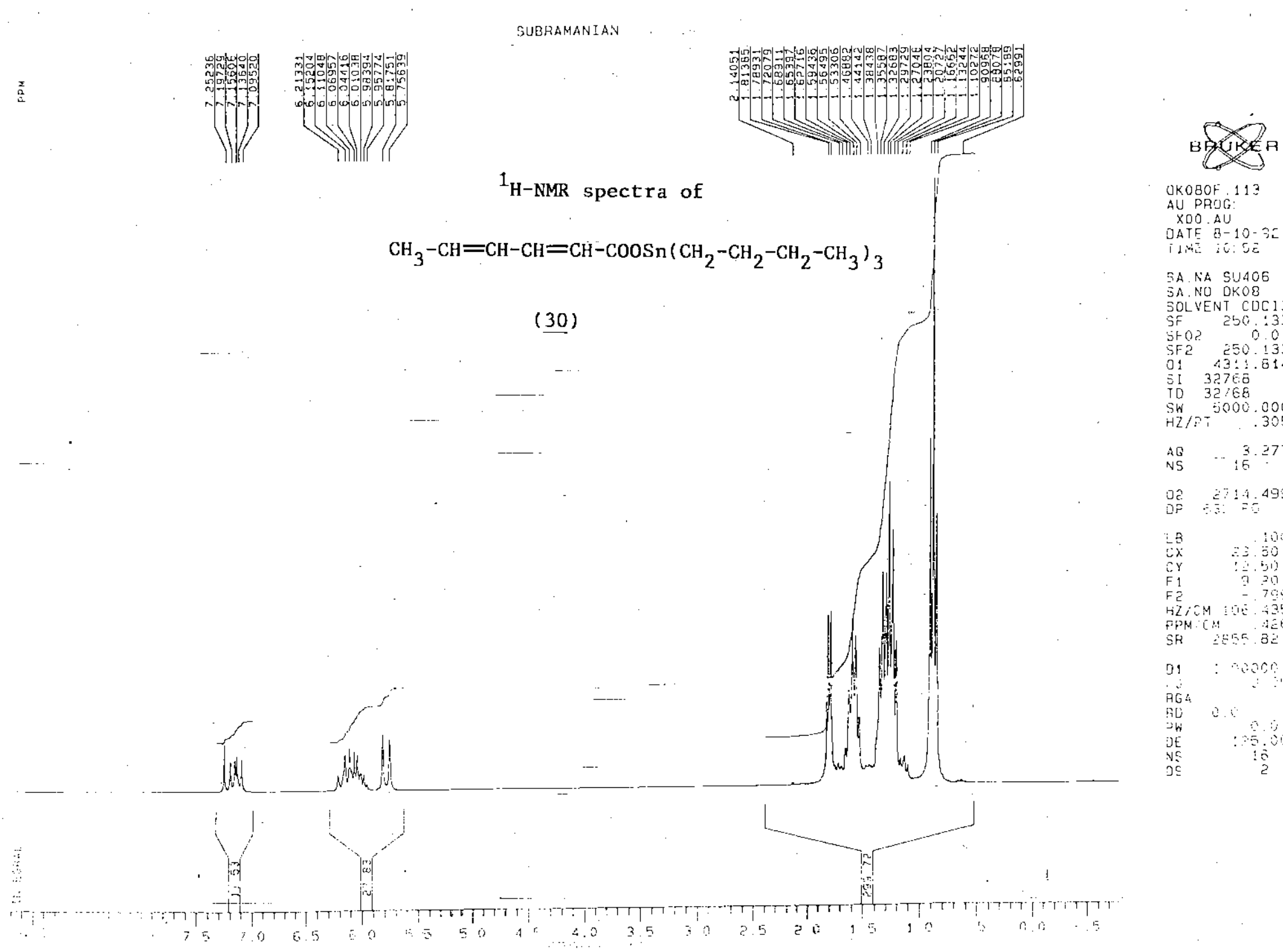


^{1}H-NMR spectra of

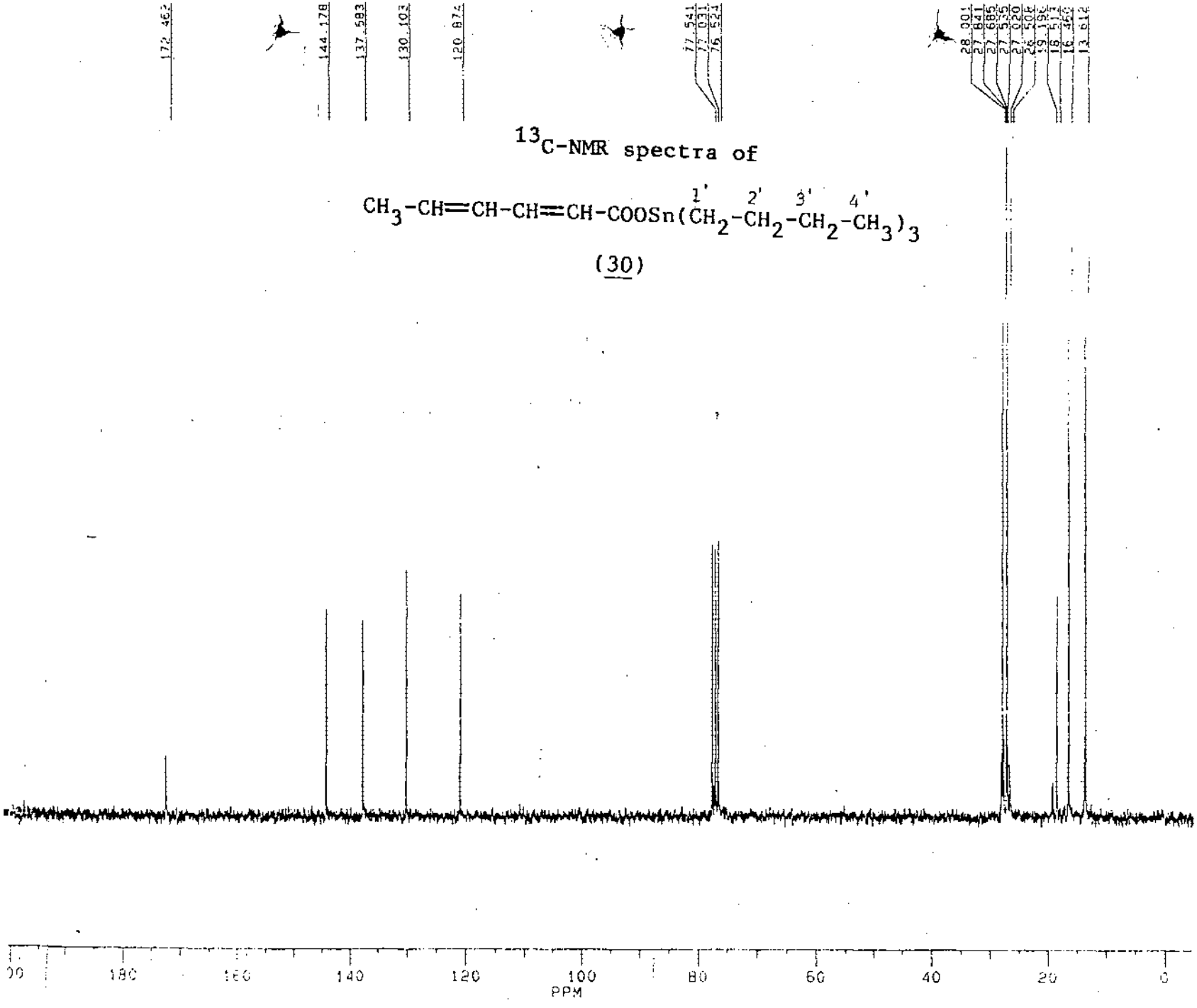
$CH_3-CH=CH-CH=CH-COOSn(CH_2-CH_2-CH_2-CH_3)_3$

(30)

^{13}C-NMR spectra of

$CH_3-CH=CH-CH=CH-COOSn(\overset{1'}{CH_2}-\overset{2'}{CH_2}-\overset{3'}{CH_2}-\overset{4'}{CH_3})_3$

(30)



BRUKER

DK08IS.113
AU PROG:
.YQ3.AU
DATE 8-10-92
TIME 11:09

SA.NA SUB406
SA.NO DK08 113
SOLVENT CDCl3
SF 62.896
SFO2
SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 256

O2 3871.265
OP 20H DO

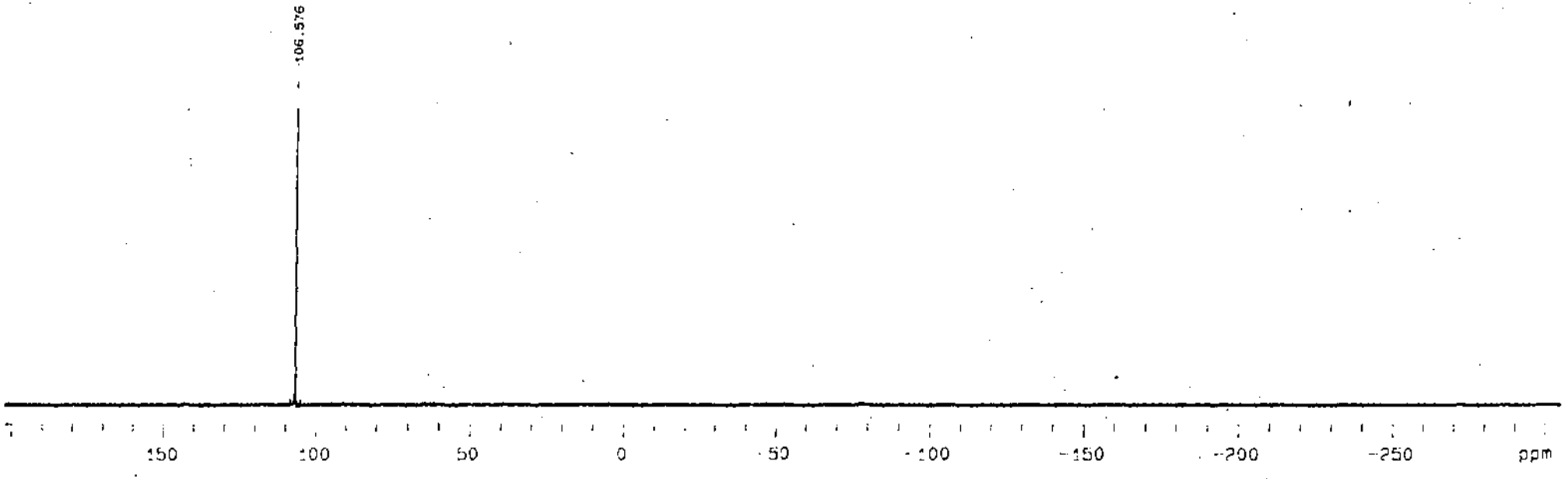
L8 1.600
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
D4 16H
D5 .0010000
S2 20H
P0 2.30
RGA
RD 0.0
PW 0 0
DE 40.00
NS 256
DS 2
D2 .0034500

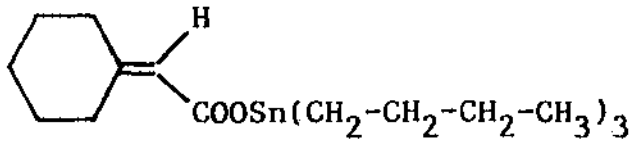
OBSERVE Sn119
Frequency 111.882 MHz
Spectral width 100.0 kHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 144
DECOUPLE H1
High power 50
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 262144
Total acquisition time 4 minutes

$CH_3-CH=CH-CH=CH-COOSnBu_3$

(30)



^{1}H-NMR spectra of



(31)

BRUKER

OK081F.110
AU PROG:
XQG.AU
DATE 9-10-92
TIME 10:25

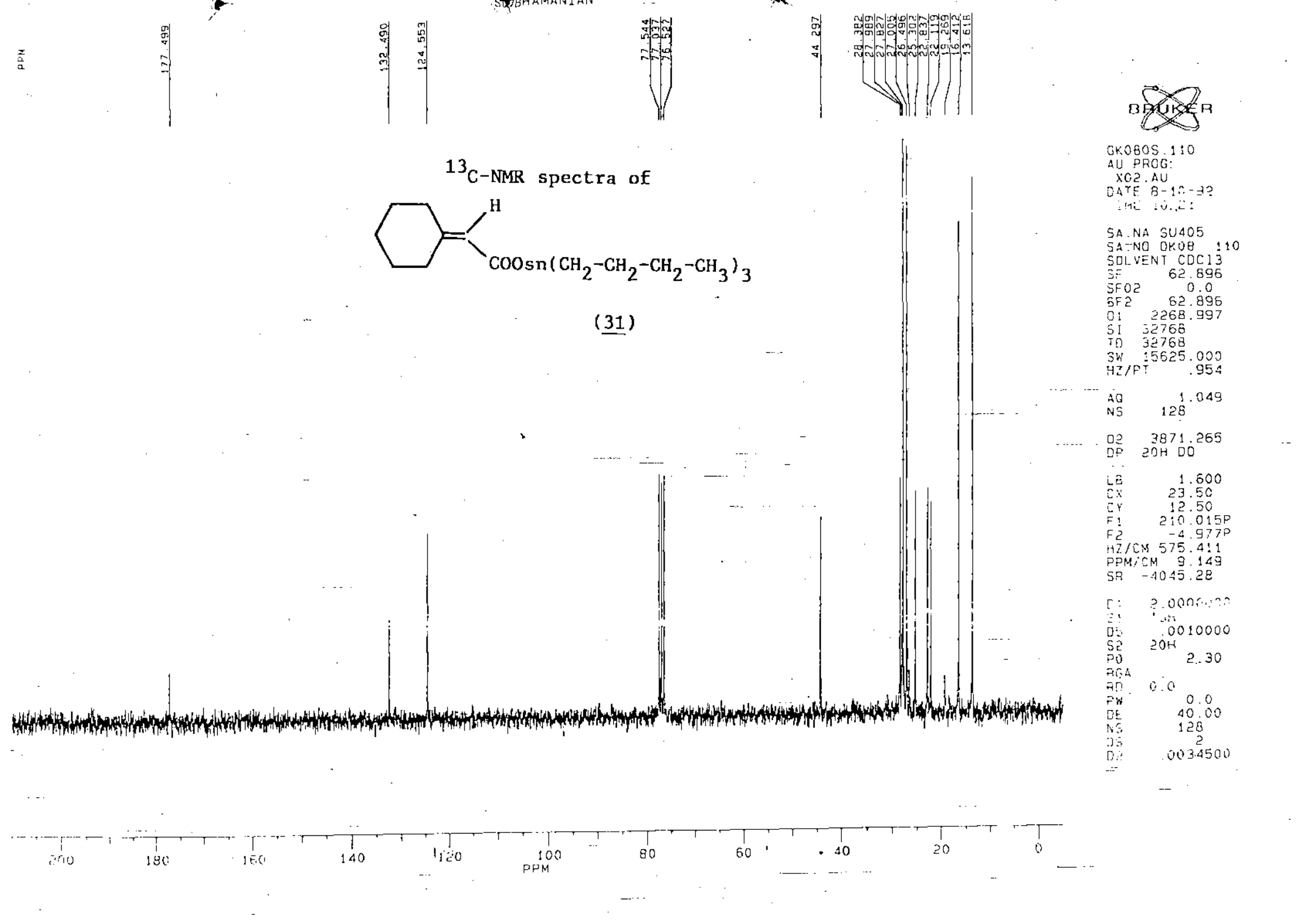
SA.NA SUB405
SA.NO OK08 110
SOLVENT CDCl3
SF 250.133
SFO2 0.0
SF2 250.133
O1 4311.814
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

AG 3.277
NS 16

O2 2714.499
DF 631.80

LB .100
GB 23.50
GC 12.80
P1 9.2019
P2 -.7998
PLW/CM 106.486
PPM/CM .426
SF 3866.50

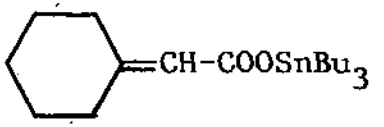
D1 1.0000000
D2 3.30
RG4
RD 0.0
PW 3.0
DE 125.00
NS 16
DS 2



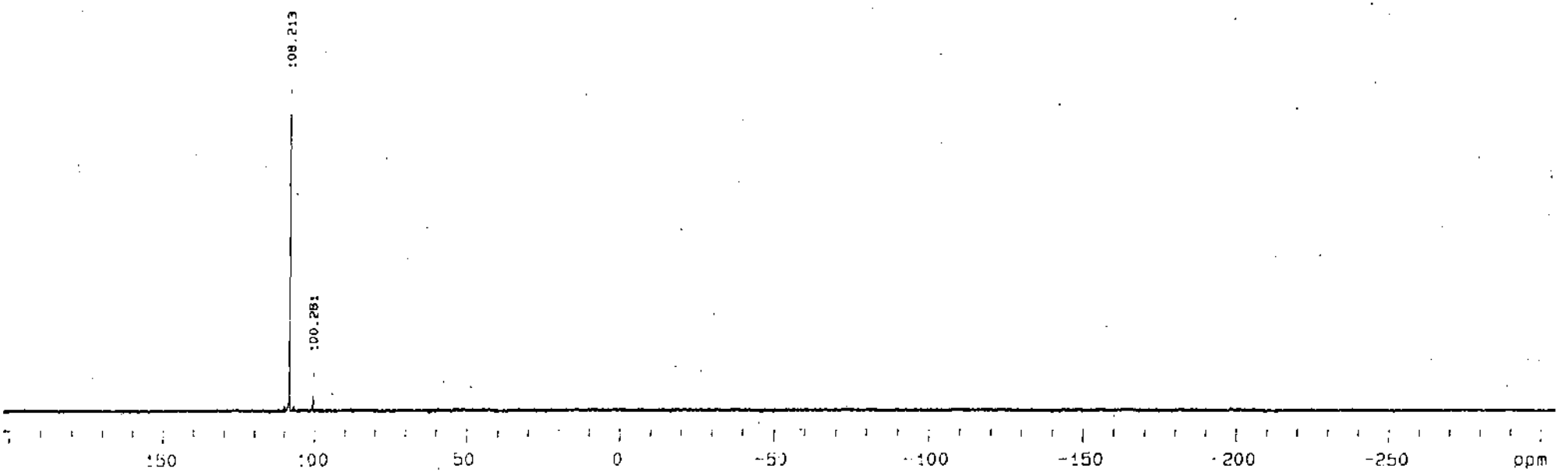
^{13}C-NMR spectra of

(31)

OBSERVE Sn119
Frequency 111.862 MHz
Spectral width 100.0 KHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 272
DECOUPLE H1
High power 50
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 262144
Total acquisition time 9 minutes



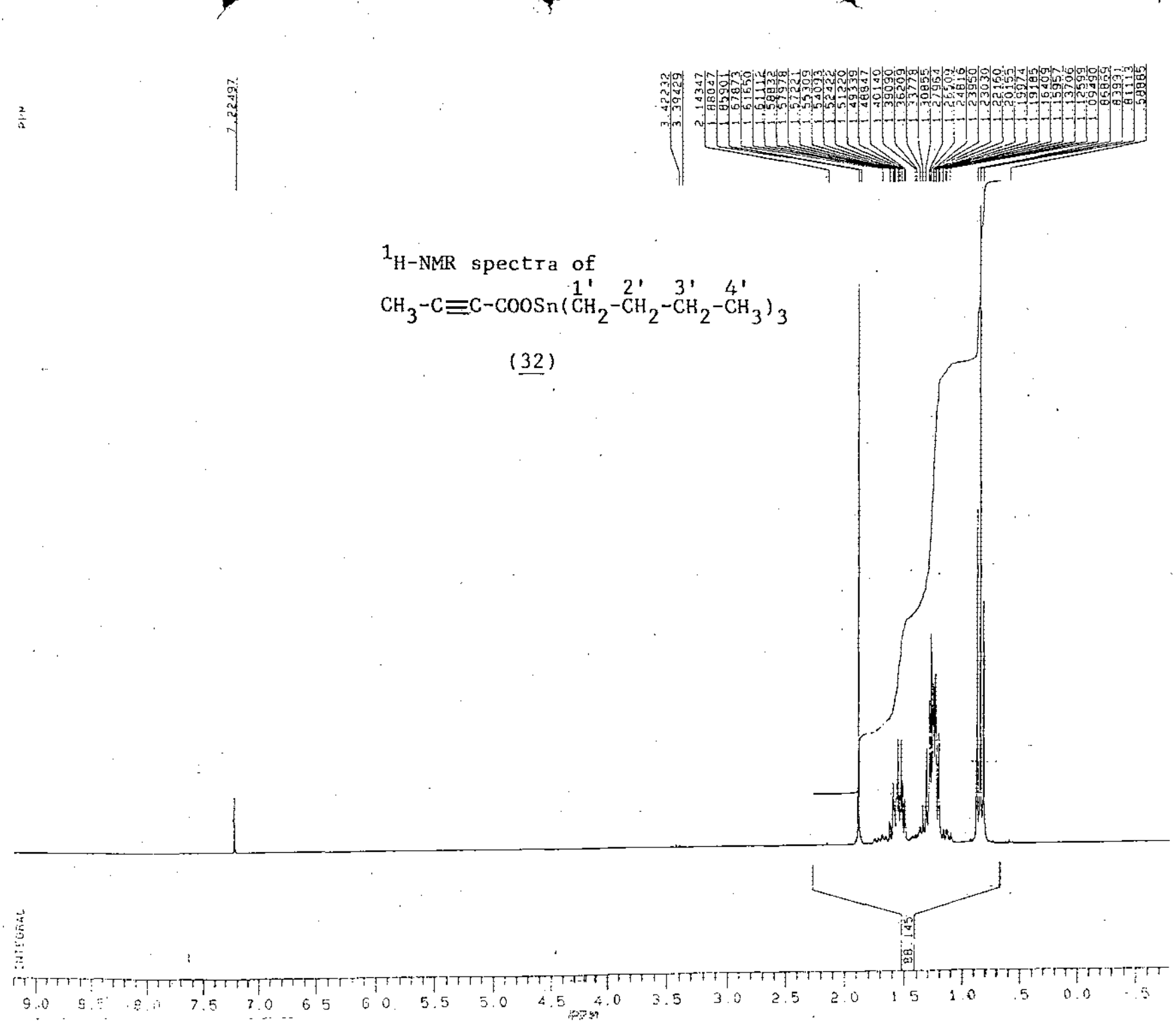
(31)



^{1}H-NMR spectra of

$CH_3-C\equiv C-COOSn(\overset{1'}{C}H_2-\overset{2'}{C}H_2-\overset{3'}{C}H_2-\overset{4'}{C}H_3)_3$

(32)



BRUKER

DK091F.109
AU PROG:
X0C.AU
DATE 9-10-92
TIME 11:01

SA.NA SUB438
SA.NO DK09 109
SOLVENT CDCl3
SF 250.133
SFO2 0.0
SF2 250.133
O1 4311.814
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

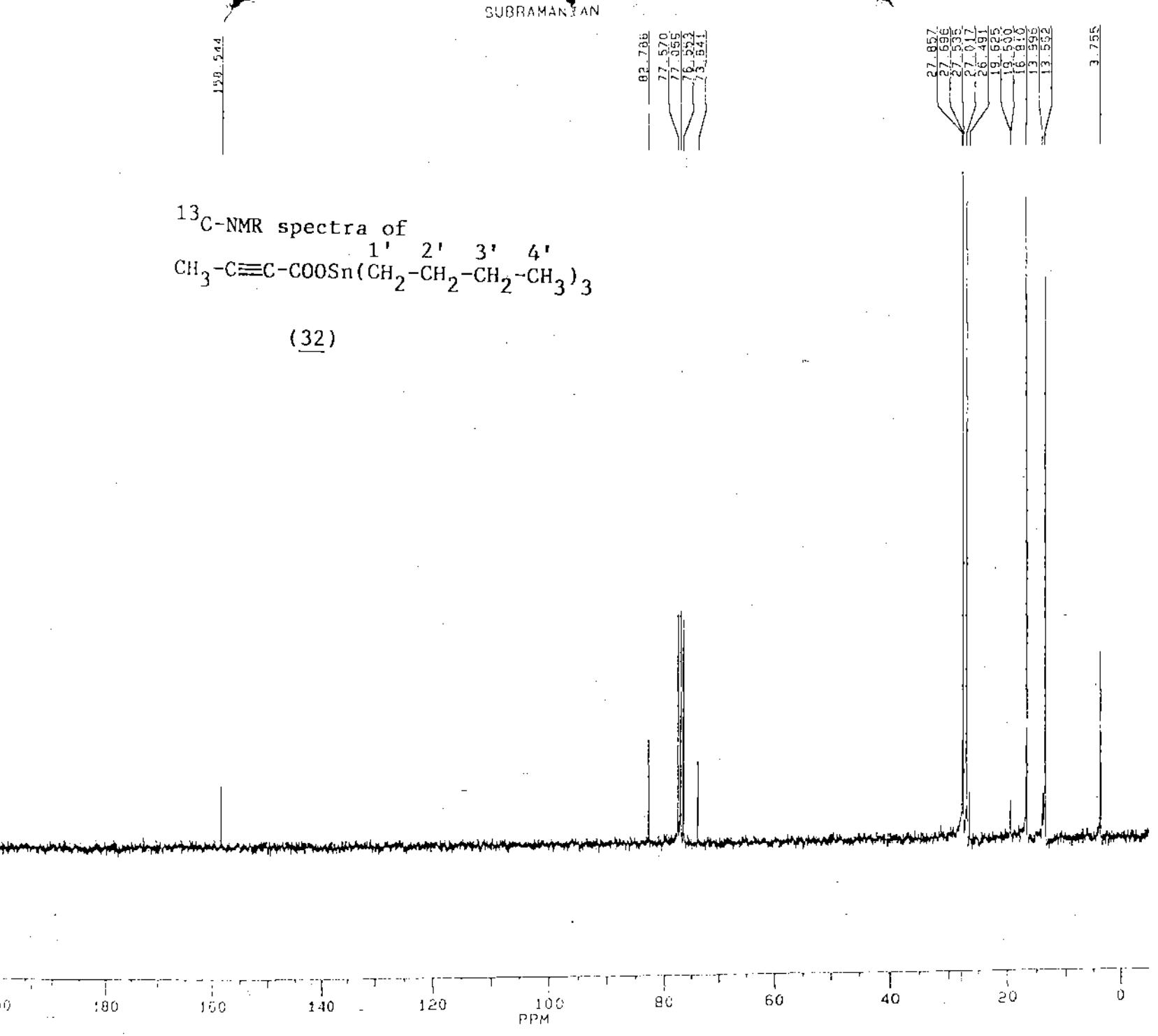
AQ 3.277
NS 16

O2 2714.499
DP 63L PO

LB .100
CX 23.50
CY 12.50
F1 9.201P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2962.84

D1 1.0000000
PO 3.00
RGA
RD 0.0
PW 0.0
DE 125.00
NS 16
DS 2

SUBRAMANIAN



^{13}C-NMR spectra of

$CH_3-C\equiv C-COOSn(\overset{1'}{CH_2}-\overset{2'}{CH_2}-\overset{3'}{CH_2}-\overset{4'}{CH_3})_3$

(32)

BRUKER

GK090S.109
AU PROG:
X02.AU
DATE 9-10-92
TIME 10:37

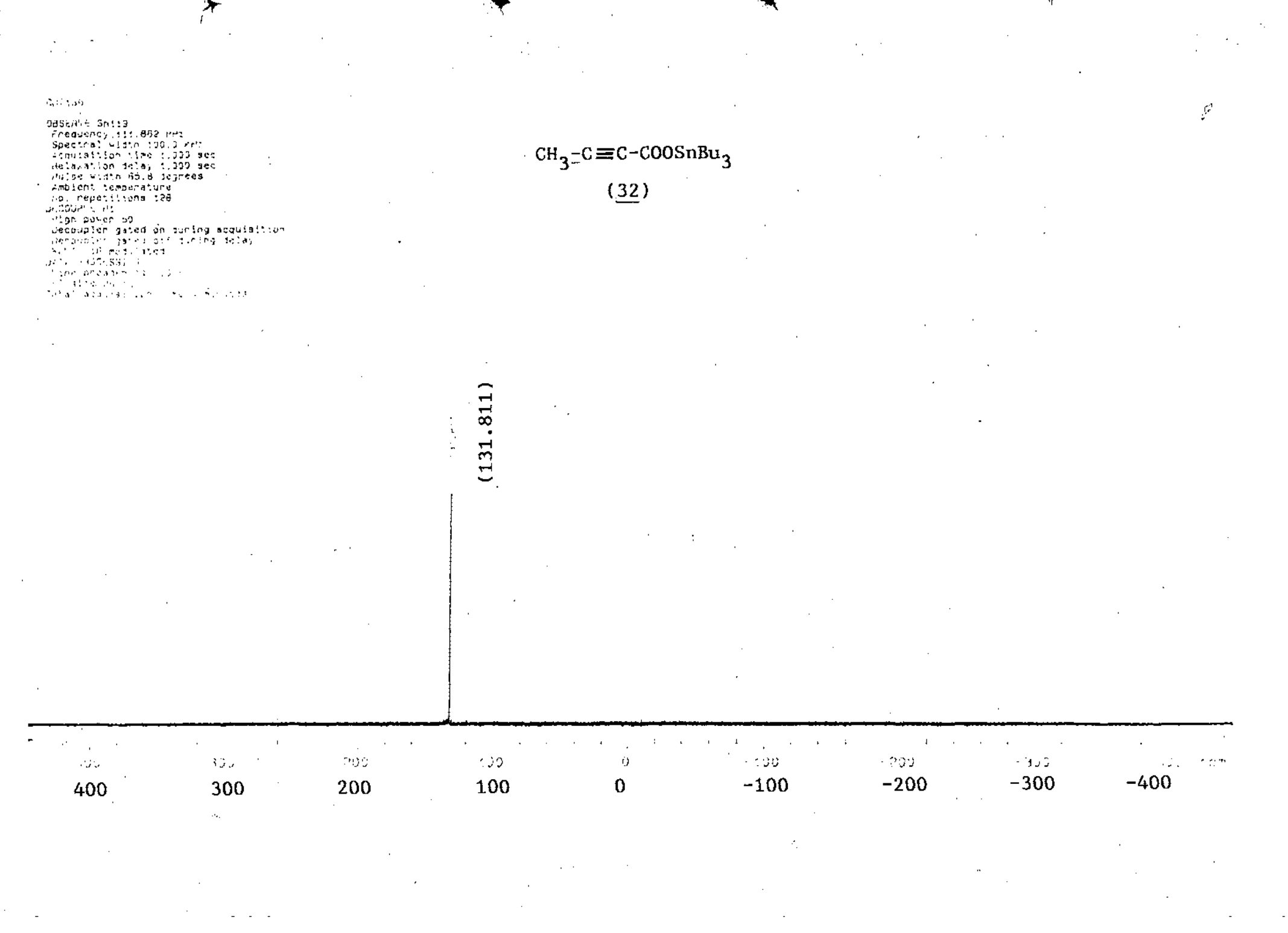
SA.NA SU438
SA.NO GK09 109
SOLVENT CDCl3
SF 62.896
SFO2 0.0
SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 256

O2 3871.265
OP 20H DO

LB 1.500
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
SI 32K
OS 0010000
S2 20H
PO 2.30
RGA
AD 0.0
PW 3.0
DE 40.00
NS 256
OS 2
O2 3871.265

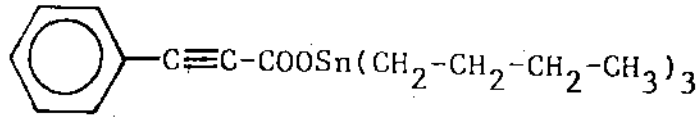


$CH_3-C\equiv C-COOSnBu_3$

(32)

SUBRAMANIAN

^{1}H-NMR spectra of



(33)

BRUKER

AP280F.112
AU PROG:
XOO.AU
DATE 28-4-93
TIME 11:48

SA:NA SU224
SA.NO AP28 112
SOLVENT CDCl3
SF 250.133
SFO2 0.0
SF2 250.133
SY 100.0
O1 4311.614
SI 32768
TD 32768
SW 5000.000
SW2 5000.000
HZ/PT .305

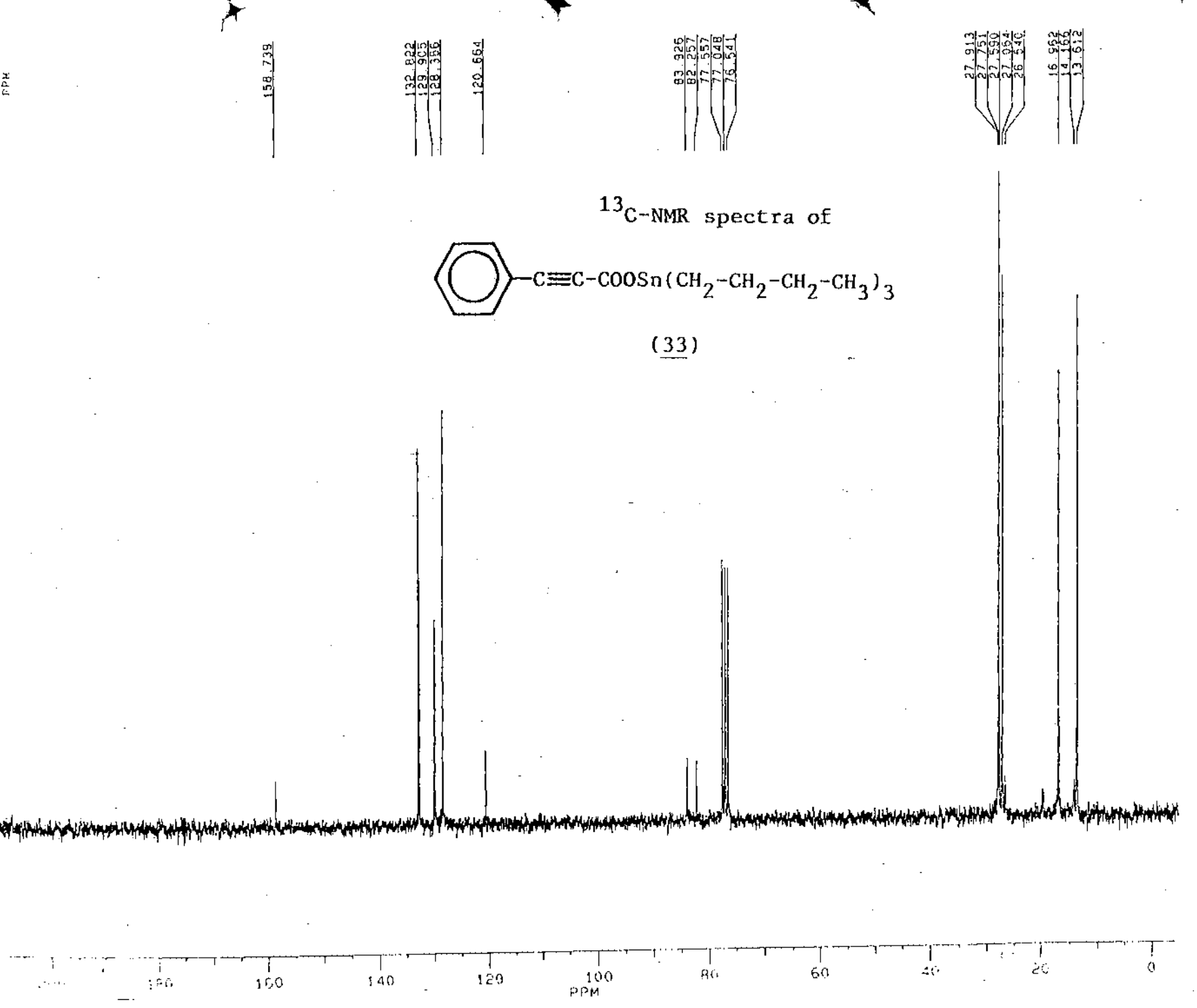
RD 0.0
AQ 3.277
RG 2
NS 16
TE 297

DE 125.0
FW 6300
O2 2714.499
DP 63L PO

LB .100
GB 0.0
NC -1
CX 23.50
CY 12.50
F1 9.201P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2855.82

D1 1.0000000
PO 3.30
RGA
RD 0.0
PW 0.0
DE 125.00
NS 16
DS 2

INTEGRAL
77.95
392.56
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0 -.5
PPM



^{13}C-NMR spectra of

(33)

BRUKER

AP2815.112
AU PROG:
.XO2.AU
DATE 28-4-93
TIME 12:06

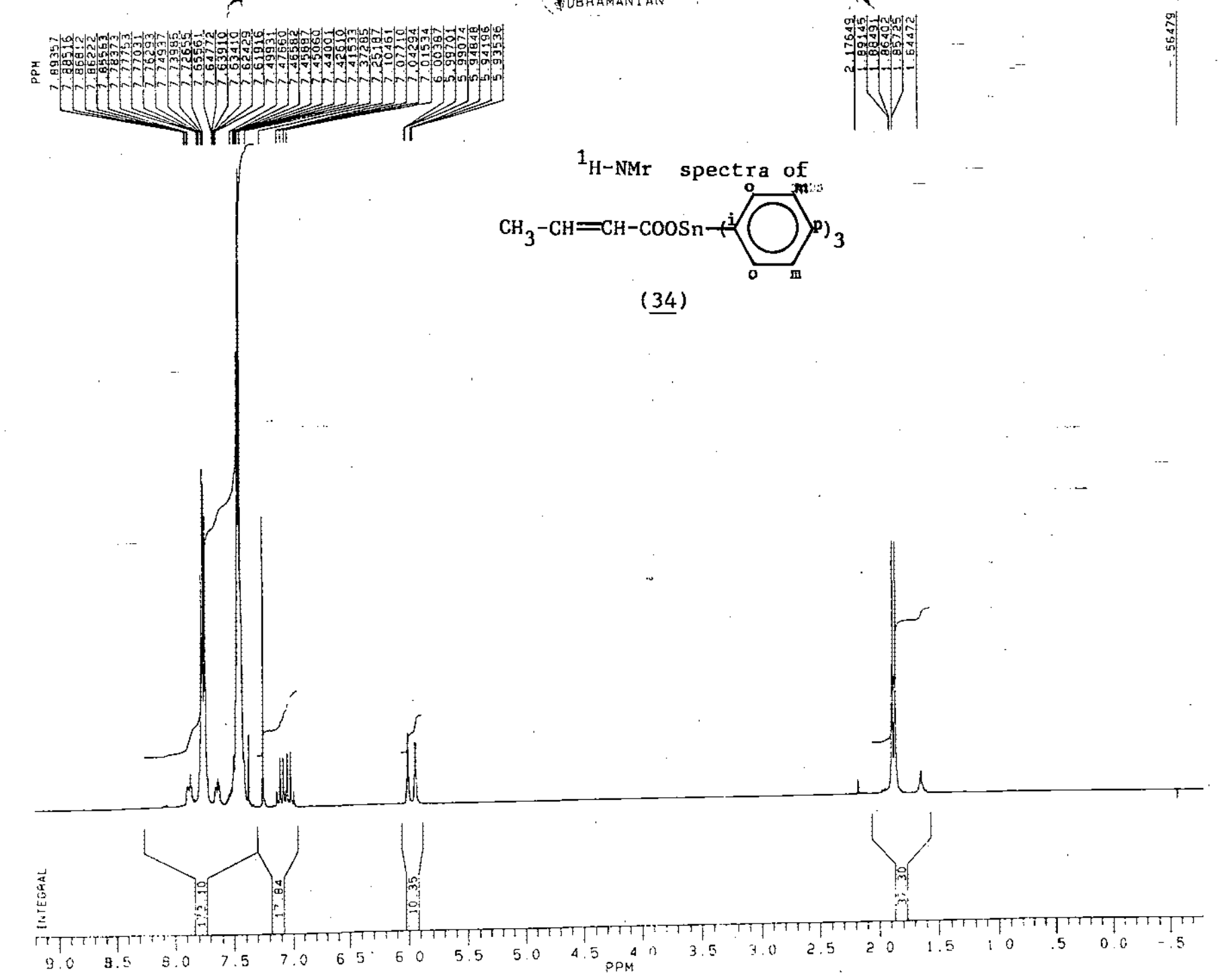
SA.NA SUB224
SA.NO AP28 112
SOLVENT CDCl3
SF 62.896
SFO2 0.0
SF2 62.896
SY 62.0
O1 2268.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 256
TE 297

DE 40.0
PW 19600
O2 3871.265
OP 20H DO

LB 1.600
GB 0.0
NC 4
CX 63.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.142
SR -4045.28

D1 2.0000000
SI 16K
D5 .0010000
SF 20M
PO 2.30
PCS
RD 0
PW
DE 40.00
NS 256
DS 2



^{1}H-NMr spectra of

(34)

BRUKER

JA120S.126
AU PROG:
XOO.AU
DATE 12-1-93
TIME 20:01

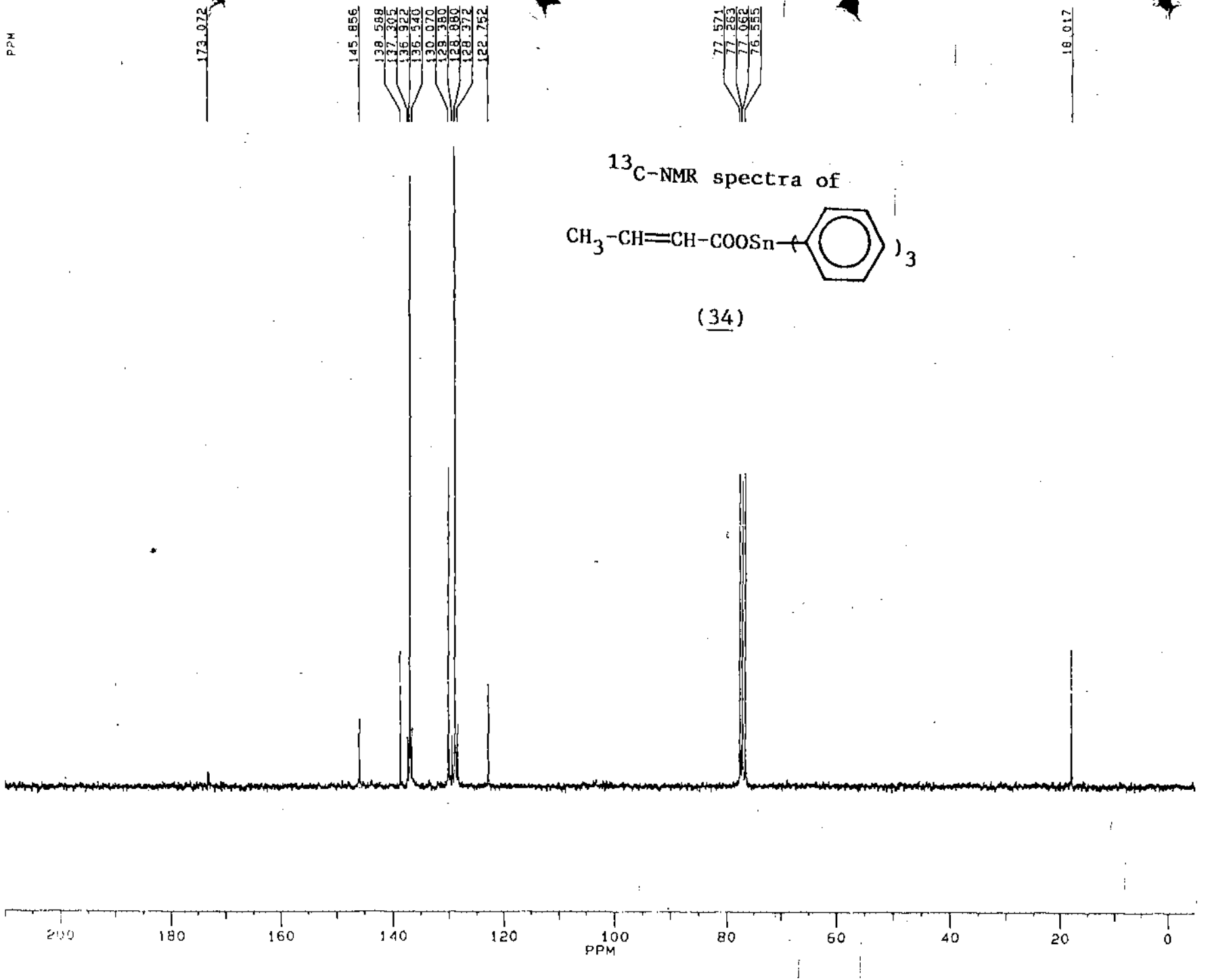
SA.NA SU628
SA.NO JA12 126
SOLVENT CDCl3
SF 250.133
SFO2 0.0
SF2 250.133
SY 100.0
O1 4311.814
SI 32768
TD 32768
SW 5000.000
SW2 5000.000
HZ/PT .305

RD 0.0
AQ 3.277
RG 10
NS 16
TE 297

DE 125.0
FW 6300
O2 2714.499
DP 63L PO

LB .100
GB 0.0
NC 1
CX 23.50
CY 12.50
F1 9.200P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2555.82

D1 1.0000000
PO 3.30
RGA
RD C 0
PW 0.0
DE 125.00
NS 16
DS 2



^{13}C-NMR spectra of

$CH_3-CH=CH-COOSn-(C_6H_5)_3$

(34)

BRUKER

JA121S.126
AU PROG:
X02.AU
DATE 12-1-93
TIME 20:56

SA.NA SUB628
SA.NO JA12 126
SOLVENT CDCl3
SF 62.896
SFO2 0.0
SF2 62.896
SY 62.0
O1 2269.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 1024
TE 297

DE 40.0
FW 19600
O2 3871.265
OP 20H DO

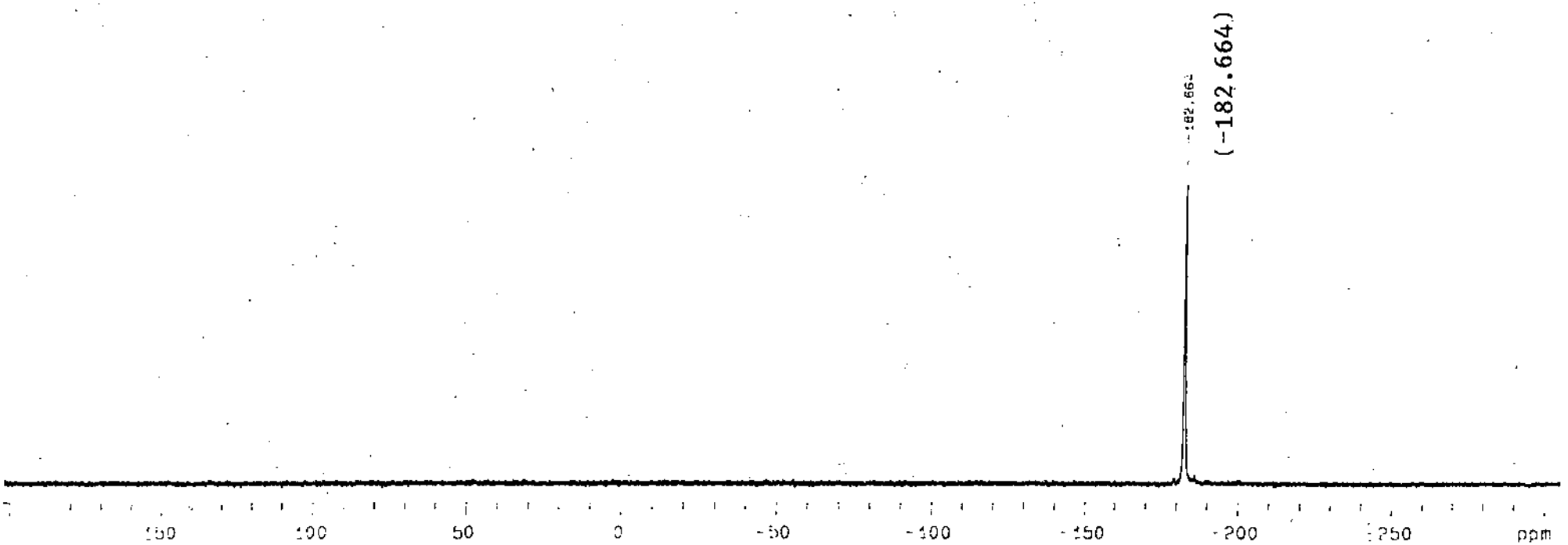
LB 1.600
GB 0.0
NC 5
CX 23.56
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.2P

D1 2.0000000
S1 16H
D5 .0010000
S2 20H
PO 2.30
BGA
RD 0 0 .
PW 0.0
DE 40.00
NS 1024
DS 2

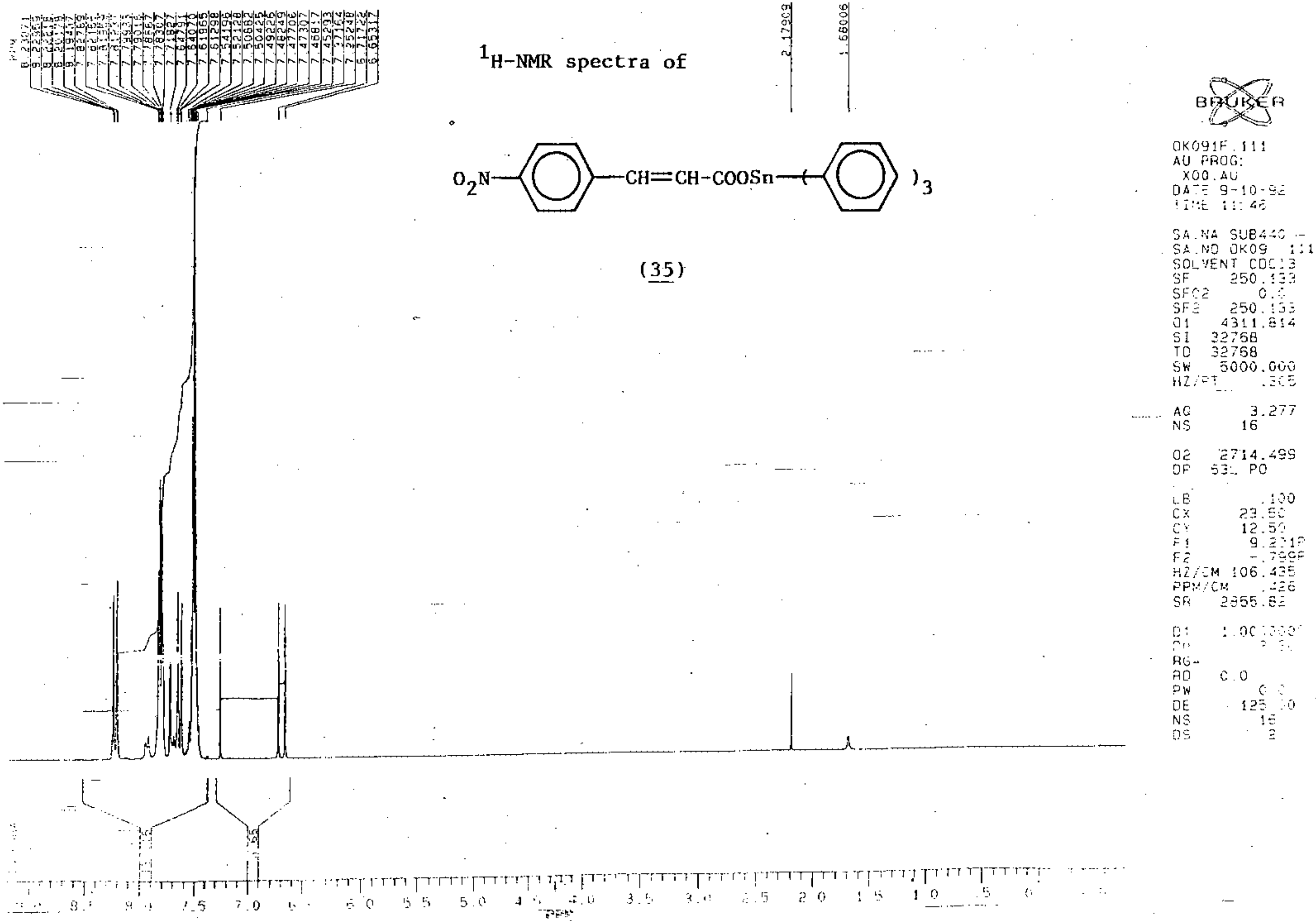
OBSERVE Sn119
Frequency 111.862 MHz
Spectral width 100.0 KHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 2656
DECOUPLE H1
High power 59
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 262144
Total acquisition time 88 minutes

$CH_3-CH=CH-COOSnPh_3$

(34)



^{1}H-NMR spectra of

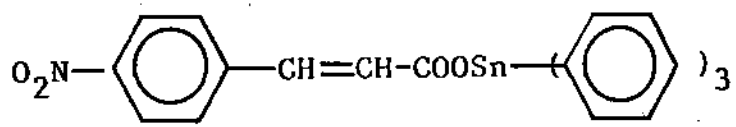


(35)

SUBRAMANIAN

171.989
148.399
142.376
140.959
138.040
137.317
136.533
136.549
130.369
129.569
129.063
128.587
124.151
123.138
77.613
77.104
76.597

^{13}C-NMR spectra of



(35)

BRUKER

OK090S.111
AU PROG:
XO2.AU
DATE 9-10-9C
TIME 11:42

SA.NA SU440
SA.NO OK09 111
SOLVENT CDCl3
SF 62.896
SFO2 0.0
SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 256

O2 3871.265
DP 20H D0

LB 1.600
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

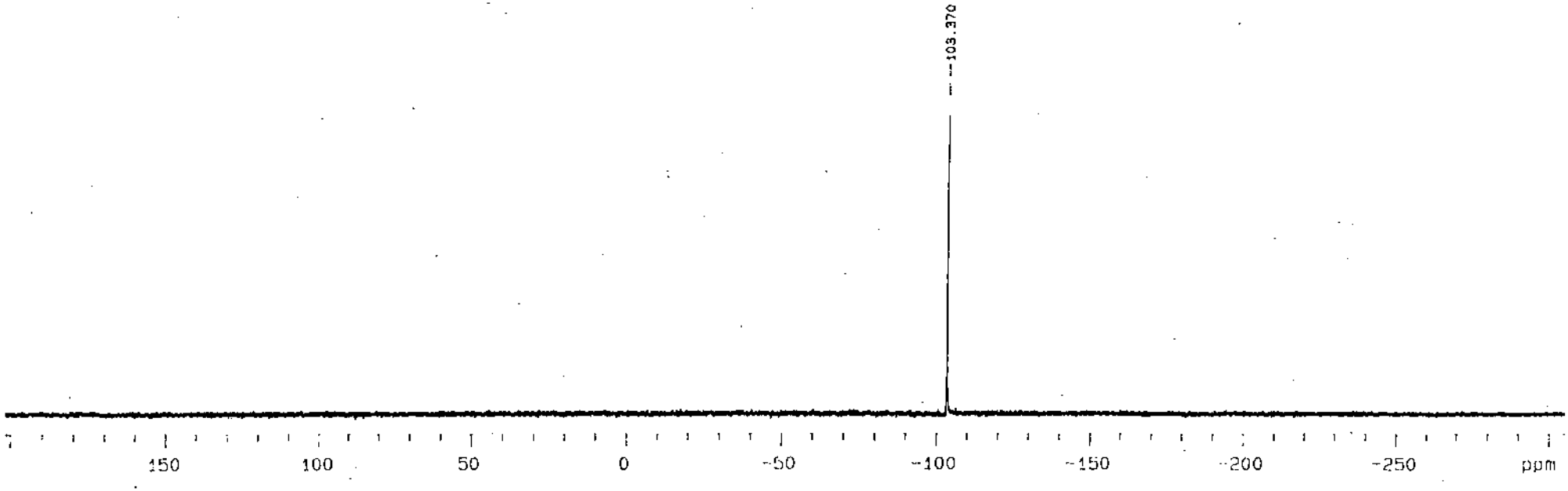
D1 2.0000000
P1 16H
D5 .0010000
S2 20H
P0 2.30
RGA
AD 0.0
PW 0.0
DE 40.00
NS 256
DS 2
D2 .0034500

CD 1?2

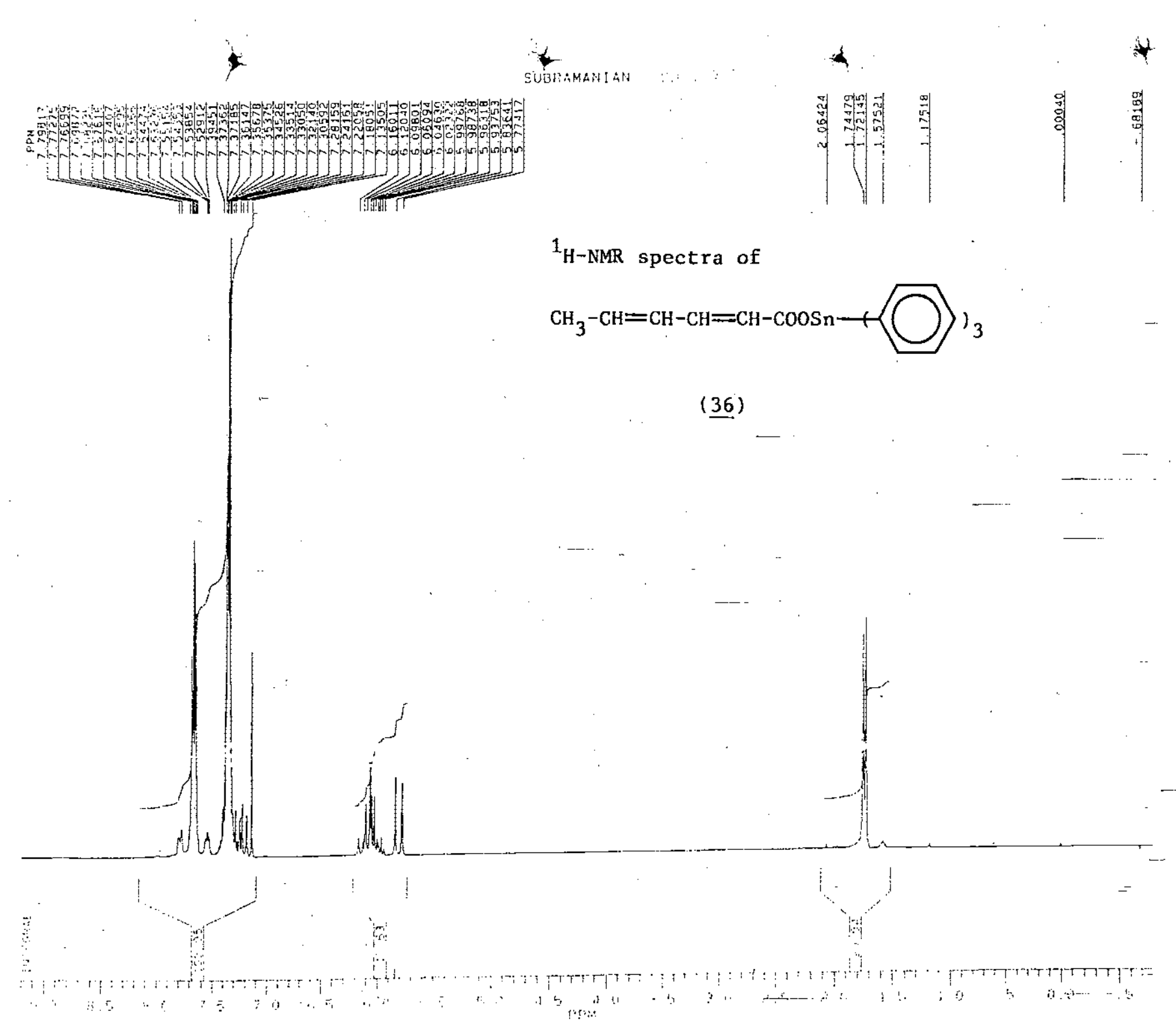
OBSERVE Sn119
 Frequency 111.862 MHz
 Spectral width 100.0 kHz
 Acquisition time 1.000 sec
 Relaxation delay 1.000 sec
 Pulse width 65.8 degrees
 Ambient temperature
 No. repetitions 240
DECOUPLE H1
 High power 50
 Decoupler gated on during acquisition
 Decoupler gated off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 4.0 Hz
 FT size 262144
Total acquisition time 8 minutes

$p\text{-}NO_2\text{-}PhCH{=}CH\text{-}COOSnPh_3$

(35)

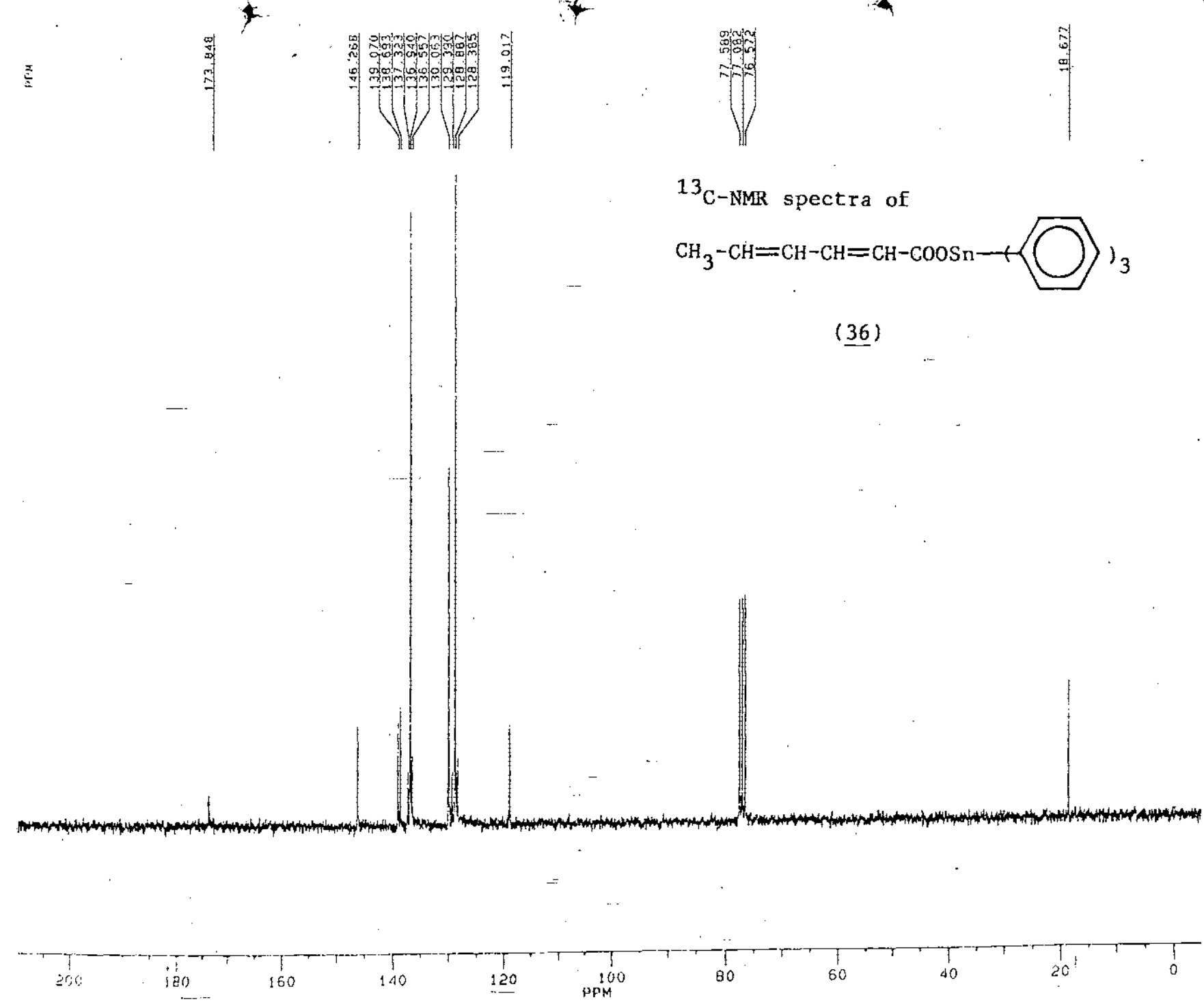


SUBRAMANIAN



^{1}H-NMR spectra of

(36)



^{13}C-NMR spectra of

CH_3-CH=CH-CH=CH-COOSn-(C$_6$H$_5$)$_3$

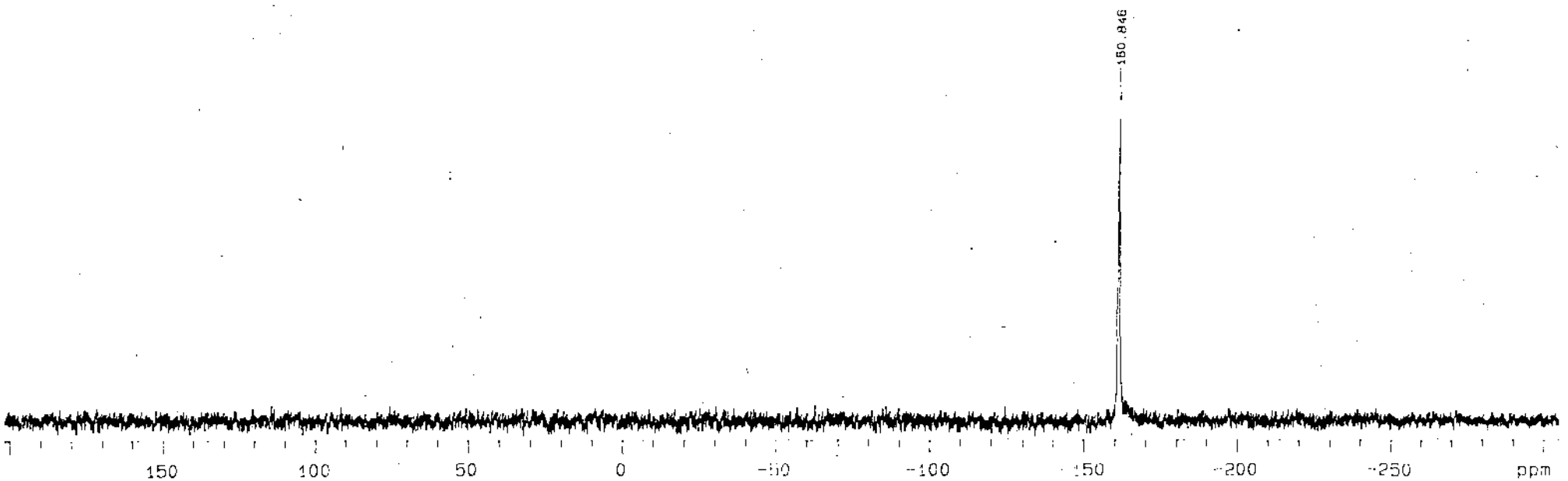
(36)


```
OK091S.110
AU PROG:
 X02.AU
DATE 9-10-92
TIME 11:24

SA.NA SUB439
SA.NO OK09  110
SOLVENT CDCl3
SF      62.896
SF02     0.0
SF2     62.896
O1    2268.997
SI   32768
TD   32768
SW   15625.000
HZ/PT     .954

AQ       1.049
NS     256

O2    3871.265
DP   20H 00

LB       1.600
CX      23.50
CY      12.50
F1     210.015P
F2      -4.977P
HZ/CM 575.411
PPM/CM  9.149
SR   -4045.28

D1    2.0000000
D5     .0010000
S2   20H
P0       2.30
RGA
RD    0.0
PW       0.0
DE      40.00
NS       256
DS         2
D2      0.34500
```

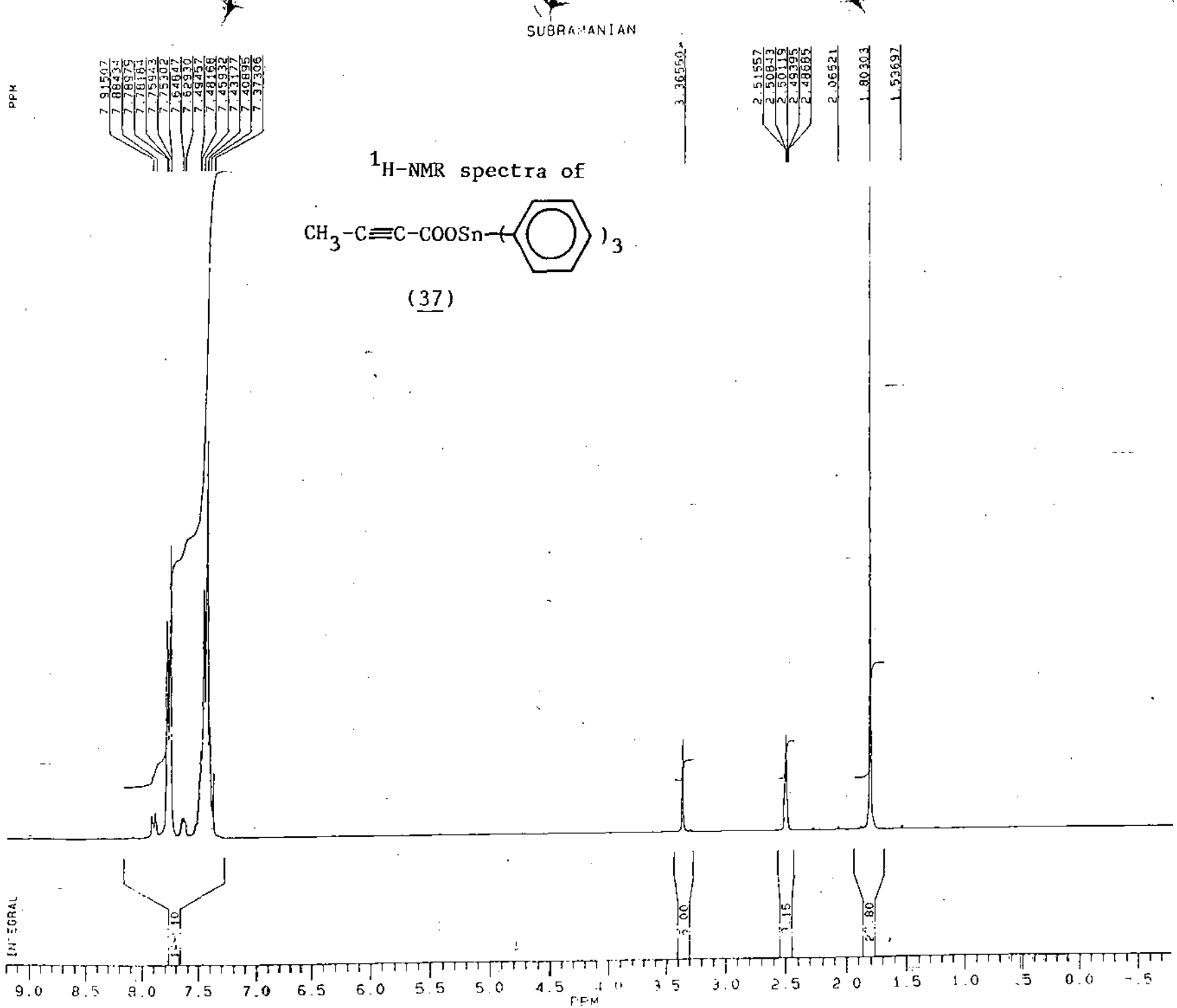
OBSERVE Sn119
 Frequency 111.862 MHz
 Spectral width 100.0 kHz
 Acquisition time 1.000 sec
 Relaxation delay 1.000 sec
 Pulse width 65.0 degrees
 Ambient temperature
 No. repetitions 1168
DECOUPLE H1
 High power 50
 Decoupler gated on during acquisition
 Decoupler gated off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 10.0 Hz
 FT size 262144
Total acquisition time 36 minutes

$CH_3-CH=CH-CH=CH-CO_2SnPh_3$

(36)



SUBRAMANIAN



^{1}H-NMR spectra of

(37)

BRUKER

OK080F.114
AU PROG:
XOO.AU
DATE 8-10-92
TIME 14:10

SA.NA SU407
SA.NO OK08 114
SOLVENT DMSO
SF 250.134
SFO2 0.000
SF2 250.134
O1 5487.59
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

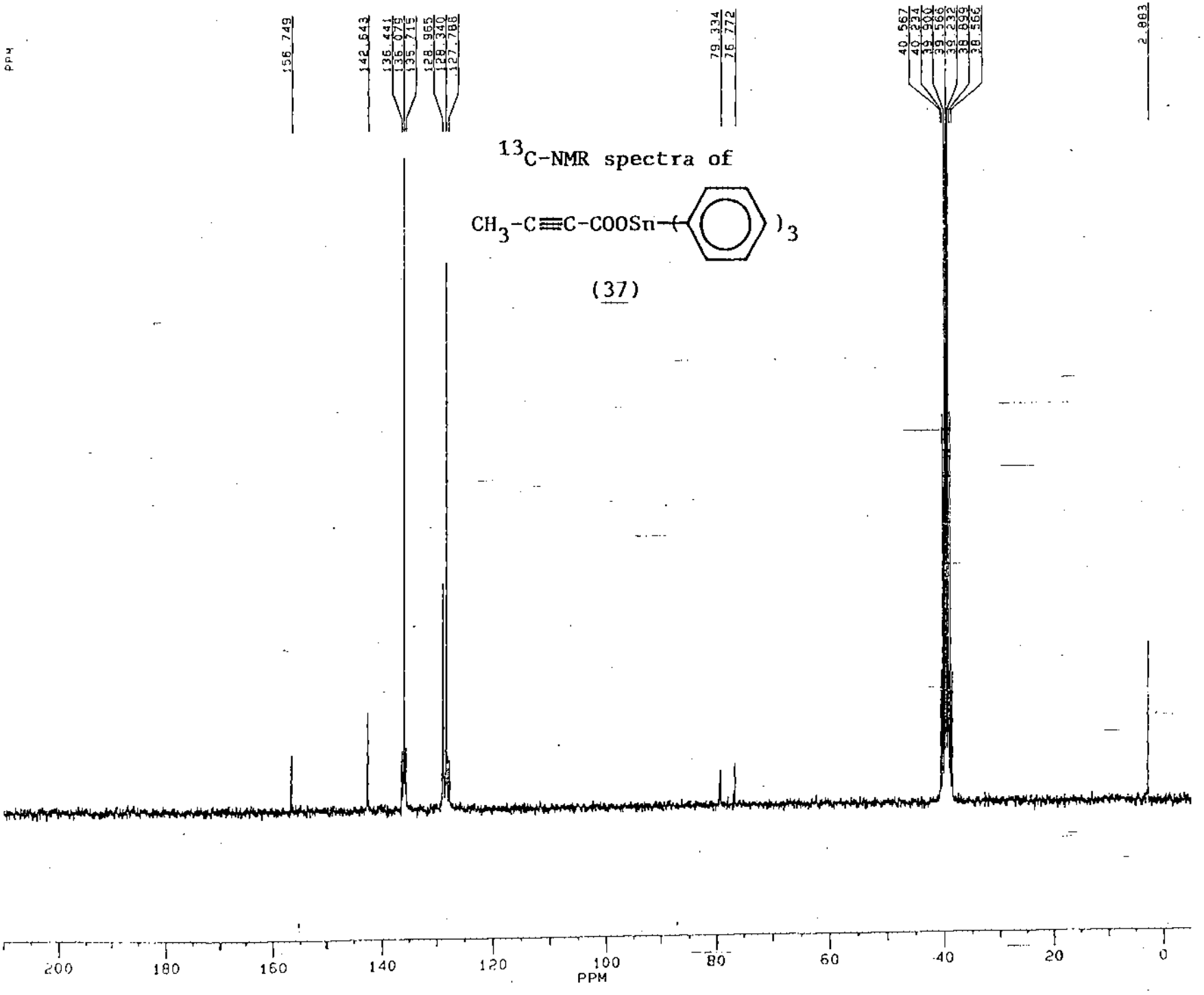
AQ 3.277
NS 16

O2 2714.499
DP 63L PO

LB .100
CX 23.60
CY 12.56
F1 9.2000P
F2 -.7999P
HZ/CM 106.435
PPM/CM .426
SR 4037.99

D1 1.00000000
[illegible]
RGA
RD 0.0
PW 0
DE 125.00
NS 16
OS 0

SUBRAMANIAN



^{13}C-NMR spectra of

(37)

BRUKER

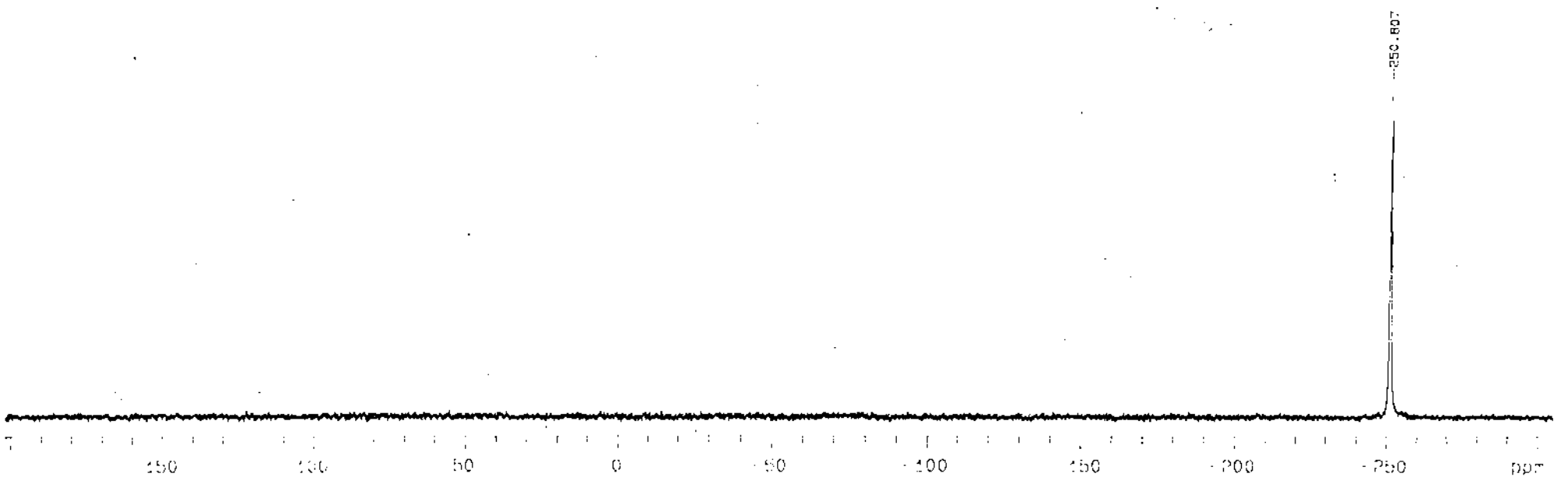
```
OK080S.128
AU PROG:
 XO2.AU
DATE 8-10-92
TIME 16:54

SA.NA SU407
SA.NO OK08  128
SOLVENT DMSO
SF      62.896
SFO2     0.0
SF2     62.896
O1    2596.808
SI   32768
TD   32768
SW  15625.000
HZ/PT    .954

AQ       1.049
NS     800

O2    5039.700
OP  20H DO

LB       1.600
CX      23.50
CY      12.50
F1    210.0102
F2     -4.9819
HZ/CM 575.411
PPM/CM  9.142
SR  -3717.47

D1    4.0000000
[illegible]
D5     .0010000
S2    20H
PO       2 30
RGA
BD    0.0
PW       0.0
DE      40.00
NS       800
DS         2
D2     .0034500
```

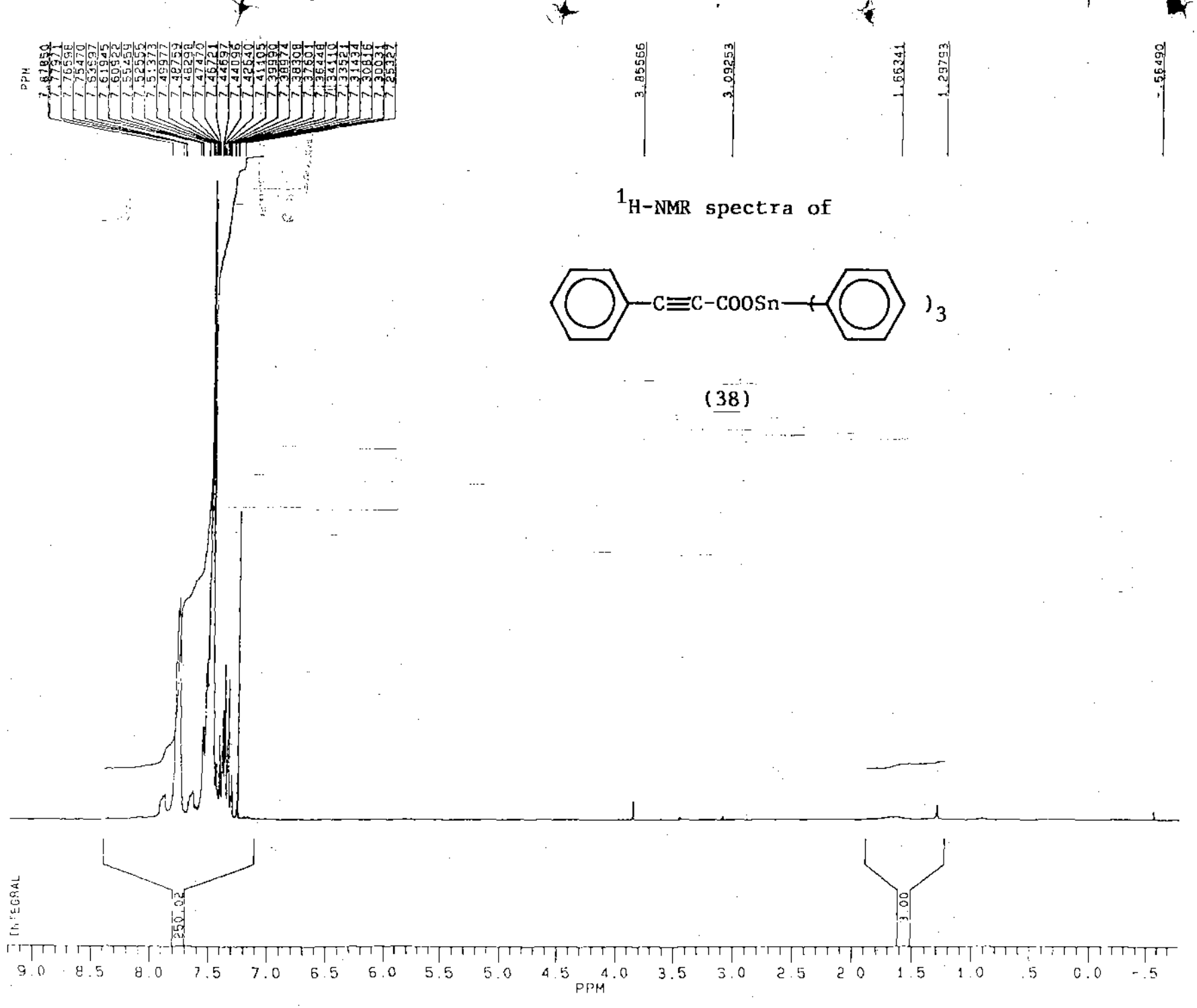
CU 1?5(14)

OBSERVE Sn119
Frequency 111.862 MHz
Spectral width 100.0 kHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 1840
DECOUPLE H1
High power 50
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 10.0 Hz
FT size 262144
Total acquisition time 61 minutes

$$CH_3-C\equiv C-CO_2SnPh_3$$

(37)





^{1}H-NMR spectra of

(38)

BRUKER

AP281F.113
AU PROG:
XOO.AU
DATE 28-4-93
TIME 12:28

SA.NA SUB225
SA.NO AP28 113
SOLVENT CDC13
SF 250.133
SF02 0.0
SF2 250.133
SY 100.0
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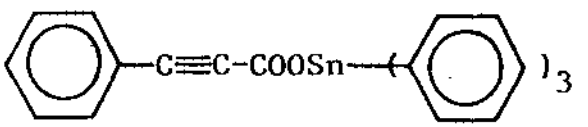

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PART – I SECTION - B

Transesterification of alkyl/aryl esters to triorganostannyl esters under neutral condition and their hydrolysis into corresponding acids using dilute acids at room temperature.

I.B-1: Introduction

The chemistry of the carboxyl group is one of the cornerstones of organic chemistry. As a consequence, in organic synthesis the procedure of selective masking and demasking of carboxyl group is an indispensable and powerful artifice at the disposal of organic chemists. As a part of our continuing interests with triorganotin esters of organic carboxylic acids, this section (SECTION-B) deals with our studies on the development of a new mild and efficient methodology for the hydrolysis of alkyl or aryl esters[1]. However, before describing our new method, it is reasonable to present a brief description on the recent developments in methods for the esterification as protection of the carboxyl group followed by its deprotection.

Many methods for the protection (as ester) and deprotection of carboxyl group of varying degree of scopes and limitations are known in the literature[2]. Recently, E.Haslam reviewed[3] this important aspects of synthetic methodologies for esterification of the carboxyl group and its removal during a synthetic sequence. While the simple alkyl or aryl esters are prepared by using the well known methods[3], their deprotection is, however, often associated with complications in terms of other acid or base sensitive functionalities present in the molecule in a multi-step synthesis. The excellence of the method, therefore, depends upon the easy accessibility of ester and the milder conditions that are being used to demask the

ester function into the acid. In this respect, several methodologies have been developed, both under the hydrolytic and non-hydrolytic conditions, which are delineated below.

The esterification of acids with alcohols can be accomplished if a means is available to drive the equilibrium to the right in equation(1). The most common and still probably most widely used catalysts are sulfuric acid and p-toluene sulfonic acid, though some reactive acids such as formic[4],

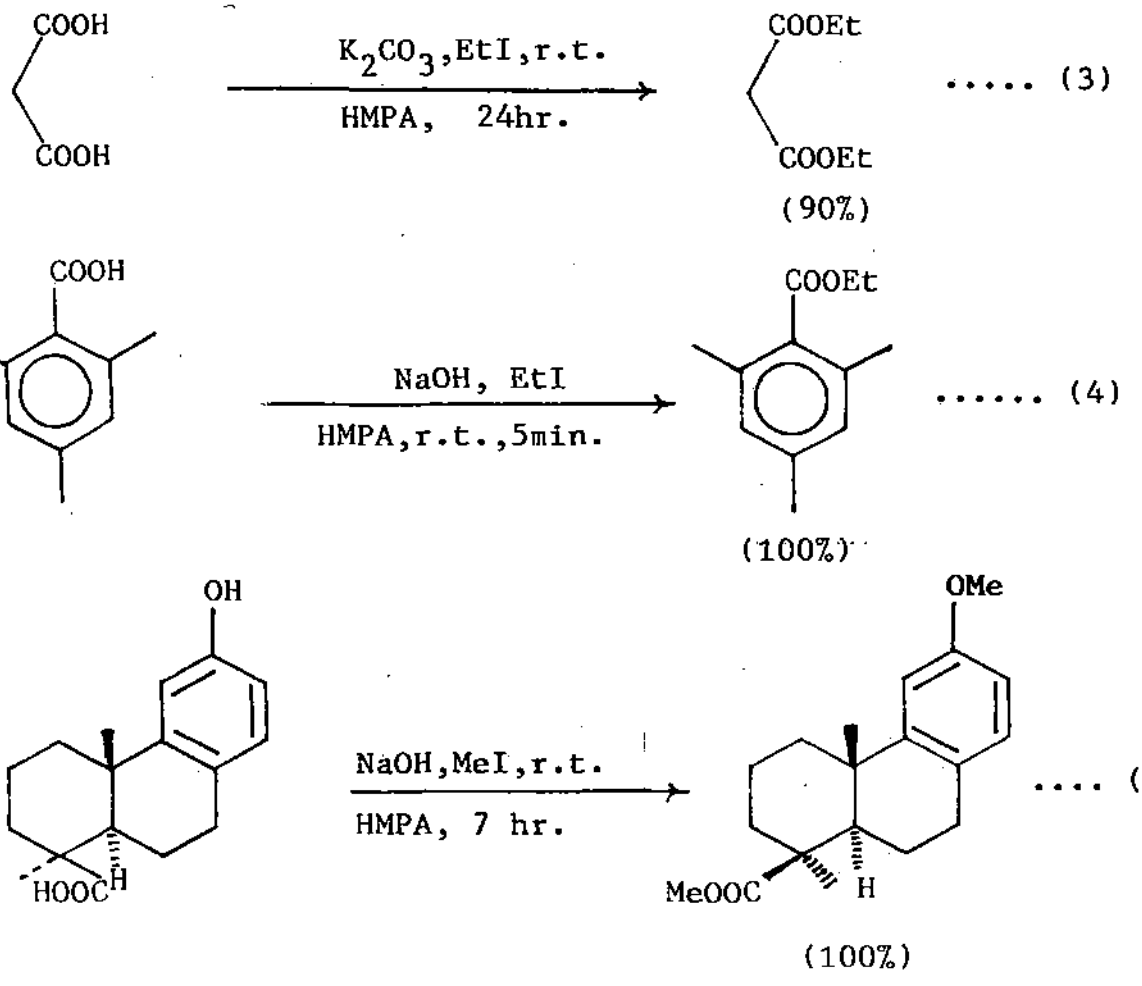
$$R\text{-}COOH + R^1OH \underset{}{\overset{H^+}{\rightleftharpoons}} R\text{-}COOR^1 + H_2O \quad \ldots\ldots\ldots(1)$$

trifluoroacetic[5] etc. do not require a catalyst. Besides methyl and ethyl, R^1 may be other primary or secondary alkyl groups, but tertiary alcohols usually afford carbocations and elimination. Allyl and cinnamyl esters are prepared from the carboxylic acid and corresponding alcohols. Engel et al.[6] prepared the allyl ester from the alkyl ester by treatment with allyl alcohol in presence of sodium hydride in excellent yields. Dimethyl copper lithium has been used to deprotect the allyl ester[7]. Corey and Tius[8] observed that the cinnamyl esters could be cleaved under nearly neutral condition by using mercuric acetate followed by treatment with potassium thiocyanate (equation 2).

$$R\text{-}COOH + HOCH_2\text{-}CH{=}CH\text{-}Ph \longrightarrow R\text{-}COOCH_2\text{-}CH{=}CH\text{-}Ph \xrightarrow[\text{r.t. 2-4 hr.}]{Hg(OAc)_2/MeOH}$$

$$R\text{-}COOCH_2\text{-}\underset{\underset{AcOHg}{|}}{CH}\text{-}\underset{\underset{OMe}{|}}{CH}\text{-}Ph \xrightarrow[\text{r.t. 12-16 hr.}]{KSCN/H_2O} \underset{(90\%)}{R\text{-}COOH} \quad \ldots\ldots\ldots(2)$$

Other than alcohols, alkyl halides have found most frequent use in the preparation of alkyl esters utilising the carboxylate group as a nucleophile. For example, Shaw and his co-workers[9] showed that aliphatic primary, sterically hindered tertiary or aromatic carboxylic acids were converted to alkyl esters by the reaction of their sodium, potassium or calcium salts with alkyl halides in HMPA, in almost quantitative yields (equation 3-5).



Similar esterification also carried out by Johnstone et al.[10] or Mehta[11] by using DMSO instead of HMPA and reported in excellent yields. Replacement of sodio- or potassio- salt of the carboxylic acid was done with quaternary alkyl ammonium ion (Me_4N^+, Et_4N^+ and $n\text{-}Bu_4N^+$) in dipolar aprotic media. The reaction rate and yields were found to be dramatically increased for n-alkyl halides in DMF, DMSO or CH_3CN[12-14].

$$MeCO_2^-Et_4N^+ + RCH_2\text{-}X \xrightarrow[r.t.]{DMF} Me.CO_2CH_2R \quad \ldots\ldots\ldots (6)$$

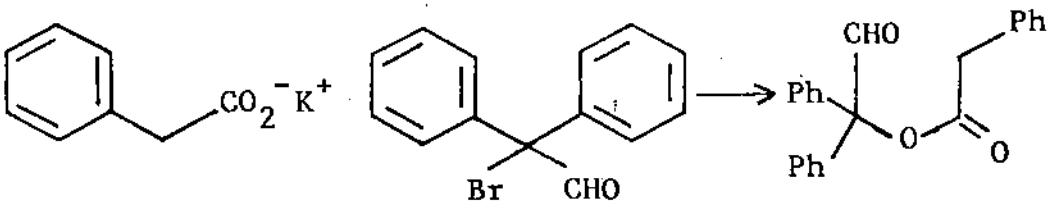
R	X	Time(hr.)	Yield(%)
n-pr	Br	0.5	90
n-pr	Cl	6	50
Ph	Cl	1	100

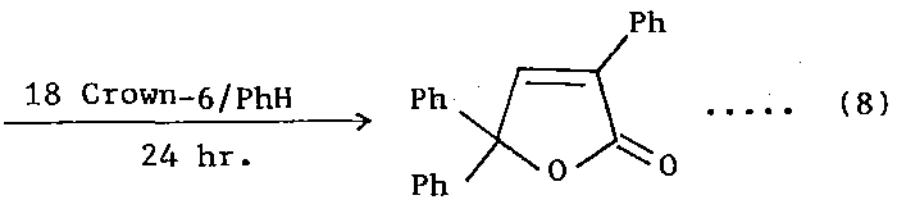
Holmberg and Hansen[14] also noted the formation of methylene diesters while using dichloromethane as solvent and they used this observation as a basis for a synthesis of a variety of methylene diesters (equation 7).

$$R.COO^-\overset{+}{N}Bu_4 + CH_2Cl_2 \longrightarrow (RCO_2)_2CH_2 \quad \ldots\ldots\ldots (7)$$
$$(\sim 60\text{-}80\%)$$

In 1978, Ono et al.[15] reported that bicyclic amidine, DBU [1,8-diazabicyclo (5.4.0) Undec-7-ene] could be used as a base in the reaction of carboxylic acid and alkyl halides to prepare alkyl esters in benzene solution.

Phase transfer catalysts (crown ethers etc.) have been used by Durst et al.[16] and other workers[17,18]. Padwa and Dehm[18] employed this technique to synthesise the α,β - unsaturated γ-lactone in one step(equation 8).





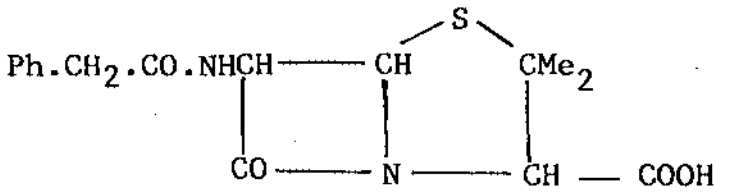
..... (8)

In the recent years, the esterification with substituted methyl groups, 2-substituted ethyl groups and substituted benzyl groups have found wide range of utilisation in synthetic organic chemistry because of the scopes and versatilities of each method. T.W.Greene reviewed these methods of protection and deprotection in the recent book[19] on "Protective Groups in Organic Synthesis".

Among the substituted methyl esters could be prepared from the reaction of ammonium salt of the carboxylic acids with alkyl halides. Jansen et al.[20] prepared the methoxymethyl(MM) ester of penicillin carboxylic acid by reaction of the triethyl ammonium salts of the acid and chloromethyl methyl ether in dimethyl formamide at room temperature (equation 9).

$$RCOO^{-}N^{+}HEt_3 + Cl.CH_2.OMe \xrightarrow[25°C,\ 1\ hr.]{DMF} RCOOCH_2.OMe \quad .....(9)$$

RCOOH ≡



To avoid the use of the carcinogen chloromethyl methyl ether, another method was developed by Dardoize et al.[21] for the preparation of methoxymethyl esters in 75-85% yield (equation 10).

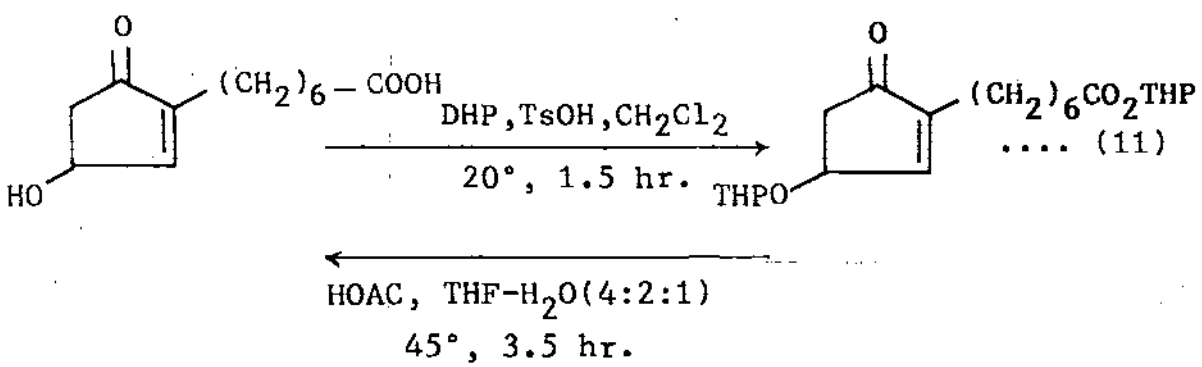
$$RCOOH + [MeO.CH_2.OMe,\ Zn/Br.CH_2.CO_2Et] \xrightarrow{0°} \xrightarrow[0 - 20°C,\ 2\ hr.]{CH_3COCl}$$

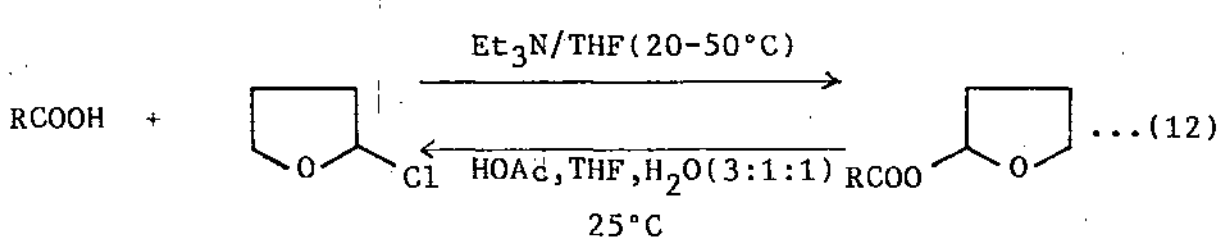
$$R.COOCH_2.OCH_3 \quad ..... \quad (10)$$

The methoxymethyl esters could be removed by silica-gel chromatography, although stable in mild acidic medium (0.01N HCl) at room temperature[22]. Masamune[23] observed

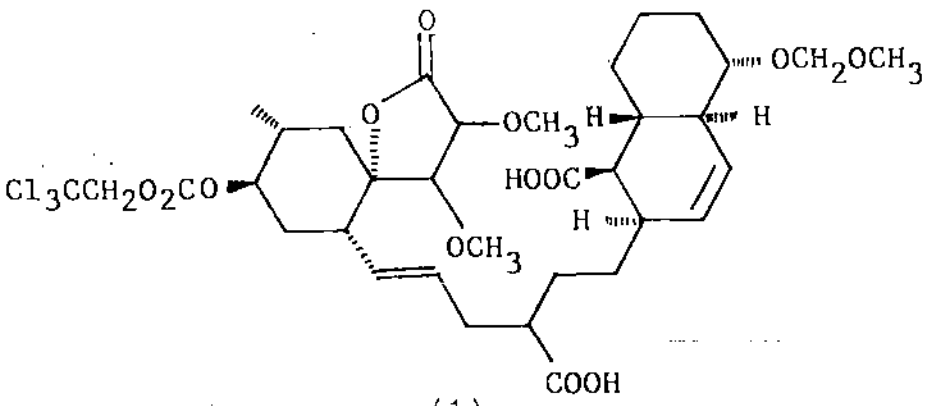
that the methoxymethyl ester was hydrolysed by using R_3SiBr in trace methanol keeping the methoxymethyl ether unreacted.

Crown ether (18-Crown-6) was used by L.G.Wade and his associates[24], for preparing methylthiomethyl esters. Several mild acidic[25] and basic [26] conditions were developed for its cleavage. Tetrahydropyranyl esters[27] (THP ester) and tetrahydrofuranyl esters[28] (THF ester) have been proved to be useful since their preparation could be achieved at room temperature and demasking occured by mild aqueous acetic acids (equation 11, 12).





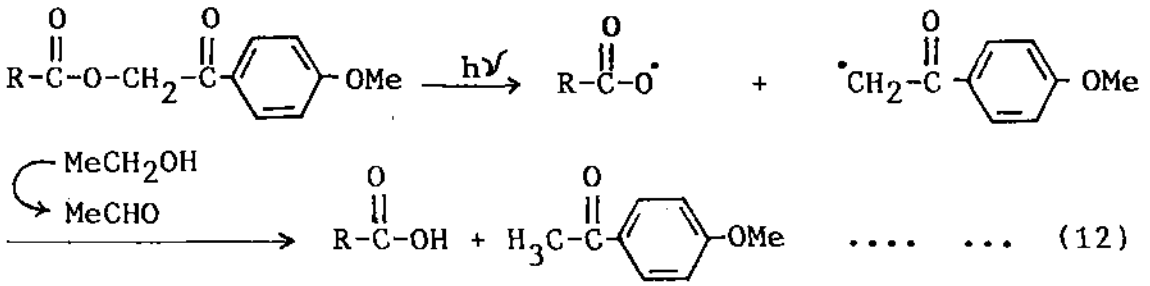
Methoxyethoxymethyl ester (MEM ester) was first prepared by Meyers et al.[29] by the reaction of carboxylic acid with MEM-chloride in presence of i-pr_2NEt at 0°C in good yield. Because of steric reasons, the MEM ester could be prepared selectively of an unhindered -COOH in presence of sterically hindered carboxylic acid group, as nicely shown by Ireland and Thompson[30] in their attempt to synthesise macrolide antibiotic chlorotricolide (1).



(1)

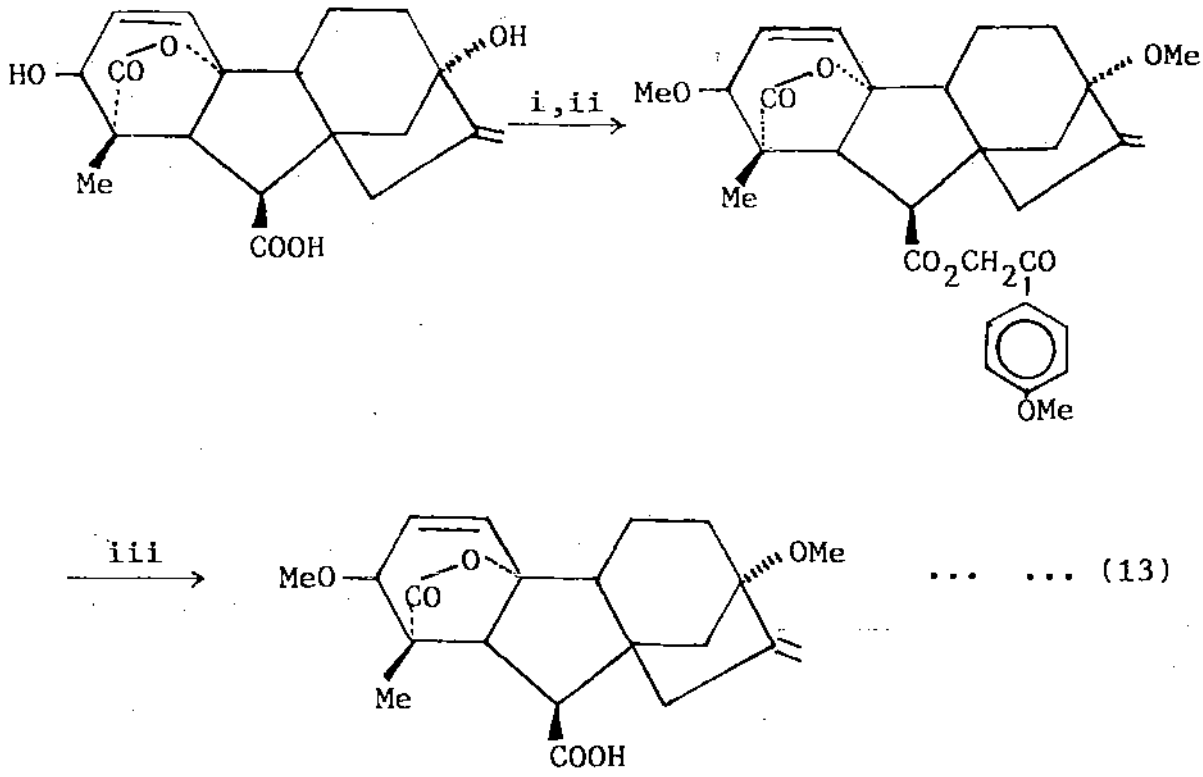
The benzyloxymethyl esters were prepared by P.A.Zoretic et al.[31] by reacting sodium carboxylates with benzyloxymethyl chloride in HMPA at 25°C. Both aromatic and aliphatic carboxylic acids were found to give their corresponding esters under this condition. Their removal, however, could be accomplished either by catalytic hydrogenolysis (non-hydrolytic) or by using aqueous acid at room temperature (hydrolytic).

Among other substituted methyl esters include phenacyl esters[32], p-bromo phenacyl esters[33], α-methyl phenacyl esters[34], p-methoxy phenacyl esters[34] and diacylmethyl esters[35]. The advantage of using the phenacyl esters is that this protective groups can be demasked photochemically. The mechanism of the photochemical removal is considered to be a simple radical scission of the carbon-oxygen bond of the ester. The other product of the photolysis is an acetophenone. Sheehan and his collaborators[34] examined both the p-methoxy phenacyl and α-methyl phenacyl functions as photolabile ester protecting groups. They observed that both types of ester were cleaved in ethanol or dioxane at 20°C by UV irradiation (equation 12). Since the sensitivity of the gibberillins to acid and



.... (12)

base was until very recently and obstacle to their recovery from alkyl ester derivatives, Russian workers[36] exploited the photolabile p-methoxy phenacyl ester group in the transformation of gibberillin A-3 (equation 13).



... ... (13)

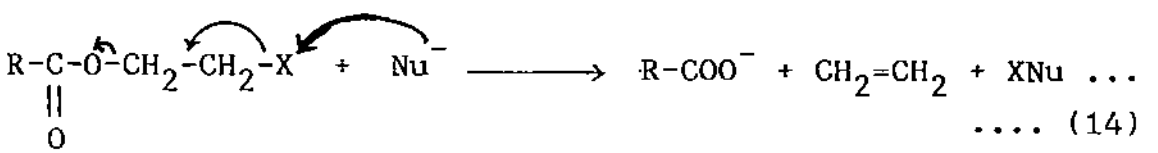
i) Et_3N-MeO-  -$COCH_2Br$-DMF-0°

ii) MeI - Ag_2O - THF

iii) hν - EtOH

The ethyl esters were prepared from the reaction of carboxylic acid and ethyl bromide by using bicyclic amidine DBU in benzene[15], dicyclohexylcarbodiimide (DCC) and 4-N,N-dimethylaminopyridine (DMAP) in ether[37] or sodium bicarbonate in dimethyl formamide[38]. All the reactions were carried out at room temperature and yields were within the range of 70-95%. Ueda[39] exhibited that the ethyl ester of amino acid could be prepared by reaction with ethyl tosylate in refluxing ethanol for 24-30 hours in excellent yields.

The attention to prepare 2-substituted ethyl esters grew from the fact that the cleavage of these esters occurred by a fragmentation reaction to generate ethylene or a ethylene derivative as outlined below (equation 14).

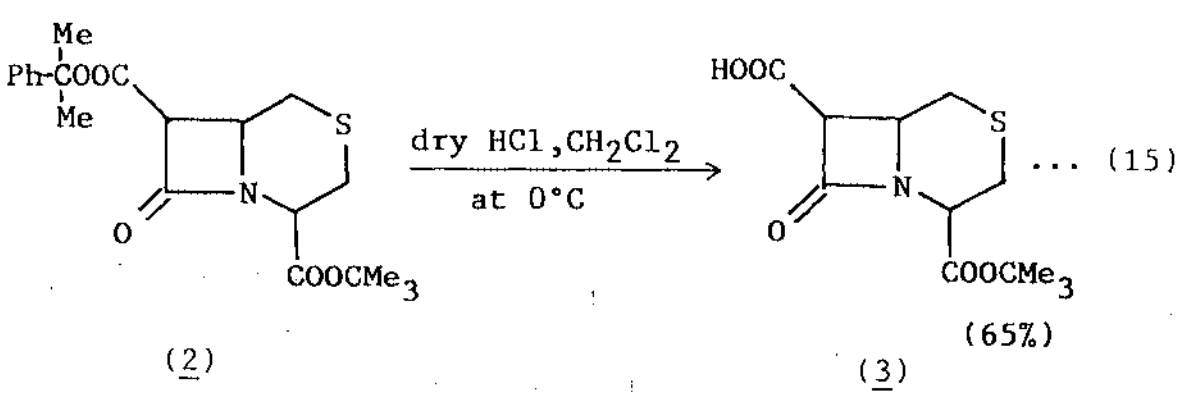


$$R\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}CH_2\text{-}X + Nu^- \longrightarrow R\text{-}COO^- + CH_2{=}CH_2 + XNu \quad \ldots\ldots (14)$$

2,2,2-Trichloroethyl ester ($RCOOCH_2CCl_3$) was prepared by Woodward *et al.*[40] using DCC in pyridine or by Carson[41] using p-toluene sulfonic acid in refluxing toluene. These esters were cleaved with Zn/THF at room temperature. Semmelhack[42] conducted electrolytic reduction at -0.70V of the corresponding tribromoethyl ester.

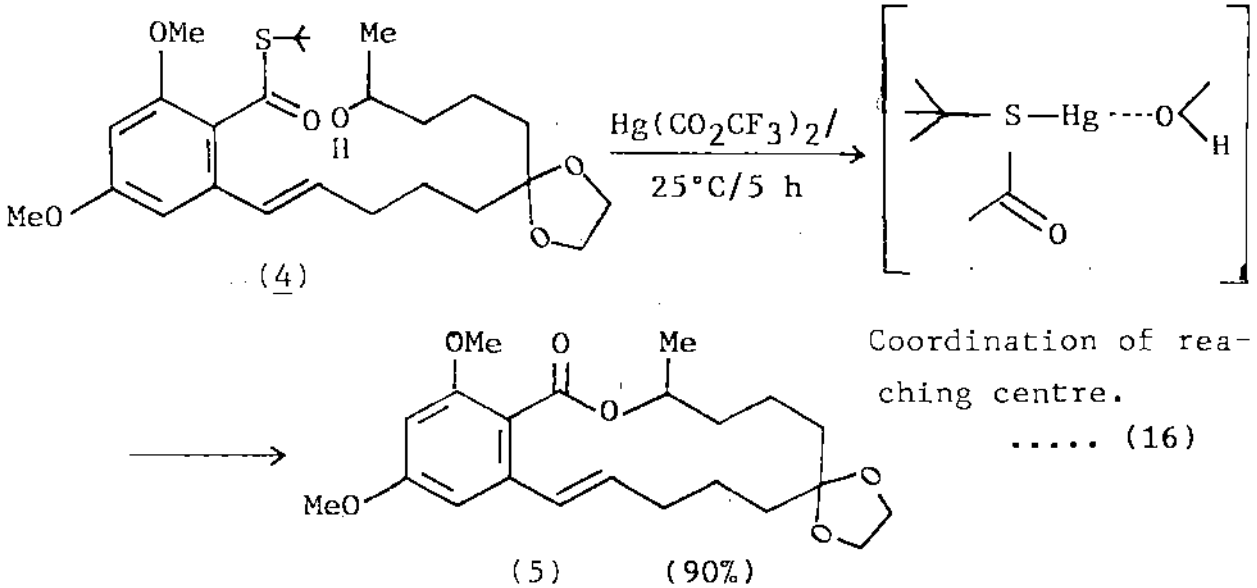
2-(Trimethylsilyl) ethyl carboxylates were prepared from the acid by P.Seiber[43] or from the acid chloride by H.Garlach[44] upon reaction with 2-(trimethylsilyl) ethyl alcohol, $Me_3SiCH_2CH_2OH$ using DCC/py in acetonitrile at 0°C or using pyridine respectively. These esters were found to be deprotected by employing fluoride ion[43] (Et_4NF or $n\text{-}Bu_4NF$).

Greatly hindered cumyl ester could be cleaved using acid and selectively in presence of t-butyl ester, as was shown by Brunwin et al.[45] in their synthesis of nuclear analouges of 7-methyl cephalosporin. Thus, compound (2) underwent hydrolysis in presence of dry acid to compound (3), effecting the hydrolysis of only cumyl carboxylate function (equation 15).



(2) (3) ... (15)

Thiol ester as a means selectively to activate a carboxylic group towards esterification and lactonisation has been proved to be of considerable importance for several reasons. While making a comparative reactivity of oxygen and thioesters, it may broadly be concluded that oxygen esters possess a relative thermodynamic stability compared to thioesters, except towards nitrogen bases, their kinetic stability is comparable[46]. Also, in the biochemical process, the thioester, in particular acetyl coenzyme A, has a role in metabolism. Chemically, a thiol ester can be catalysed[47] by coordination of the sulfur atom with a "soft" thiophilic metal ion such as Hg^{+2}, Cu_2^{+2}, Cu^{+2}, Ag^{+} and Tl^{+4}. Masamune and his collaborators[48] exploited this feature, for instance, using t-butyl thiol ester (4) in association with thiophilic metal ions to effect the formation of macrocyclic lactone zearalenone dimethyl ether (5) (equation 16).



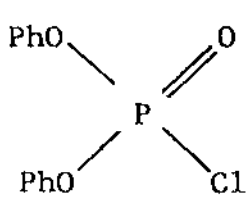
(4)

(5) (90%)

Coordination of reaching centre.

..... (16)

Initially thiol esters preparation directly from carboxylic acids and thiols were tried and found to be unrewarding because of small equilibrium constants for the reactions[3]. However, newer methods have been developed to synthesise thiolesters in which the carboxylic acid function was activated towards nucleophilic attack by several means. These included preparation of acid chloride, imidazolide[49], triazolide[49] or generation of 2-acyloxypyridinium salts followed by treatment with a thiol and an organic base or the thallium salt of a thiol. Activation of acids were also done by forming mixed anhydride with the phosphates such as,diphenylchlorophosphate(6), diphenylphosphorylazide(7)[50], diethylphosphorylcyanide(8)[50,51], phenyldichlorophosphate (9)[52], N,N-dimethylphosphoramidic dichloride (10)[52 53] etc.



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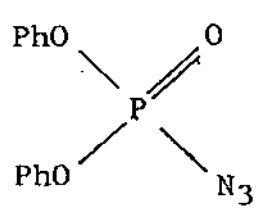

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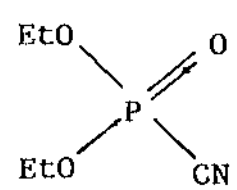

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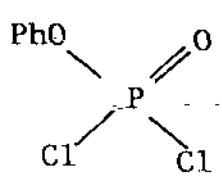

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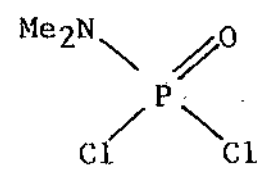
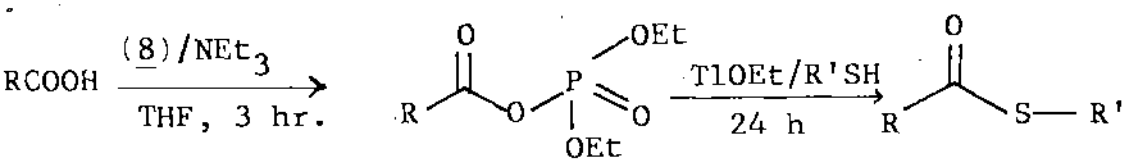


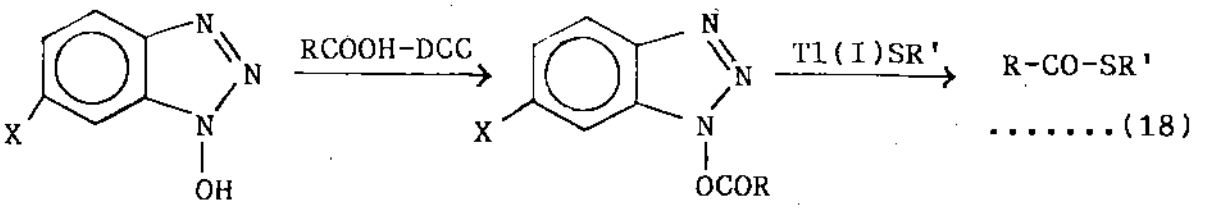
(10)

Esterification to thiol ester was reported to take place as depicted in equation (17).



..... (17)

Although dicyclohexylcarbodiimide (DCC) was observed to be a condensing agent for carboxylic acids and thiols to prepare thiol esters, there were certain limitations to its use. Baig and Owen[54] found difficulties in purification of the products. Grunwell and Forest[55] reported that thio phenols were more effective in the condensation than alkane thiols and that primary alkane thiols were more reactive than secondary and tertiary thiols. Lloyed et al.[56], however, successfully employed the reagent to prepare various 2-pyridyl thiol esters of amino acids. Horika[57] reported preparation of analogous active esters of 1-hydroxybenztriazole (11) and 1-hydroxy 6-chlorobenztriazole (12) using DCC. These esters reacted with thallium (I) thiolate to produce thiol esters (equation 18).

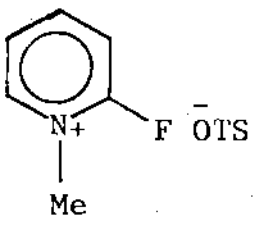


.....(18)

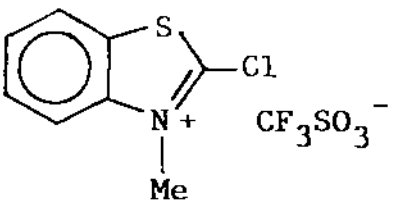
(11) , X = H

(12) , X = Cl

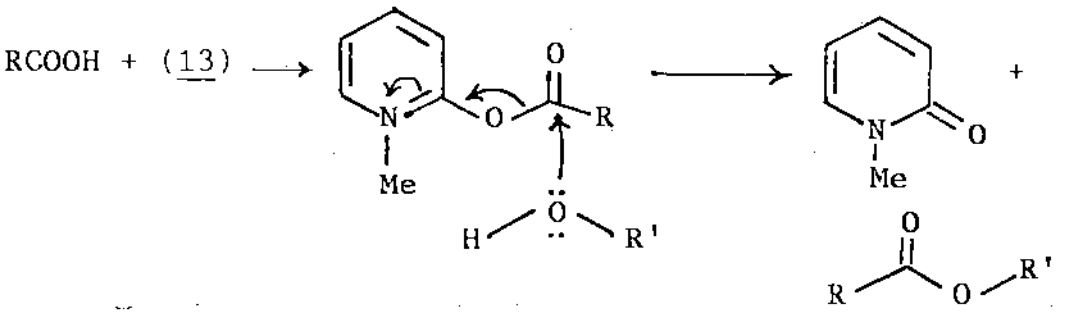
Mukaiyama used a halopyridinium salt (13) and related compound (14) in the preparation of thiol esters, as described in the following reaction (equation 19).



(13)

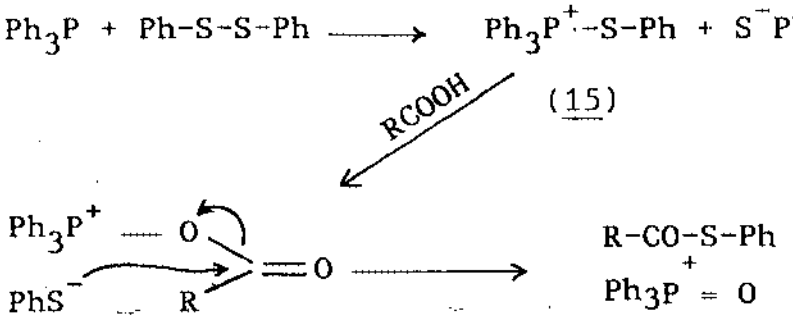


(14)



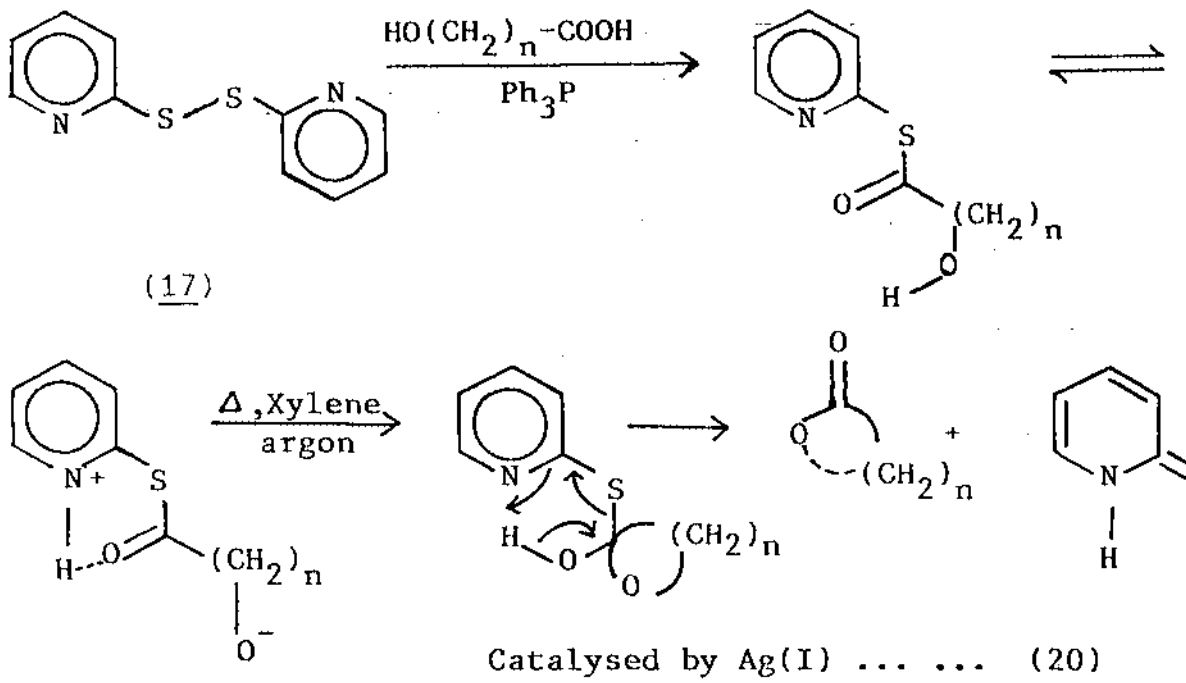
... .. (19)

In 1970, Mukaiyama et al.[58] accounted that thiol ester could be prepared from reaction of carboxylic acid with diphenyl disulphide and triphenyl phosphine in refluxing acetonitrile. The reaction pathway was formulated by assuming the initial formation of the phosphonium salt (15) which in turn was transformed by attack of the carboxylic acid to give (16). However, they suggested that



(16)

the reactivity of disulphide in this reaction was dependent on its oxidising power which in turn decreases with decreasing stability of the thiolate anion. Corey et al.[59] and Gerlach et al.[60] independently published the preparation of 2-thiopyridine esters of carboxylic acids using this reaction with 2,2'-pyridyldisulphide(17) (equation 20).

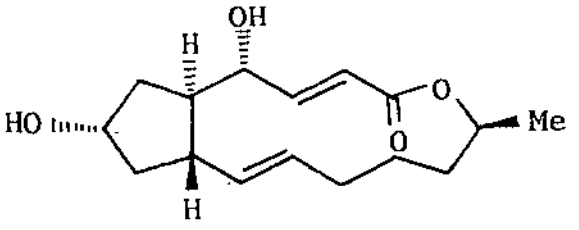


(17)

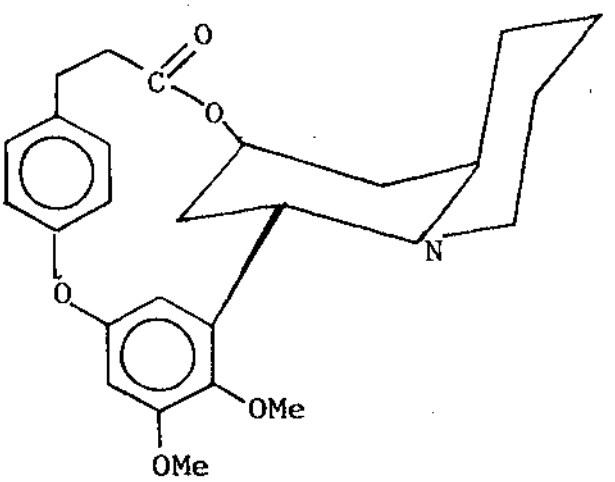
Catalysed by Ag(I) ... ... (20)

n	ring	Yield(%)
5	7	71
7	9	8
10	12	47
12	14	68
14	16	80

Corey[61] and Gerlach[60] illustrated the applicability of this method in the synthesis of macrocylic lactones and in the synthesis of natural products such as brefeldin A(18) and vertaline (19).

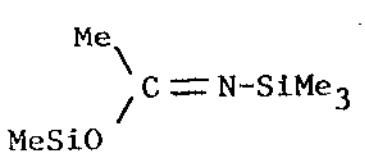


(18)

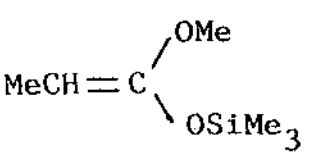


(19)

Silyl esters have found wide applications in multi-step organic synthesis because of their extreme susceptibility to cleavage by water, while stable to non-aquous reaction conditions.[19] The trimethylsilyl ester could be cleaved by refluxing in alcohol while more substituted silyl esters required mild acidic or basic medium for hydrolysis. In 1968, Fechtig et al.[62] prepared trimethylsilyl ester by treating carboxylic acid with trimethylsilyl chloride in presence of pyridine at room temperature.Other methods[63-65] developed later are mentioned here;



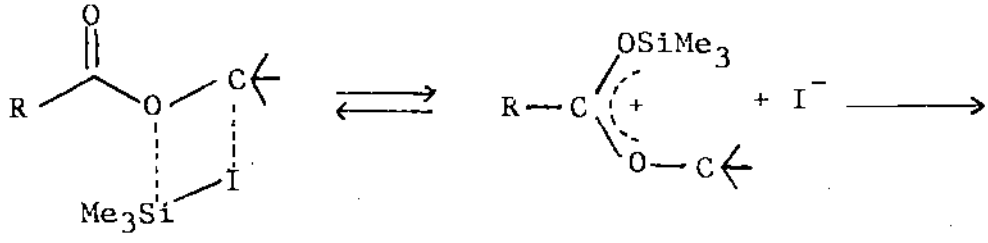
in Ether at 25°C



in CH_2Cl_2 at 15-25°C

$Me_3SiNHSO_2OSiMe_3$ in CH_2Cl_2 at 30°C.

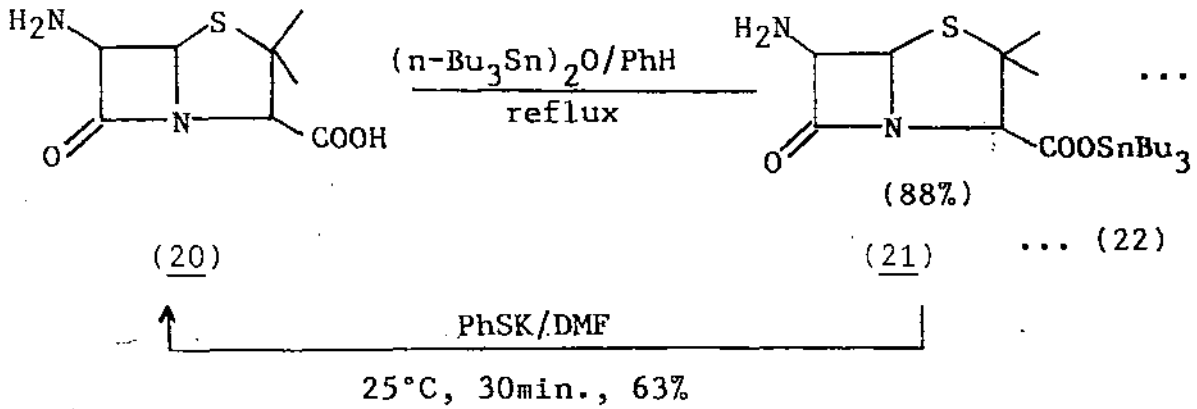
All the methods gave trimethylsilyl esters in nearly quantitative yield. Olah et al.[66] prepared trimethylsilyl esters from the alkyl esters by reacting with trimethylsilyl iodide in neat or in solution. They reported[67] that alkyl esters undergo transesterification to silyl esters in presence of trimethylsilyl iodide (generated in situ from the mixture of hexamethyldisilane and iodine in chloroform solution) followed by hydrolysis in aqueous medium. Jung and Lyster[68] displayed that hindered esters e.g., t-butyl ester was hydrolysed by using iodotrimethylsilane in 0.5 hour at room temperature. The reaction is believed to proceed as follows (equation 21).



$$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OSiMe_3 + \rightarrow C\text{-}I \xrightarrow{H_2O} (Me_3Si)_2O + RCOOH \quad \ldots\ (21)$$

However, too lability of TMS esters in aqueous medium, which may be considered as anhydride[69], creates problems on some occasions. E.J.Corey[70], therefore, used isopropyldimethylsilyl ester in prostaglandin synthesis. Besides, more hindered t-butyl dimethylsilyl esters were also used in many cases[71,72]. These silyl protective groups could be removed by aqueous acetic acid[71], tetrabutyl ammonium fluoride[71] or potassium carbonate in aqueous methanol[72].

Triorganostannyl groups ($-SnR_3$) have been employed as protecting group for the carboxyl function. Owing to high electropositivity of the tin atom, these esters could be readily hydrolysed by treatment with dilute acid or base. In 1965, Frankel *et al.*[73] first utilised $-SnR_3$ group as protecting carboxyl function of amino acids in presence of a free amino group. Bamberg *et al.*[74] prepared the stannyl ester (21) in 88% yield by refluxing the acid (20) with bis-tributyltin oxide in benzene. Its removal, however, was achieved with potassium salt of thiol at room temperature (equation 22).



Frankel[73] also prepared the triethyl ester of N-protected amino acid which was then deprotected by acetic acid keeping the N-protection intact (equation 23).

$$(R_3Sn)_2O + R'CH(NHR'')COOH \longrightarrow R'CH(NHR'')COOSnR_3 + H_2O \quad \ldots\ldots(23)$$

R=Et, n-Bu

R''=H, CH_3CO, C_6H_5CO, $C_6H_5CH_2OCO$.

I.B-2: Present work: Objective, Results and discussion

From the foregoing discussions it is apparent that although there are many new reagents for blocking the carboxyl group as ester and better methods for demasking available in the literature, the need for developing more milder and specific methods for the protection and activation of the carboxyl group is still on.

The criteria of a good protective group (as ester) of carboxyl function are (i) the reagent(s) for esterification should be readily available, stable and non-toxic; (ii) the reagent(s) should neither possess nor introduce a chiral centre ; (iii) the protective ester should be stable throughout the required reaction sequence; (iv) the reagents should be capable of being put on, and removed from, the carboxyl group in virtually quantitative yields; and (v) after removing the protective group moiety should be readily separable from the freed compound.

We considered that the masking of carboxyl function with $-SnR_3$ group might satisfy more or less all these criteria. The tin esters may be easily prepared[75] from the carboxylic acid by heating with bis(tributyltin) oxides in good to excellent yield. Bis(tributyltin) oxides are easily accessible, stable, do not introduce a chiral centre. Again,

owing to high electropositivity of the tin atom the tri-alkyltin esters are attacked readily by an electrophilic or nucleophilic reagents as follows:

$$R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-}OSnR_3 + {}^-OH \longrightarrow R^1\text{-}COO^- + R_3SnOH$$

$$R^1\text{-}\underset{\underset{O}{\|}}{C}\text{-}OSnR_3 + HX \longrightarrow R^1\text{-}COOH + R_3SnX$$

These reactions are very fast and Frankel et al.[73] showed that these reactions could be used also for the rapid quantitative volumetric determination of organotin esters. And finally the tin residue, after hydrolysis, can be removed in many ways[73] and the recovery of the acid is simple and in good to excellent yield. In our case, however, we[1] have separated the acid by extracting with aqueous sodium bicarbonate followed by acidification or directly by crystallisation.

According to Haslam[3,76], the continued and vigorous searches by the organic chemist for methods to protect the carboxyl group as an ester function and then to remove the protecting group and regenerate the free carboxyl group at a subsequent stage are broadly based on two approaches.

1. The first is to use readily available or readily prepared esters such as ethyl- and methyl- and to devise novel, mild and if possible non-hydrolytic conditions for

de-esterification such that other acid or base sensitive groups in the molecule may survive.

2. The second approach is to devise novel ester protecting groups which are removable under non-hydrolytic conditions, such as hydrogenolysis, photolysis,oxidation etc. (a few examples have been mentioned in Part I.B-1 of this dissertation).

The prime advantage of the first approach is the ready availability or formation of ester starting material in synthesis. On the other hand, the use of stannyl esters, being relatively more labile in acid or base media, may creat the question of survival throughout the required reaction sequence. It occurred to us that if we can convert the alkyl esters directly into its triorganostannyl esters, subsequent hydrolysis by using acid or base might provide a new mild method for bringing about demasking of alkyl esters.

Going through the literature, it was found that during the period of 1954-1957, Anderson[77] reported the reaction of alkyl esters with bis(tributyltin) oxide and the products were dialkyl ether and triorganotin carboxylate (equation 24). Thus ethyl acetate and bis(triethyltin) oxide

$$2R^1\text{-}COOR^2 + (R_3Sn)_2O \longrightarrow 2R^1\text{-}COOSnR_3 + R^2\text{-}O\text{-}R^2 \quad \ldots (24)$$

were reported to give diethyl ether and triethyl tin acetate. However, while studying the reaction of organotin oxides with carbamic esters on the one hand, and carboxylic esters on the other, Davies et al.[78] could not be able to confirm the Anderson's report. They reasoned that the formation of an ether (from equation 24) implies the alkyl-oxygen fission of a simple alkyl ester ($R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2$) under surprising mild condition. Davies and his associates therefore re-examined the reaction between carboxylic ester and bis(trialkyltin) oxides and reported the formation of trialkyltin carboxylates and trialkyltin alkoxide and no

$$R^1COOR^2 + (R_3Sn)_2O \longrightarrow R^1COOSnR_3 + R_3SnOR^2 \quad \ldots (25)$$

$R^1=CH_3$, $R^2=Et$, $R=n\text{-}Bu$

ether could be detected (equation25). They used a trap cooled in liquid nitrogen to collect any volatile material. Under reduced pressure, some liquid collected in the trap and was shown by the NMR spectra to contain ethyl acetate but no diethyl ether. In the case of ethyl acetate the reported yield of the triethyltin acetate was 81%, while the yield of tributyltin acetate was not given. It seemed from the study of Davies et al. that their aim was to detect the formation

of the products, but not to standardise the transesterification reaction. We therefore thought that if we can develop the procedure of transesterification of alkyl ester to triorganostannyl ester, subsequent hydrolysis of the tin carboxylate using dilute acid or base should provide a mild, convenient and new method for the hydrolysis of alkyl esters. The use of bis(tributyltin) oxide for transesterification should maintain strictly a neutral condition which is in contrast with the usual procedure of transesterification. Normally, the transesterification requires heating of the alkyl ester with a large excess of the alcohol in the presence of a catalyst (such as sulfuric acid[79]). However, the bis(tributyltin) oxide - mediated transesterification may be compared with the iodotrimethylsilane - mediated transesterification of alkyl to silyl ester, as reported by Olah and his collaborators[67].

I.B-2.1: Transesterification of alkyl/aryl carboxylates to triorganotin carboxylates and their hydrolysis :

For the present work, initially we had chosen to investigate the reaction of ethyl acetate with bis tri-n-butyltin oxide. Although Davies *et al.*[78] conducted this reaction by heating a mixture of ethyl acetate and bis tri-n-butyltin oxide, we opted a solvent, carbon tetrachloride, to carry out this reaction. Halogenated solvent was selected since this was used on several occasion to prepare triorganostannyl esters from their corresponding carboxylic acids or metal salts[75]. After having refluxed an equimolar mixture of ethyl acetate and bis tri-n-butyltin oxide in carbon tetrachloride, we were able to isolate the tri-n-butylstannyl acetate(22) in 82% yield.

$$CH_3\text{-}COOC_2H_5 + (Bu_3Sn)_2O \xrightarrow[CCl_4]{\text{Reflux}} \underset{(22)}{CH_3\text{-}COOSnBu_3} + C_2H_5OSnBu_3$$

The compound (22) had m.p. 85°C (lit.[75] 85°C). The IR spectra of triorganotin esters usually have characteristic ν_{max} for CO_2 group, depending on their molecular association (already discussed in pages 12 & 13 of this dissertation). The compound(22) showed ν_{max} at 1575(s) and 1555(s) cm^{-1} as CO_2

stretching bands which were consistent with the literature observation[80]. In ^{1}H-NMR spectrum of (22), the methyl proton exhibited a sharp singlet at δ 1.95 while the butyl protons appeared as multiplets in the region of δ0.70-1.90.

As our main objective was to optimise the right condition for obtaining the transesterified product, i.e., the tin ester, we were less concerned with the formation of the other product i.e., the tin alkoxide. Moreover, because of high sensitivity of the tin alkoxides to moisture and carbon dioxide[81], we did not try to isolate it(23) or the resulting hydroxide.

In order to explore the generality of this transesterification reaction under mild and strictly neutral condition, we then turned our attention to check the following aspects of the reaction, outlined in equation (25).

$$R^1COOR^2 + (R_3Sn)_2O \longrightarrow R^1COOSnR_3 + \underset{(23)}{R_3Sn\text{-}OR^2} \quad \ldots\ (25)$$

1. Change of R^1; we considered carboxyl group attached to primary and tertiary alkyl [compounds; ethyl acetate, (24), (26), (32), (36), (38) and (32), (34)], α,β - unsaturated aliphatic ((27) and aromatic (30) and aryl (40) functions.

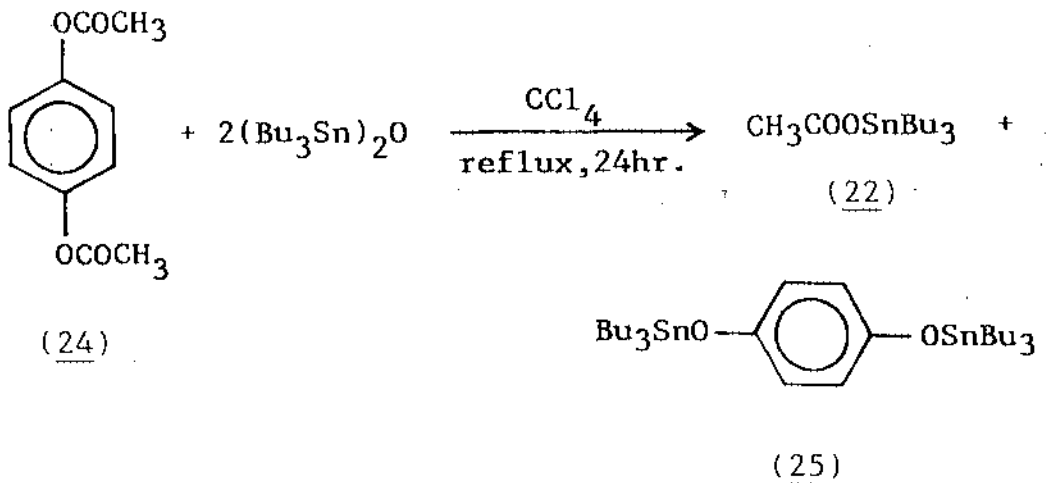
2. Change of R^2; we considered alkyl (Me and Et), benzyl (26) and phenyl (24) functions.

3. Change of solvent; we carried out the reaction in carbon tetrachloride, toluene and also in neat-mixture.

4. Esters of dibasic acid; we selected easily accessible diethyl malonate (36), 2,2-dimethyl succinate (32) and dimethyl adipate (38).

5. Change of R; we used n-butyl and phenyl groups [bis tri-n-butyltin oxide and bis (triphenyltin oxide)].

To change the R^2 from alkyl to phenyl, we studied the reaction of easily accessible hydroquinone diacetate (24). A mixture of (24) and bis tri-n-butyltin oxide, in 1:2 ratio, was heated under reflux in carbon tetrachloride for 24 hours.



(24) (22)

(25)

After removing the volatiles, the residue was chromatographed through silica gel and the compound (22) was isolated by eluting with 10-25% benzene-light petroleum in 96% yield. The m.p., m.m.p., IR and PMR data were all consistent with the tri-n-butyltin acetate (22) obtained from ethyl acetate. The other product (25) was not characterised. It was presumed that while performing chromatography on silica-gel the compound(25) was converted[81a] into hydroquinone. Although we could not isolate the hydroquinone, this reaction, however, indicated that acetate ester of hydroxyl group could be transesterified. Subsequent hydrolysis of the resulting alkoxide to alcohol which could be an ease process, would provide a method for the hydrolysis of the acetates. Further studies in this regard would be undertaken in our laboratory.

Similar reaction of benzyl acetate(26) (R^2=CH_2Ph) with bis tri-n-butyltin oxide was carried out and the tri-n-butyltin acetate(22) was afforded in 90% yield.

$$\underset{(26)}{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2Ph} + (Bu_2Sn)_2O \longrightarrow \underset{(22)}{CH_3-\overset{O}{\overset{\|}{C}}-O-SnBu_3} + PhCH_2-OSnBu_3$$

We then tried this reaction of ehtyl crotonate(27) with bis tri-n-butyltin oxide and bis (triphenyltin) oxide in carbon tetrachloride, toluene and also by heating their

mixture in neat. In all the cases, the corresponding tri-n-butylstannyl crotonate(28) and triphenylstannyl crotonate(29) were obtained in very good to excellent yields.

--The IR spectra of tri-n-butyltin crotonate(28) showed ν_{max} for the CO_2 and C=C at 1655(s), 1555(s) and 1535(s)cm^{-1}, while for the corresponding triphenyltin crotonate(29), the CO_2 and C=C absorptions appeared at 1650(s), 1570(s), 1545(s), and 1515(s)cm^{-1}. The detail spectral(^1H, ^{13}C and ^{119}Sn NMR) and analytical data were discussed in the SECTION-A of this dissertation(p.34-38)in connection with other studies and also given in the experimental part of the SECTION-B(p. 124-125).

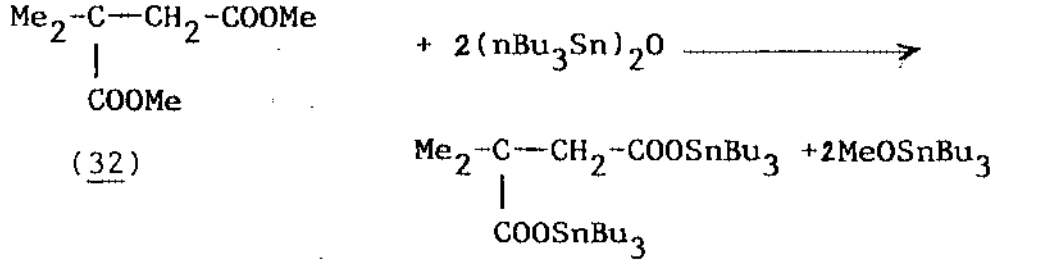
$$R^1\text{-CH=CH-COOR}^2 + R_3Sn\text{-O-}SnR_3 \longrightarrow R^1\text{-CH=CH-COOSn}R_3 + R^2OSnR_3$$

	R^1	R^2	R	
(27)	CH_3	Et	n-Bu	(28)
(27)	CH_3	Et	Ph	(29)
(30)	Ph	Me	n-Bu	(31)

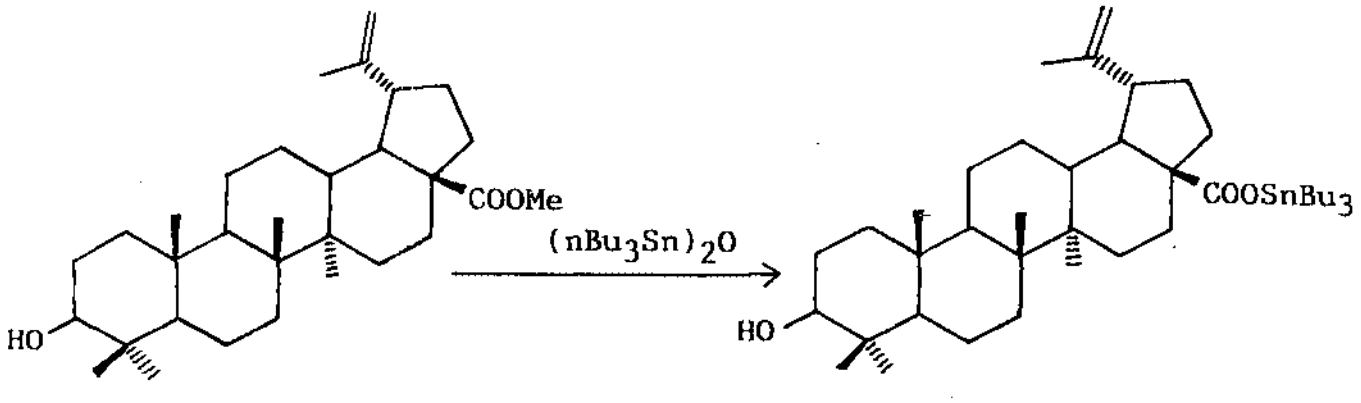
In the case of tri-n-butyltin cinnamate(31), obtained from methyl cinnamate(30), the IR absorption of CO_2 and C=C appeared at 1640(m) and 1538(s)cm^{-1}. In the PMR spectrum, the β-proton showed a doublet at δ 7.61 (J=15.94 Hz). The aromatic protons appeared in the region of δ7.33-7.52. The ^{13}C- and ^{119}Sn-NMR data were given in p.60.

Among the hindered tertiary esters, we attempted this transesterification reaction with two compounds, methyl 2,2-dimethyl succinate(32) and methyl betulinate(34). The compound (32) was prepared according to the literature procedure[82] and compound(34) was gifted[83].

The compound(32) is also an ester of dibasic acid, one being primary and the other tertiary carboxylic acid. We used two equivalent of bis tri-n-butyltin oxide and the reaction was carried out in toluene. The corresponding tri-n-butylstannyl 2,2-dimethyl succinate(33), afforded in 82% yield and had m.p. 205-208°C(d).



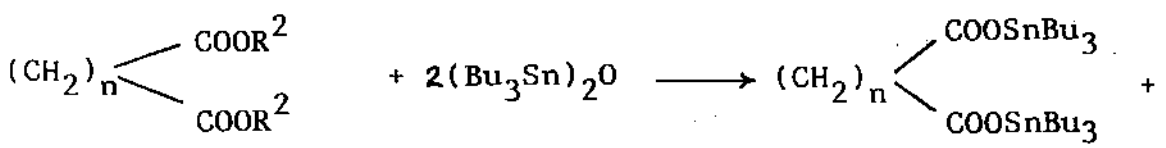
(32) (33)



(34) (35)

Its IR spectrum displayed absorption maxima for CO_2 at 1600(w) and 1525(w)cm^{-1}. The PMR spectrum of (33) could not be recorded because of its poor solubility in $CDCl_3$, D_6-DMSO and D_6-acetone. The reaction of methyl betulinate(34) with bis tri-n-butyltin oxide was conducted in carbon tetrachloride and the resulting tri-n-butylstannyl betulinate(35), isolated in 79% yield, m.p. 70-73°C, had the ν_{max} in IR at 3430(w) (for hydroxyl function), 1658(s) and 1635(s) (for the CO_2 and the C=C function). Its PMR was given in the experimental part of this SECTION-B.

Other two esters of dibasic acid were diethyl malonate(36) and dimethyl adipate(38) and both the esters gave the tin esters(37) and (39) respectively in good to excellent



(36) ; n = 1 , R^2 = Et ; (37) ; n = 1

(38) ; n = 4 , R^2 = Me ; (39) ; n = 4

yields. Their m.p.s are reported in the literature, prepared from their corresponding acids. For(37) m.p. 85-87°C(lit.[84] 87°C), IR: ν_{max} for CO_2, 1585(s) and 1565(s)cm^{-1} and the methylene protons appeared as a singlet at δ3.18. For(39); m.p.104-105°C(lit.[85] 105°C), IR: ν_{max} for CO_2, 1560(s) and 1540(s)cm^{-1} and the ^{1}H-NMR : δ 2.10-2.48(m, 4H), 0.70-1.90(m, 58H).

Triorganostannyl esters of benzoic acids are usually readily hydrolysed. We, therefore, tried this transesterification of methyl p-hydroxy benzoate(40) with bis tri-n-butyltin oxide, by heating their mixture in neat. After heating for 15 hours, the mixture was cooled and the residual solid was crystallised from ethanol to afford the tin ester(41) in 81% yield, m.p. 281°C(d). The tri-n-butylstannyl p-hydroxy benzoate was highly insoluble in $CDCl_3$, D_6-DMSO and D_6-acetone and therefore its NMR spectra could not be recorded.

Having succeded to obtain a standard, easy condition for this transesterification reaction, we were interested to see the hydrolysis of these triorganostannyl carboxylates under acid medium.

It is known that most triorganotin carboxylates are relatively more hydrolytically stable than diorganotin dicarboxylates[$R_2Sn(OCOR')_2$] or monoorganotin tricarboxylates

$[RSn(OCOR')_3]$[75]. The latter derivatives are readily hydrolysed in ethanol to form the monoorganotin oxycarboxylates, which were suggested to exist as polymers or oligomers in the solid state, $[RSn(O)OCOR']_n$. However, as discussed in the **Introduction** part of this **SECTION-B**, the triorganotin carboxylates could be hydrolysed readily by electrophilic(HX) or nucleophilic(OH^-) reagents.

We carried out the hydrolysis of these triorganotin carboxylates(**TABLE-I**) by using dilute hydrochloric acid(5N) or glacial acetic acid and at room temperature. The details of the reaction condition and procedure for work-up are described in the **Experimental Part**. We obtained the carboxylic acid in all the cases almost quantitatively.

I.B-2.2: Conclusion :

In conclusion, it was observed that alkyl, benzyl or aryl esters of several carboxylic acids (primary, tertiary, aryl, α,β -unsaturated) could be transesterified into their triorganotin carboxylates by using bis(triorganotin) oxides under strictly neutral condition. Subsequent hydrolysis of these tin esters using mild acids at room temperature afforded the acids in overall excellent yields. It was thus found feasible to use this method to hydrolyse the alkyl/aryl esters through their corresponding triorganotin esters followed by treatment with dilute acid. As such, a new facile and mild method for the hydrolysis of alkyl/aryl esters has been developed during the present study.

TABLE-I

R^1—COO—	Alkyl/Aryl R^2	Stannyl Ester $-SnR_3$	Hydrolysis Condition/ Stirred at r.t	Yield(%) of acid
CH_3-COO-	Et	(22) $SnBu_3$	HCl (5N)	92
CH_3-COO-	p-C_6H_4	(24) $SnBu_3$	HCl (5N)	92
CH_3-COO-	CH_2-Ph	(26) $SnBu_3$	HCl (5N)	92
CH_3-CH=CH-COO-	Et	(28) $SnBu_3$	HCl(5N)/ CH_2Cl_2	90
CH_3-CH=CH-COO-	Et	(29) $SnPh_3$	HCl(5N)/ $CHCl_3$	92
Ph-CH=CH-COO-	Me	(31) $SnBu_3$	HCl(5N)/ CH_2Cl_2	91
$Me_2C(COO-)-CH_2-COO-$	Me	(33) $SnBu_3$	HCl (5N)	89
Betulinate	Me	(35) $SnBu_3$	HCl (5N)	86
$CH_2(COO-)_2$	Et	(37) $SnBu_3$	Glacial AcOH/CH_2Cl_2	88
$(CH_2)_4(COO-)_2$	Me	(39) $SnBu_3$	Glacial AcOH/CH_2Cl_2	88
p-OH-C_6H_4COO-	Me	(41) $SnBu_3$	HCl (5N)/ $CHCl_3$	86

I.B-2.3: Experimental

I.B-2.3.1: General Procedure: Transesterification in Carbon Tetrachloride or Toluene

A solution of alkyl/aryl ester(0.5g-2g scale) and bis tri-n-butyltin oxide or bis (triphenyltin) oxide(1:1 equivalent for monoesters) in carbon tetrachloride or toluene was heated under reflux for several hours (noted for each compound below) using a Dean-Stark water separator. The completion of the reaction was monitored by checking TLC(developed in iodine chamber). After the reaction was complete, the solvents were distilled off and the triorganotin carboxylate was obtained from the residue as follows:

Tri-n-butylstannyl acetate(22)

i) From ethyl acetate: Ethyl acetate (2g,13.2 mmole), bis tri-n-butyltin oxide(7.92g, 13.2 mmole) in Carbon tetrachloride(40ml) were refluxed for 12 hrs. The compound(22) was isolated as colourless crystals by chromatography over silica-gel(eluant 25% benzene-light petroleum) yield=82%, m.p.. 85°C(lit.[1] m.p. 85°C).

IR: ν_{max} 1555(s), 1575(s)cm^{-1}

^{1}H-NMR($CDCl_3$):δ 0.70-1.90(m, 27H, $C_{1'}$, $C_{2'}$, $C_{3'}$ & $C_{4'}$), 1.95(s, 3H, C2).

% Analysis for $C_{14}H_{30}SnO_2$:

Found:	C	48.20	H	8.75	Sn	34.19
Calcd.:	C	48.17	H	8.66	Sn	34.00

ii) From hydroquinone diacetate : Hydroquinone diacetate (2g, 10.2 mmole), bis tri-n-butyltin oxide(12.26g, 20.4 mmole) in carbon tetrachloride(50 ml) were refluxed for 24 hours. The crude residue was purified by column chromatography on silica-gel. Elution with 20% benzene-light petroleum gave 96% colourless crystals of tri-n-butylstannyl acetate(22). The m.p., m.m.p., IR and PMR data all were identical with the values of tri-n-butylstannyl acetate(22) obtained from ethyl acetate.

iii) From benzyl acetate : Benzyl acetate(1.5 g, 9.9 mmole), bis tri-n-butyltin oxide(5.95g, 9.9 mmole) in 30 ml carbon tetrachloride were refluxed for 12 hours. Colourless crystals of tri-n-butylstannyl acetate(22) were isolated by performing silica-gel column chromatography (25% benzene-light petroleum was used as eluant) in 90% yield. Physical and spectral data of which were similar to that of the compound(22) obtained from ethyl acetate.

Tri-n-butylstannyl crotonate (28) from ethyl crotonate (27)

A mixture of ethyl crotonate (1 g, 8.7 mmole) and bis tri-n-butyltin oxide (5.22 g, 8.7 mmole) in 20 ml carbon tetrachloride was refluxed for 12 hours. The residue was purified by column chromatography. Elution with 40% benzene-light petroleum afforded (28) which was recrystallised from light petroleum to furnish colourless needle shaped crystals of tri-n-butylstannyl crotonate(28), yield=95%, m.p. 81°C(lit.[86] m.p. 84°C).

UV(EtOH) λ_{max} 224(ϵ=1,618)

IR: ν_{max} 1535(s), 1555(s), 1655(s) cm^{-1}

^{1}H-NMR($CDCl_3$): δ 0.85(t, J=7.25 Hz, 9H, $C_{4'}$), 1.20-1.39 (m,12H, $C_{1'}$ & $C_{3'}$), 1.54-1.74(m, 6H, $C_{2'}$), 1.81(d, J=1.70 Hz, small allylic coupling and 6.90 Hz, 3H, C4), 5.84(d, J=1.7 Hz, small allylic coupling and 15.40 Hz, 1H, C2), 6.84(m, 1H. C3).

Triphenylstannyl crotonate (29) from ethyl crotonate (27)

Ethyl crotonate (1g, 8.7 mmole), bis triphenyltin oxide (6.27 g, 8.7 mmole) in toluene (20 ml) were refluxed for 24 hours. An oily mass was obtained which was solidified on scratching. The crude was crystallised from chloroform-

benzene mixture to furnish colourless solids of (29), yield = 78%, m.p. 141-142°C.

UV($CHCl_3$): λ_{max} 241 (ϵ = 1,182).

IR : ν_{max} 1515(s), 1545(s), 1570(m), 1650(s)cm^{-1}

^{1}H-NMR($CDCl_3$): δ 1.87(d, J=1.7 & 6.9 Hz, 3H, C4), 5.97(d, J=1.70 Hz, small allylic coupling & 14.0 Hz, 1H, C2), 7.06 (m, 1H, C3), 7.37-7.50(m, 9H, Aromatic), 7.62-7.89(m, 6H, Aromatic).

Tri-n-butylstannyl cinnamate(31) from methyl cinnamate(30)

Methyl cinnamate(2g, 12.3 mmole) and bis tri-n-butyltin oxide(7.35g, 12.3mmole) in 40 ml carbon tetrachloride were refluxed for 12 hours. The residue was charged into silica-gel column packed with light petroleum. The desired product was eluted with 40% benzene-light petroleum. Recrystallisation from light petroleum provided an analytical sample(31), yield 80%, m.p. 71°C(lit.[86] 69-70°C).

UV(EtOH) : λ_{max} 215(ϵ 5,250), 270(ϵ 6,700)

IR: ν_{max} 1555(s), 1580(m), 1640(s)cm^{-1}

^{1}H-NMR($CDCl_3$): δ 0.92(t, J=7.22 Hz, 9H, C_4,), 1.27-1.42(m, 12H, C_1, & C_3,), 1.58-1.71(m, 6H, C_2,), 6.49(d, J=15.94 Hz, 1H, C2), 7.33-7.39(m, 3H, Aromatic), 7.47-7.52(m, 2H, Aromatic), 7.61(d, J=15.94 Hz, 1H, C3).

Preparation of 2,2-dimethyl succinic acid, used here following the literature procedure[82]

In a 100 ml round bottom flask, fitted with a double surface condenser, 10g(12.6 ml, 0.172 mole) of pure dry acetone, 10g(9.4 ml, 0.088 mole) of ethyl cyanoacetate and 0.5g of piperidine were placed. The mixture was allowed to stand for 72 hours and then heated on water bath for 1 hour. After cooling, 50 ml ether was added to the cold reaction mixture and washed with dilute hydrochloric acid and then with water. The organic layer was dried(Na_2SO_4), evaporation of the solvents provided a liquid residue which was distilled under reduced pressure and collected the desired product, ethyl isopropylidene cyanoacetate at 90-100°C/2.5-4 mm Hg (8.5g, 63%).

8g(0.052 mole) of the aforementioned cyano ester was dissolved in 40 ml of rectified spirit and an aqueous solution of KCN (8g KCN dissolved in 16 ml of water) was added. It was allowed to stand for 48 hours. After that, alcohol was distilled off and the residue was refluxed for 3 hours by adding a large excess of concentrated hydrochloric acid. The reaction mixture was diluted with water and extracted with ether(3 x 50ml) after saturating with ammonium sulphate. The combined etherial layer was dried(Na_2SO_4) and the solvents were distilled out. The residue was

recrystallised from excess concentrated hydrochloric acid and dried at room temperature to furnish pure 2,2-dimethyl succinic acid(4.8g, 63%), m.p. 139-140°C(lit.[82] m.p.141-142°C)

The foregoing 2,2-dimethyl succinic acid was esterified by heating gently for 12 hours with bidistilled methanol in presence of a few drops of concentrated sulfuric acid and worked-up following the usual procedure. The residue was sublimed at 100-110°C/2-3 mm of Hg afforded pure dimethyl 2,2-dimethyl succinate. IR: ν_{max} 1715(s), 1745(s)cm^{-1}. ^{1}H-NMR($CDCl_3$) : δ 1.23(s, 6H, gem-CH_3), 2.50(s, 2H, -CH_2), 3.45(s, 3H, -$COOCH_3$), 3.48(s, 3H, -$COOCH_3$).

Tri-n-butylstannyl 2,2-dimethyl succinate(33) from dimethyl 2,2-dimethyl succinate(32)

A solution of dimethyl 2,2-dimethyl succinate(1g, 5.7 mmole) and bis tri-n-butyltin oxide(6.84g, 11.7 mmole) in 20 ml toluene was refluxed for 36 hours. After cooling to room temperature a small amount of white solids was settled down which was eliminated by filtration. Filtrate was concentrated and allowed to stand for overnight. Powdery, pale yellow coloured solid was appeared and filtered off, washed with benzene, dried in vacuo to furnish the compound (33) in 82% yield, m.p. 205-208°C(dec.).

IR(KBr): ν_{max} 1525(w), 1600(w)cm^{-1}

^{1}H-NMR spectra of (33) could not be recorded due to its poor solubility in $CDCl_3$, D_6-DMSO and D_6-acetone.

% Analysis for $C_{30}H_{62}Sn_2O_4$:

Found :	C	49.83	H	8.82	Sn	32.85
Calcd.:	C	49.75	H	8.63	Sn	32.78

Tributylstannyl betulinate(35) from methyl betulinate(34)

Methyl betulinate(0.5g, 0.6 mmole), bis tri-butyltin oxide(0.39g, 0.6 mmole) in 5 ml carbon tetrachloride were refluxed for 18 hours. Colourless needle shaped crystalline compound(35) was obtained by recrystallisation twice from light petroleum, yield=79%, m.p. 70-73°C.

IR($CHCl_3$): ν_{max} 1605(s), 1635(s), 1658(s)cm^{-1} for CO_2 and 3430(m)cm^{-1} for -OH.

^{1}H-NMR($CDCl_3$): δ 0.86-2.08(m, 67H), 2.18(s, 3H), 4.43(m, centered at, 1H), 5.88(s, 1H), 6.13(s, 1H).

% Analysis for $C_{42}H_{74}SnO_3$:

Found :	C	67.50	H	9.87	Sn	16.05
Calcd.:	C	67.64	H	10.00	Sn	15.91

Tri-n-butylstannyl p-hydroxy benzoate(41)from methyl p-hydroxy benzoate(40)

A mixture of Methyl p-hydroxy benzoate(1g, 6.5 mmole), and bis tri-n-butyltin oxide(3.92g, 6.5 mmole) was

heated in neat for 15 hours. Borwn-coloured crude solid was dissolved in ethanol, a small amount of insoluble solid was removed by filtration. The filtrate was concentrated and allowed to stand for overnight. Powdery pale yellow coloured solids were obtained and dried in vacuo to furnish compound(41), in 81% yield, m.p. 281°C(dec.). Probably the p-OH group has been converted into p-$OSnBu_3$, as the product did not give colouration with $FeCl_3$.

IR: ν_{max} 1510(m), 1535(w), 1605(s)cm^{-1}.

^{1}H-NMR spectra of the sample could not be recorded because of poor solubility in $CDCl_3$, D_6-DMSO and D_6- Acetone.

Tri-n-butylstannyl malonate(37) from diethyl malonate(36)

Diethylmalonate(1.5g, 9.3 mmole) and bis tri-n-butyl tin oxide (11.09g, 18.6 mmole) in 30 ml carbon tetrachloride were refluxed for 12 hours. The residue was recrystallised twice from light petroleum afforded stannyl malonate(37), yield=65%, m.p. 85-87°C (lit. [84] 87°C).

IR: ν_{max} 1565(s), 1585(s)cm^{-1}

^{1}H-NMR($CDCl_3$):δ0.66-1.90(m, 54H), 3.18(s, 2H).

% Analysis for $C_{27}H_{56}Sn_2O_4$

Found :	C	47.62	H	8.31	Sn	34.92
Calcd.:	C	47.54	H	8.27	Sn	34.80

Tri-n-butylstannyl adipate(39) from dimethyl adipate(38)

Dimethyl adipate(2 g, 11.4 mmole), bis tri-butyltin oxide(13.6 g, 22.9 mmole) were refluxed in 40 ml carbon tetrachloride for 12 hours. The compound(39) was isolated as colourless crystals by chromatography over silica-gel (eluant 25% benzene-light petroleum), yield=91%, m.p. 104-105°C (lit.[85] 105°C).

IR : ν_{max} 1540(s), 1560(s)cm^{-1}.

^{1}H-NMR($CDCl_3$) :δ0.70-1.90(m, 58H), 2.10-2.48(m, 4H).

% Analysis for $C_{30}H_{62}Sn_2O_4$:

Found :	C	49.61	H	8.49	Sn	32.78
Calcd.:	C	49.75	H	8.63	Sn	32.85

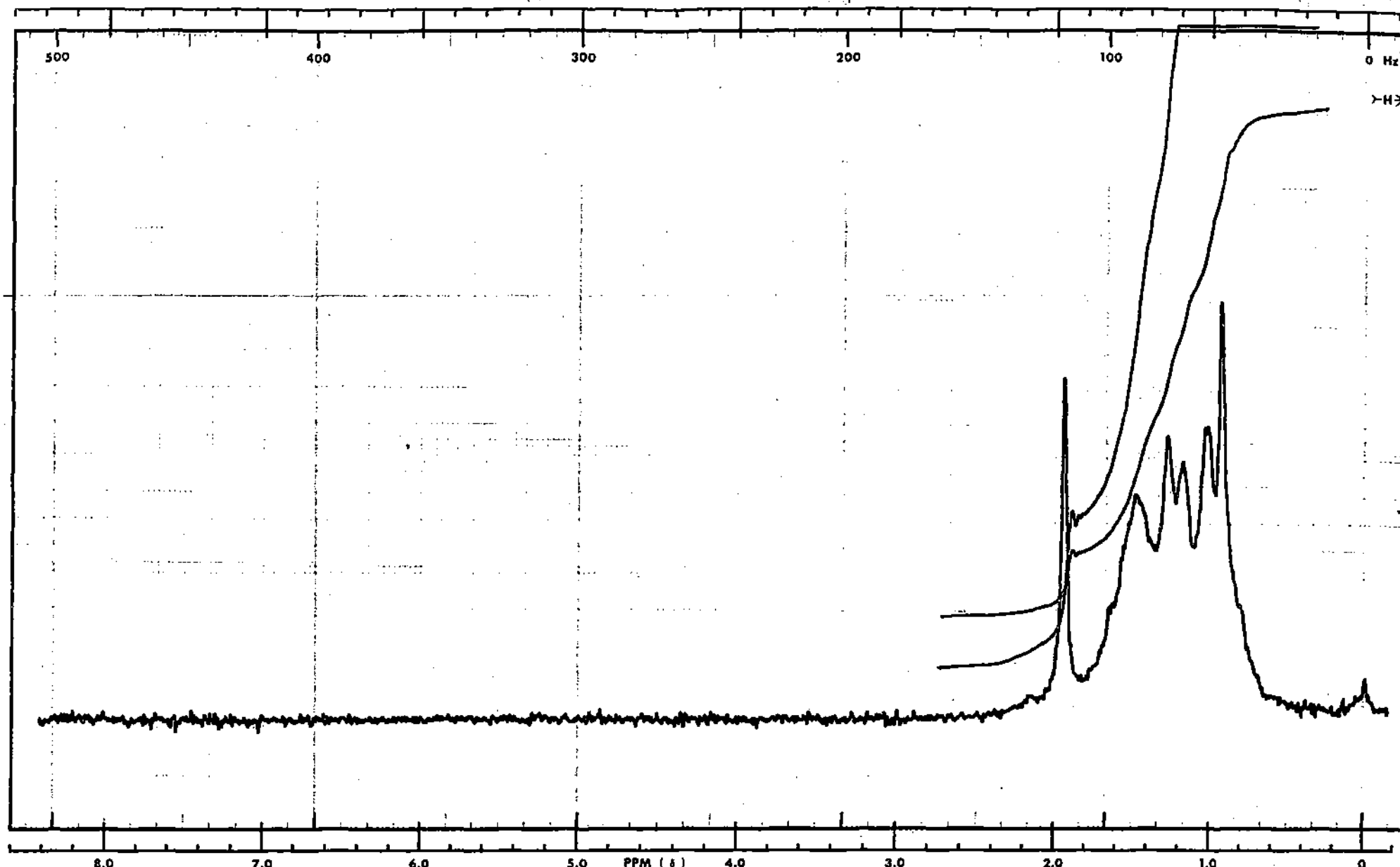
I.B-2.3.2: Hydrolysis of Triorganotin carboxylates (22, 28, 29, 31, 33, 35, 37, 39, 41) into their corresponding Acids

General Procedure :

I. The stannyl esters(2g) were taken in 2 ml dilute hydrochloric acid(5N) or in glacial acetic acid(2ml) (TABLE-I) as a suspension and stirred overnight at room temperature. The volatiles were removed under reduced pressure, the acids were obtained either by extracting with ether(2 x 25 ml) or by crystallisation from benzene-light petroleum. Yields(%)of acids were recorded in (TABLE-I).

II. To a stirred solution of stannyl esters(2g) in either dichloromethane (5 ml) or chloroform(5 ml), 2 ml of dilute hydrochloric acid(5N) or glacial acetic acid(2 ml) was added. The heterogeneous solution was stirred overnight at room temperature . The reaction mixture was diluted with ether (10 ml) and washed with aqueous sodium bicarbonate solution (2 x 10 ml). Then the aqueous phase was acidified by dropwise addition of dilute hydrochloric acid(5N) in an ice-cold condition and extracted with ether (2 x 25 ml). Combined etherial layers were washed with brine, and dried over anhydrous Na_2SO_4. Volatiles were removed and the residue was dried under vacuo. Recrystallisation from benzene-light petroleum afforded the acids in quantitative yields. TLC, m.p., IR of the acids, all were identical with the authentic sample. The yields(%) of the acids were given in TABLE-I.

CHART 5-60T
MADE IN U.S.A.



MANUAL | AUTO ☐

SWEEP OFFSET (Hz): _____
SPECTRUM AMPLITUDE: _____
INTEGRAL AMPLITUDE: _____
SPINNING RATE (RPS): _____

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

SAMPLE: S. Dek. C. DEB

SOLVENT: CCl4

REMARKS:

$CH_3COOSnBu_3$

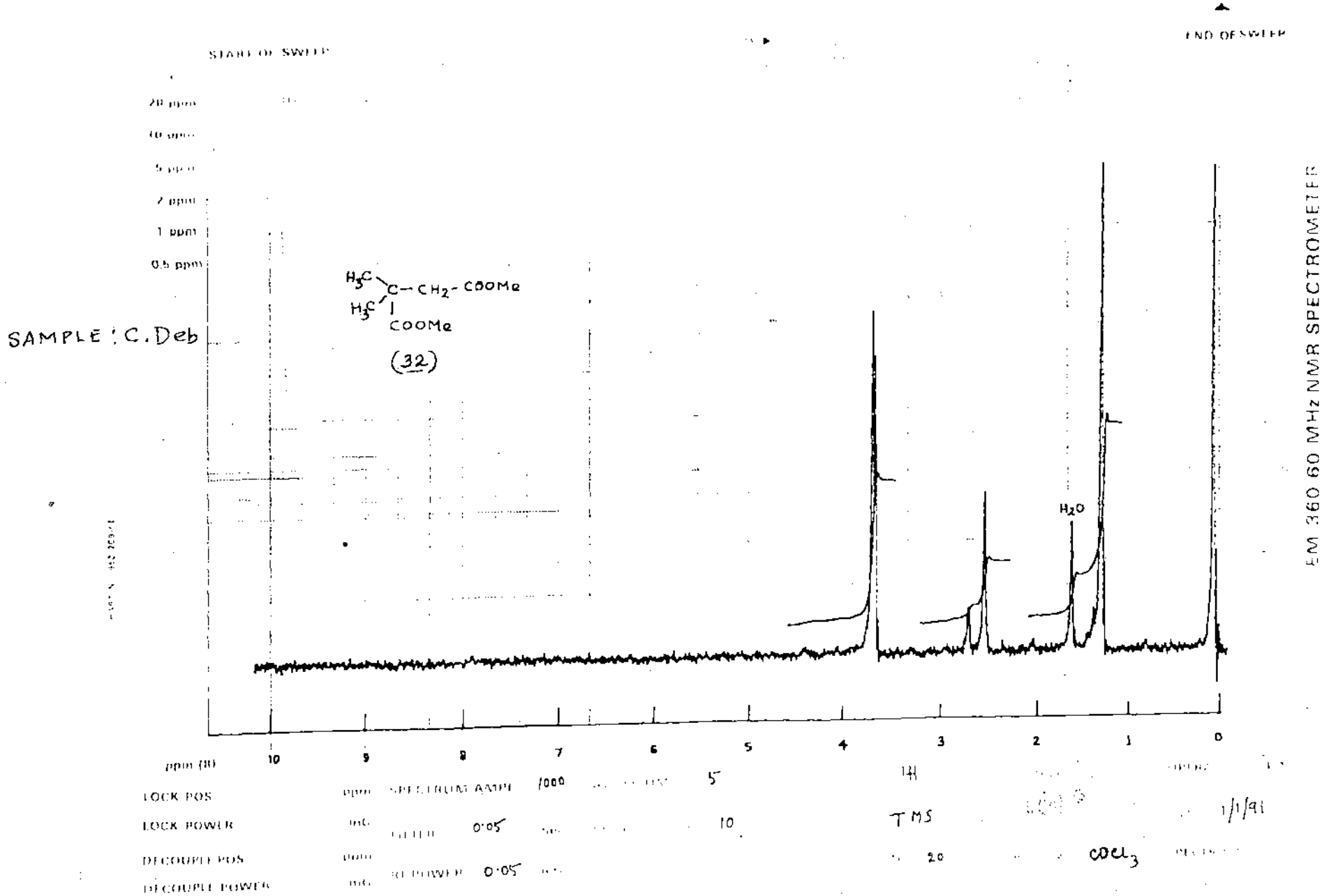
(22)

varian
analytical instrument division

DATE: 08/8/90

OPERATOR:

60 MHz NMR
SPECTRUM NO.


START OF SWEEP
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(32)
H_2O
ppm (δ)
10
9
8
7
6
5
4
3
2
1
0
TMS
$CDCl_3$
1/1/91
LOCK POS
LOCK POWER
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DECOUPLE POWER
0·05
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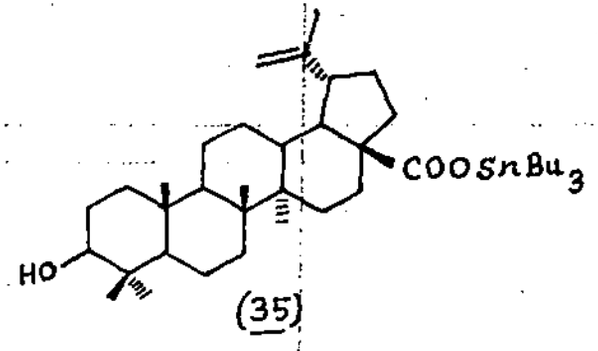
EM 360 60 MHz NMR SPECTROMETER

CHART 5-60T
MADE IN U.S.A.



(35)

500 400 300 200 100 0 Hz

8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0

MANUAL AUTO ☐ SAMPLE: C. Deb REMARKS:

SWEEP OFFSET (Hz): _____
SPECTRUM AMPLITUDE: 16
INTEGRAL AMPLITUDE: 3
SPINNING RATE (RPS): _____

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

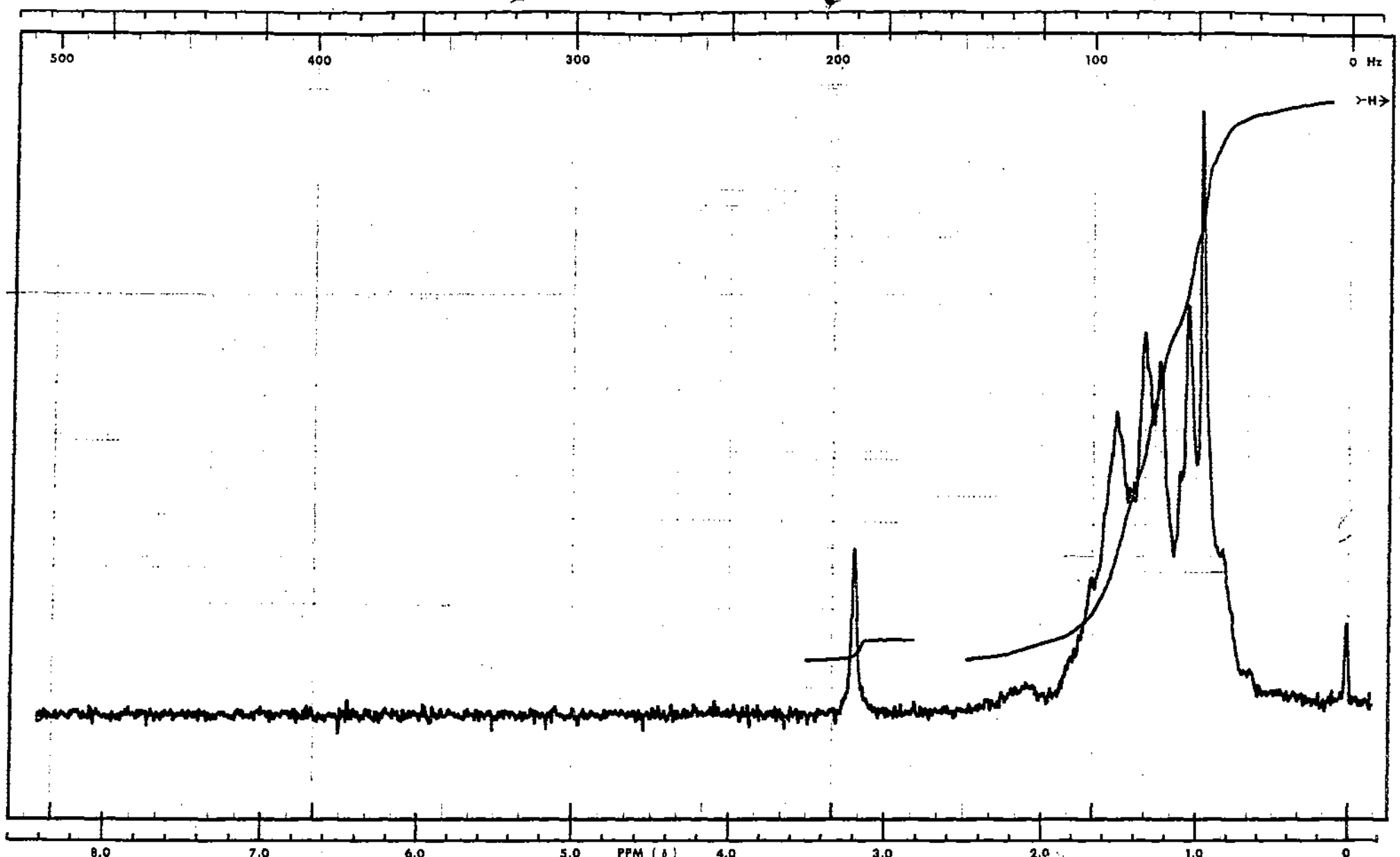
SOLVENT: $CDCl_3$

varian
analytical instrument division

DATE: _____ OPERATOR: _____

60 MHz NMR
SPECTRUM NO. _____

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



SWEEP OFFSET (Hz): _____

SPECTRUM AMPLITUDE: _____

INTEGRAL AMPLITUDE: _____

SPINNING RATE (RPS): _____

MANUAL

SWEEP TIME (SEC): 50 | 250

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

FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8

RF POWER LEVEL: _____

AUTO ☐

(250)

(500)

(2)

(.05)

SAMPLE: S. Dcl. C. DEB

SOLVENT: cdcl3

REMARKS

CH_2(COOSnBu$_3$)$_2$

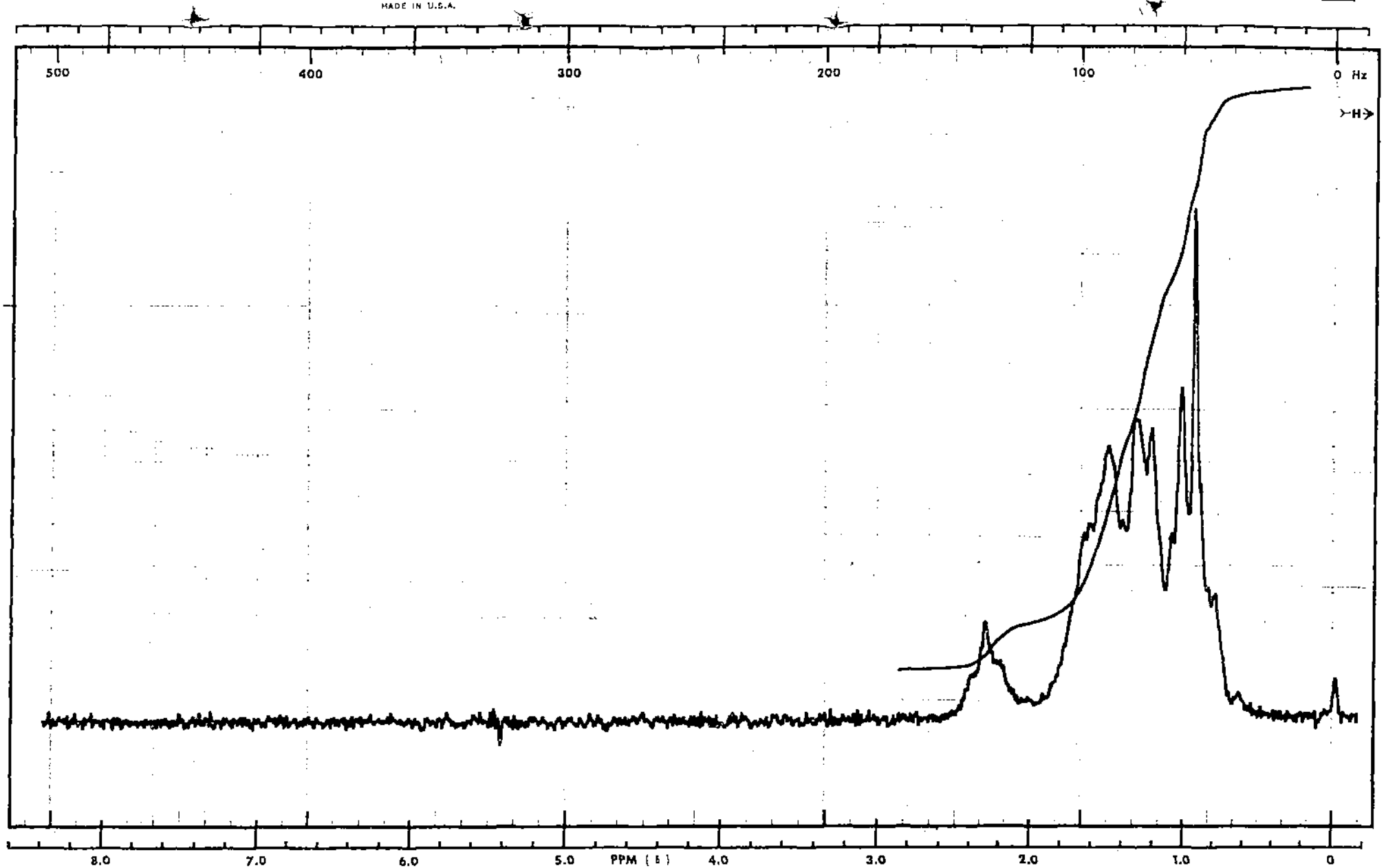
varian
analytical instrument division

DATE: 09/8/90.

OPERATOR: _____

60 MHz NMR SPECTRUM NO. (37)

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



SWEEP OFFSET (Hz): _____
SPECTRUM AMPLITUDE: 16
INTEGRAL AMPLITUDE: 3
SPINNING RATE (RPS): _____

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

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: S. Dele
C. DEB

SOLVENT: ~~dry~~ $CDCl_3$.

REMARKS:

$(CH_2)_4$ with $COOSnBu_3$ and $COOSnBu_3$

varian
analytical instrument division

DATE: 08/6/70

OPERATOR: _____

60 MHz NMR
SPECTRUM NO. (39)

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PART -- I SECTION - C

Toxicity (fungicidal and phyto-) of a series of α,β-unsaturated triorganostannyl carboxylates against some phytopathogenic fungi.

I.C-1: Studies on Toxicity of a Series of Unsaturated Triorganotin Carboxylates against Phytopathogenic Fungi

I.C-1.1: Introduction

In the earlier section (SECTION-A) of the thesis, preparation, spectroscopic characterisation and regioselective reaction with mercury(II) salts of some α,β-unsaturated (both olefinic and acetylenic) triorganostannyl esters have been presented. Since triorganotin carboxylates are known to exhibit a wide range of biological effects[1-3], some studies were undertaken to screen the fungicidal and phytotoxicity of a series of unsaturated triorganostannyl carboxylates during the course of the present study. As a prelude to the present work, it is necessary to describe a concise review on the previous applications of related compounds.

Organotin compounds after their discovery around 1850, long remained of purely scientific interest. A systematic investigation of the antifungal effectiveness of organotin compounds was started in 1950 by van der Kerk and Luijten[4]. They evidenced the high fungitoxicity of compounds of the type R_3SnX(triorganotin derivatives) compared to tetra- (R_4Sn), di- (R_2SnX_2), and mono-($RSnX_3$), substituted

organotin compounds. From their studies[5-7] with trialkyltin compounds(R_3SnX), the nature of the X group did not appear to have, in general, any particular effect on the activity. With regard to alkyl groups, e.g. with trialkyltin acetates($CH_3COO-SnR_3$), it was revealed that not the nature of the individual groups, but the total number of carbon atoms in the three groups was decisive. For a high antifungal toxicity the total number of carbon atoms in the alkyl groups of a trialkyltin compound should be about nine to twelve[6]. Thus dimethyloctyltin acetate(1) had the same high activity as tri-n-propyltin acetate(2) or as tri-n-butyltin acetate(3). They inhibited the growth of test fungi at concentration of 1mg/L or lower[5,8]. Tricyclopentyl(4) or tricyclohexyltin acetates(5) were more active than the n-alkyl derivatives[7].

$$CH_3-\overset{O}{\overset{\|}{C}}-O-SnR_2R^1$$

(1) R=Me, R^1=Octyl

(2) R = R^1 = n-Pr

(3) R = R^1 = n-Bu

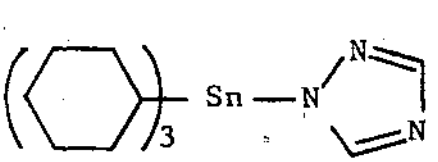
(4) R=R^1=Cyclopentyl

(5) R=R^1=Cyclohexyl

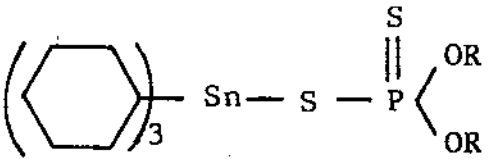
(6) R=R^1= Phenyl

In the case where R=aryl, introduction of functional groups did not lead to a significant improvement in activity over that of the unsubstituted triphenyltin derivative[5,9,10]. Triphenyltin acetate(6), the first agricultural organotin

fungicide(BRESTAN®), was developed by Hoechst in 1960[11,12]. Shortly afterwords, a second organotin fungicide, triphenyltin hydroxide, with a spectrum of activity similar to that of acetate[13], achieved commercialisation[3]. Among other triorganotin compounds, the major agricultural application was realised in tricyclohexyltin hydroxide(PLICTRAN)[14] and compounds(7)[15] and (8)[16].

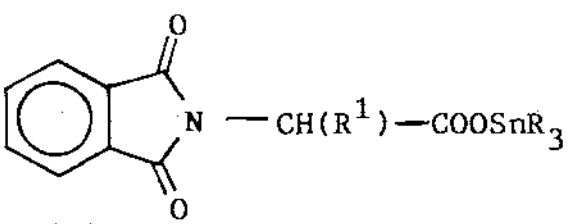


(7) Tricyclazole



(8) R-28627

Several articles on applications and biological effects of organotin compounds are available in the literature[1-3,17]. In the recent years, Shcherbakov & his workers[18] and M. Gielen & his associates[19,20] carried out investigation on the biological activity of trialkyltin esters of N-phthaloyl-protected amino acids(9) and triphenyltin carboxylates(10) of substituted salicylic acids[19] respectively.



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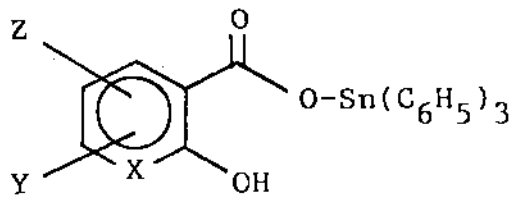


(10a) X=CH, Y=4-Me, Z=H

(10b) X=CH, Y=5-OMe, Z=H

(10c) X=CH, Y=5-NH_2, Z=H

(10d) X=CH, Y=5-SO_3H, Z=H

(10e) X=CH, Y=3-$CHMe_2$, Z=$CHMe_2$

(10f) X=N, Y= Z = H

Shcherbakov et al.[18] observed that their compounds were indicative of the average fungicidal activity[21]. However, the phthaloyl protection of the amino group increased to some extent the fungitoxicity relative to the organotin analogue with the unprotected amino group. In their studies with compounds(10a-10f), Gielen et al.[19] noticed that compounds(10c) and (10e) displayed highest toxicity against Gaeumannomyces graminis while compounds (10b) and (10c) were most toxic against Fusarium avenacearum fungi.

The principal advantages of the organotin agrochemicals (which mainly possess prophylactic action[22]) are their relatively low phytotoxicity, their generally low toxicity to

non-target organisms and the lack of resistance by crop pests to these chemicals. Furthermore, triorganotin compounds possessing relatively weak nature of Sn-C bond, undergo degradation in the environment, eventually to form harmless inorganic tin residues.

The mode of action or metabolism of organotin compounds has been the subject of much discussion. It was suggested [8,23] that inhibition of oxidative phosphorylation in the case of the trialkyltin compounds might be the case of the observed inhibition of fungal growth. In vivo animal studies, little informations were derived regarding the dealkylation or dearylation products formed from the organic moieties. However, work by Prough et al.[24] on the NADPH- and oxygen dependent microsomal metabolism of the ethylene series Et_nSnX_{4-n}(n=2-4) demonstrated that the major organic metabolite was ethylene and the minor product, ethane.

I.C-2: Present work: Results and discussion

From the preceding discussion it was evident that for trialkyltin acetates to exhibit antifungal activity, the nature of alkyl groups had a great role. At the same time, the influence of the nature of the carboxylate group on the activity was also studied[25]. In connection with our interest

with α, β -unsaturated triorganostannyl carboxylates, we focussed our attention on the fungicidal activities in vitro of the compounds(11-20). Early studies[26] on the fungitoxicity of unsaturated trialkyltin carboxylates, e.g., acrylate, methacrylate etc. were associated with a problem relating to their stability. These esters are known[27] to be polymerised even at room temperature. The tin carboxylates, comprised of the present investigation, were isolated in pure form conveniently and stable enough to conduct the biological studies. The in vitro tests of fungicidal activity of the organotin compounds have limited value to the organotin pesticide chemist unless their phytotoxicity are determined[3]. We also studied the phytotoxicity of these unsasturated triorganostannyl esters (11-20).

I.C-2.1: Biocidal Activity

The compounds(11-16) were screened for their fungicidal effectiveness in vitro against Alternaria solani and the esters(17-20) were screened against Piricularia oryzae. The poison food technique [28] was followed for testing and the growth inhibition was evaluated using the formula[29]: % inhibition=C-T/C x 100, where C and T are growth of fungus under control and treated plates respectively. All the carboxylates(11-16) were found to be active against A. solani

and compounds(17-20) against P. oryzae. The % of growth inhibition was measured at different concentration at different time (24hrs, 48hrs and 72hrs.) and the ED_{95} values were obtained by calculating these results by least square regression analysis. The results were summarised in TABLE I & II.

For phytotoxicity study of these unsaturated tin carboxylates(11-20), rice seeds were dipped in compound suspension at different concentration (25, 50 and 100 ppm) for one, four and eight hours. The treated seeds were allowed to germinate for eight days and germinated seeds were counted against control. The percentage of germinated seed at different concentrations and times were presented in TABLE-III.

From the results (ED_{95} values) in TABLE-I it was found that compound(11), the tri-n-butylstannyl crotonate, showed maximum inhibition after incubation for 24 hours and 72 hours while the tri-n-butylstannyl p-nitro cinnamate(15), inhibited the growth at 4.96 ppm after 48 hours against A. solani. On the other hand, triphenylstannyl crotonate(12) was found to be least active. From TABLE-II, triphenyltin but-2-ynoate(20), was the most active against P. oryzae after 24 hours incubation(1.95 ppm) and least active after 72 hours

incubation(12.87 ppm). The tri-n-butyltin cyclohexylidene acetate(18) inhibited the growth of the fungi (P. oryzae)with doses within the range 5.93-7.00 ppm, an average acitivity relative to other tin esters.

With regard to the assessment of phytotoxicity of these unsaturated tin carboxylates(11-20) (TABLE-III), it was revealed that tri-n-butylstannyl but-2-ynoate(19) did not have practically any phytotoxicity even at doses 100 ppm. The compounds(11) and (15) were most fungitoxic against A. solani, and at the same time their phytotoxic effects were almost nil. Again, the compound(20) exhibited highest fungicidal effectiveness and its phytotoxicity was nil. Among these esters studied, the tri-n-butylstannyl sorbate(13) showed highest phytotoxicity for 8 hours dipping at the concentration 50 and 100 ppm.

Despite the effectiveness of tripropyl- and tri-n-butyl-tin compounds in vitro, field trials demonstrated that not only are they very phytotoxic, but their ability to control fungi is reduced. In contrast, triphenyltins were found to be tolerated by the plants to a greater degree and were highly fungistatic. In our studied compounds, for example the tri-n-butylstannyl but-2-ynoate(19) and triphenyltin but-2-ynoate(20), the butyl group showed less phytotoxicity than the phenyl group. However, the

triphenyltin ester(20) exhibited most fungitoxicity (1.95 ppm for 24 hrs.) compared to the butyltin ester(19) (4.37 ppm for 24 hrs.) against P. oryzae.

I.C-3: Experimental

Materials and Methods

Antifungal Activities

i) Compounds: Tri-n-butylstannyl crotonate(11), Triphenylstannyl crotonate(12), Trin-butylstannyl sorbate(13), Triphenylstannyl sorbate(14), Tri-n-butylstannyl p-nitrocinnamate(15), Triphenylstannyl p-nitro cinnamate(16), Tri-n-butylstannyl cinnamate(17), Tri-n-butylstannyl cyclohexylidene acetate(18), Tri-n-butylstannyl but-2-ynoate(19), Triphenylstannyl but-2-ynoate(20) reported earlier in SECTION-A, and have been tested for fungitoxicity and phytotoxicity.

ii) Organisms:

a) Alternaria solani (EII and Mart) Jones and Grout -causal organism of early blight disease of potato.

b) Piricularia oryzae cav-causal organism of blast disease of rice.

iii) Culture media : Solid media[malt extract agar[30]]

20g malt extract (Difco) was boiled in water till dissolved. 20g agar agar(Kobe-Japan) was added and boiled until agar agar was well dissolved. 0.05g chloramphenicol was

suspended in 5 ml of 95% alcohol and added to the medium as antibacterial agent. The volume of the medium was then made upto 1 litre by addition of water, P^H of the medium was adjusted with sodium hydroxide to 6.5. Medium was sterilised at 15 p.s.i. for 20 minutes.

I.C-3.1:

Antifungal Activities of some α,β -Unsaturated Organotin carboxylates in vitro

Acetone solution of suitable quantity of the compounds(11-20) in sterile distilled water was incorporated into melted malt agar so as to get the desired concentrations of the compound in the media. Media with desired concentrations of compounds were poured in petriplates and after solidification were incubated at the centre with uniform discs(7 mm) of mycelia, punched out with a sterile cork borer from the advancing zone of the culture test fungus. Three replications on each test with appropriate control under same conditions were maitained. The petriplates were then incubated at 30±1°C in dark. Linear growth of the fungal discs were measured after regular interval and the percentage of growth inhibition over control was calculated and finally ED_{95} values(ppm) were recorded in TABLE I & II.

TABLE-I

Effect on growth of A. solani

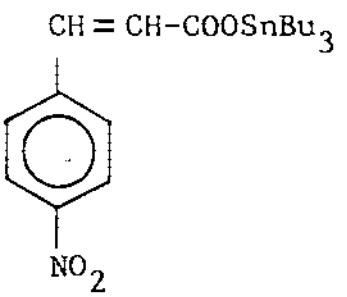
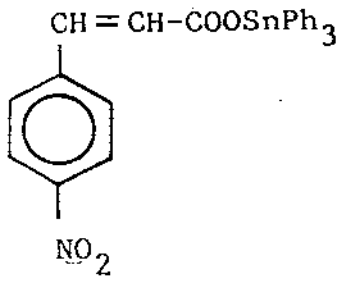
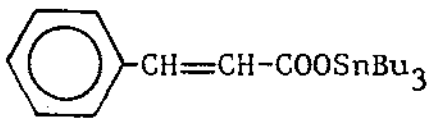
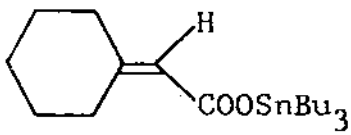
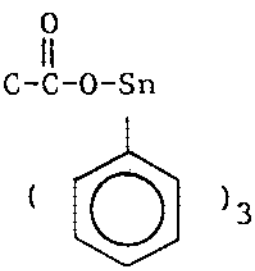
Compound	ED_{95} value(ppm) for incubation period		
	24hrs	48hrs	72hrs
(11) $CH_3-CH=CH-COOSnBu_3$	4.4	5.7	6.34
(12) $CH_3-CH=CH-COOSnPh_3$	9.92	10.00	10.00
(13) $CH=CH-COOSnBu_3$ $\vert$ $CH=CH-CH_3$	-	6.57	7.42
(14) $CH=CH-COOSnPh_3$ $\vert$ $CH=CH-CH_3$	-	5.74	5.80
(15) 	4.8	4.96	9.14
(16) 	9.24	9.36	10.00

TABLE-II

Effect on growth of P. oryzae

Compound	ED_{95} values(ppm) for incubation period		
	24hrs	48hrs	72hrs
(17) 	6.22	6.47	7.19
(18) 	5.93	6.50	7.00
(19) $CH_3-C\equiv C-COOSnBu_3$	4.37	8.45	9.22
(20) 	1.95	9.20	12.87

I.C-3.2: Phytotoxicity on Rice

i) Seed Sample :

Healthy rice seeds of PUSA 2-21 variety collected from Chinsurah Rice Research Farm, Hoogly, West Bengal were used in the investigation.

ii) Compound numbers (11-20)

iii) Effect on seed germination

Healthy rice seeds were dipped in compound suspension of 25, 50 and 100 ppm concentrations for 1, 4 and 8 hours. For control, water with requisite amount of acetone was used. The treated seeds were then placed on moist three layered filter paper in closed petriplates. Plates were incubated at 30 1°C. 100 seeds were maintained for each treatment. After 8 days the germinated seeds were counted. Seeds producing a root or a coleoptile were recorded as germenated. Three replications of each test with appropriate control under same conditions were maintained. The percentage of germinated seeds were counted with respect to control (results were placed in TABLE-III).

TABLE-III

Effect of the compounds on rice seed germination

Compound	Concn. (ppm)	% of germinated seeds with respect to control treated for		
		1hr	4hrs	8hrs
(11) Tri-n-butyltin crotonate	100	91	81	75
	50	93	83	82
	25	96	89	85
(12) Triphenyltin crotonate	100	91	88	88
	50	93	88	88
	25	98	90	89
(13) Tri-n-butyltin sorbate	100	83	79	66
	50	87	83	76
	25	96	95	79
(14) Triphenyltin sorbate	100	90	89	88
	50	92	90	88
	25	95	92	88
(15) Tri-n-butyltin p-nitro cinnamate	100	87	87	82
	50	89	91	90
	25	83	93	94
(16) Triphenyltin p-nitro cinnamate	100	86	88	81
	50	91	82	78
	25	95	90	83

Contd...

TABLE-III

Contd...

Compound	Conc^{n}. (ppm)	% of germinated seeds with respect to control treated for		
		1hr	4hrs	8hrs
(17) Tri-n-butyltin cinnamate	100	90	80	80
	50	91	82	78
	25	92	84	76
(18) Tri-n-butyltin cyclohexylidene acetate	100	100	93	90
	50	100	95	92
	25	100	96	93
(19) Tri-n-butyltin but-2-ynoate	100	100	100	98
	50	100	100	100
	25	100	100	100
(20) Triphenyltin but-2-ynoate	100	93	95	90
	50	97	95	91
	25	97	97	91

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JOM 23212PC

Preliminary Communication

Selectivity of mercury(II) salts in reactions with α,β-unsaturated stannyl esters

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(Received June 12, 1992; in revised form September 18, 1992)

Abstract

Demetallation reactions of tri-n-butyltin carboxylates of some α,β-unsaturated carboxylic acids (acrylic, crotonic, cinnamic, sorbic and cyclohexylidene acetic) with mercury(II) salts (HgX_2; X = Cl, OAc) occurred selectively, and no mercuration of the olefinic double bond was detected.

1. Introduction

The mercuration of olefins (isolated/conjugated) with mercury(II) salts is a well documented reaction [1]. The resulting organomercurials have found many applications in organic synthesis [2]. For example, the preparation of serin [3] involves the solvomercuration of the carbon–carbon double bond of methyl acrylate upon treatment with mercuric acetate in methanol, whereas organotin carboxylates undergo demetallation with mercury(II) salts as reported by Roy *et. al* [4]. With these observations in mind, it is of interest to investigate the reactions between α,β-unsaturated stannyl carboxylates and mercury salts. We report here the difference in reactivity towards mercury(II) salts observed in the case of stannyl esters and their alkyl esters, and we believe that this portends certain potential in organic synthesis.

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2. Results and discussion

Our investigation embodied several types of α,β-unsaturated tin carboxylates of unsubstituted (acrylic), β-monosubstituted (crotonic, cinnamic and hexa-2,4-dienoic) and β,β-disubstituted (cyclohexylidene acetic) carboxylic acids. The reactions of these esters with

TABLE 1.

Entry	Tin carboxylates	HgX_2	Solvent	Time/Temp.	Yield [a] of BuHgCl (%)	Yield [a] of Acid (%).
1	$CH_2=CH-COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	89	42
		X = Cl	CH_3CN	6 h/reflux	86	40
		X = OAc	MeOH	48 h/r.t.	84	30
		X = OAc	CH_3CN	6 h/reflux	82	42
2	$CH(CH_3)=CH-COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	40	45
		X = Cl	PhH	4 h/reflux	88	43
		X = OAc	CH_3CN	4 h/reflux	96	47
		X = OAc	PhH	4 h/reflux	84	48
3	$CH(Ph)=CH-COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	96	45
		X = Cl	CH_3CN	6 h/reflux	94	48
		X = OAC	MeOH	48 h/r.t.	85	46
		X = OAC	CH_3CN	6 h/reflux	90	49
4	$CH(CH=CH-CH_3)=CH-COOSnBu_3$ [c,e]	X = OAc	MeOH	48 h/r.t.	71	50
		X = Cl	PhH	4 h/reflux	76	43
		X = Cl	CH_3CN	6 h/reflux	92	59
5	 [d,e]	X = OAc	MeOH	48 h/r.t.	73	48
		X = Cl	PhH	4 h/reflux	78	44

[a] Yield of isolated pure product. [b] M.p. 69–70°C (Lit. [8] 69–70°C). [c] M.p. 84–85°C. [d] M.p. 80°C. [e] Compounds listed in entries 1, 4 and 5 gave satisfactory ^{1}H-NMR spectral data.

0022-328X/93/$6.00

mercuric chloride and mercuric acetate were studied in different solvents ranging from protic/aprotic polar to aprotic nonpolar (Table 1). In each case, butyl mercuric chloride and the corresponding acids were obtained after hydrolysis in fair to excellent yields. The formation of butyl mercuric chloride in the case of using mercuric acetate probably occurred [5] during washing of the reaction mixture with brine. Although change in the solvents did not significantly affect the yields of the products, the use of methanol, however, required a lower temperature. The results are summarised in Table 1.

While the alkyl esters of α,β-unsaturated acids, upon treatment with mercury(II) salts, undergo solvomercuration of carbon–carbon double bonds [2,3], the corresponding stannyl esters, upon similar treatment, react preferentially at the ester function keeping the olefin unreacted. Thus, by using the stannyl esters we were able to protect the carbon–carbon double bond and thereby provide a useful approach for preferential reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts. This method also provides a mild and neutral condition for hydrolysis of alkyl or aryl esters [6].

3. Experimental details

General procedure

To a solution of tri-n-butylstannyl carboxylates (2 mmol) in a solvent (10 ml) were added mercury(II) salt (2 mmol) (HgX_2; X = Cl, OAc) and the mixture was stirred under the conditions noted in Table 1. A small amount of white solids precepitated during the reaction which were filtered off. The filtrate was diluted with ether, and the organic layer was then washed with aqueous sodium chloride and dried over anhydrous Na_2SO_4. Evaporation of volatiles afforded the residue, which was crystallized from light petroleum to give BuHgCl as shining flakes in excellent yields.

M.p. 128°C (lit. [7] 127–130°C). ^{1}H-NMR (270 MHz, $CDCl_3$, ppm): δ 2.1 (t, 2H, J = 7.13 Hz), 1.78–1.67 (m, 2H), 1.48–1.34 (m, 2H), 0.95 (t, 3H, J = 7.29 Hz). ^{13}C-NMR (22.40 MHz, $CDCl_3$, ppm for APT spectra a (+) indicates 0 or 2 attached protons and a (−) indicates 1 or 3 attached protons): δ 33.06 (+), 30.09 (+), 27.81 (+), 13.47 (−). Anal. Found: C, 16.08; H, 3.17. C_4H_9HgCl calcd.: C, 16.38; H, 3.07%.

The mother liquor was diluted with ether and washed with saturated aqueous sodium bicarbonate. The aqueous phase was made acidic (3 N HCl) and extracted with ether. The organic phase was washed with aqueous sodium chloride, dried (Na_2SO_4) and evaporated to afford the corresponding acids, then recrystallized from benzene–light petroleum. Physical and spectral data of all acids isolated are identical with those of authentic samples.

Acknowledgements

We wish to thank Mr. T. Hinomoto, Jeol Ltd., Japan and RSIC, I.I.Sc., Bangalore for spectral analysis and CDRI, Lucknow for elemental analysis. One of us (CD) is grateful to the University of North Bengal for financial assistance.

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Indian Journal of Chemistry
Vol. 31B, February 1992, pp. 131-132

A mild and facile method for hydrolysis of esters†

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Received 10 May 1991; accepted 18 July 1991

A mild method for the hydrolysis of primary, tertiary and aromatic esters through their corresponding triorganostannyl esters is reported.

A number of mild hydrolytic and non-hydrolytic approaches are available for masking and demasking of carboxyl group (alkyl, aryl, etc.)[1,2]. Despite this, the search is on for still milder methods to bring about the demasking of carboxylate groups. We present herein a new two-step sequence for deprotection of alkyl/aryl carboxylates under mild acidic condition.

In the first step the alkyl/aryl carboxylates are transesterified to the trialkylstannyl esters under completely neutral conditions, such as (i) by azeo-

Table 1—Characterization data of triorganostannyl carboxylates (**2**)

Entry No.	Esters **1** R^1-COO-	R^2	Solvent	Reflux time (hr)	Yield of **2** (%)[a]	m.p.[b] (°C) (Lit.)	IR[c] of **2** (C=O) in cm^{-1} (Nujol)	PMR[d] of **2** in δ (ppm) (J = Hz); Solvents[e]
1a	$Ph-CH=CH-COO-$	Me	CCl_4	12	80	71	1640	0.70-1.90 (m, 27H), 6.35 (d, 1H, J = 16), 7.10-7.60 (m, 5H), 7.56 (d, 1H, J = 16)
1b	$Ph-CH=CH-COO-$	Me	Ph·Me	12	93	"	"	"
1c	$Ph-CH=CH-COO-$	Me	Neat	12	82	"	"	"
2	$CH_3-CH=CH-COO-$	Et	CCl_4	12	95	81	1655	0.66-1.75 (m, 27H), 1.82 & 1.86 (two ds, 3H, J = 7), 5.63-6.15 (m, 1H), 6.61-7.20 (m, 1H)
3	CH_3-COO-	Et	CCl_4	12	82	85 (85)[5]	1575, 1555	0.70-1.90 (m, 27H), 1.95 (s, 3H)
4	CH_3-COO-	CH_2-Ph	CCl_4	12	90	"	"	"
5	CH_3-COO-	p-C_6H_4	CCl_4	24	96	"	"	"
6	$Me_2C(CH_2-COO-)(COO-)$	Me	Ph·Me	36	82	205-208(d)	1600, 1525 (KBr)	f
7	Betulinate[4]	Me	CCl_4	18	79	70-73	3430 (−OH), 1658, 1635 ($CHCl_3$)	0.86-2.08 (m, 67H), 2.18 (s, 3H), 4.43 (m, centered at, 1H), 5.88 (s, 1H), 6.13 (s, 1H)
8	$p-OH\cdot C_6H_4\cdot COO-$	Me	Neat	15	81	281(d)	1605	f, g
9	$H_2C(COO-)_2$	Et	CCl_4	12	65	85-87 (87)[5]	1585, 1565	0.66-1.90 (m, 54H), 3.18 (s, 2H)
10	$(H_2C)_4(COO-)_2$	Me	CCl_4	12	91	104-105 (105)[6]	1560, 1540	0.70-1.90 (m, 58H), 2.10-2.48 (m, 4H)

(a) Yield of isolated pure product; (b) Uncorrected; (c) Recorded on a Pye Unicam SP 3-300S spectrophotometer; (d) Recorded on Varian T-60 or EM-360 spectrometer using TMS as internal standard; (e) CCl_4 used for Entry No. 1-5 & 9 and $CDCl_3$ used for Entry No. 7 & 10; (f) PMR spectra could not be recorded because of poor solubility in $CDCl_3$, D_6-DMSO & D_6-Acetone; (g) Probably the p-OH group has been converted into p-$OSnBu_3$ as the product did not give colouration with $FeCl_3$.

† A part of the work was presented in the 27th Annual Convention of Chemists, Dec. 26-30, 1990 (Abstract No. OS-13).

tropic distillation of esters **1** with bis-trialkyltin oxide in carbon tetrachloride or toluene or (ii) by heating their neat mixture. The corresponding triorganostannyl carboxylates **2** so formed undergo easy hydrolysis to acids **3** by treatment with dilute acid at room temperature (Table 1). In all the cases facile formation of stannyl esters and their facile hydrolysis are observed in overall excellent yields.

$$\underset{\mathbf{1}}{R^1COOR^2} + (n\text{-}Bu_3Sn)_2O \rightarrow \underset{\mathbf{2}}{R^1COOSn(n\text{-}Bu)_3} \rightarrow \underset{\mathbf{3}}{R^1COOH}$$

$$+ n\text{-}Bu_3OR^2 \qquad + n\text{-}Bu_3SnX\ (X = Cl, OAc)$$

R^1 = alkyl (primary, tertiary), aryl, α,β-unsaturated functions.
R^2 = alkyl, phenyl and benzyl groups.

Experimental

Transesterification of alkyl/aryl carboxylate **1**: *General procedure*

A solution of **1** and bis-tri-*n*-butyltin oxide (1:1 equivalent for monoesters) in carbon tetrachloride or toluene was heated under reflux for several hours (see Table 1) using a Dean-Stark water separator. The solvents were distilled off and the residue was chromatographed over silica-gel. Elution with 20-50% benzene-light petroleum afforded the tri-*n*-butylstannyl esters **2**.

The stannyl ester **2** was taken in dil. hydrochloric acid (5*N*) or in glacial acetic acid as a suspension and stirred overnight at room temperature. After removing the aqueous acids under reduced pressure the acid **3** was obtained either by extracting with ether or by crystallisation. The transformation was almost quantitative.

Acknowledgement

One of the authors (CD) is thankful to the North Bengal University for financial assistance. The authors are thankful to Mr P Ghosh, Department of Chemistry, N.B.U. for a gift of methyl betulinate[4] listed in Entry No. 7 in Table 1.

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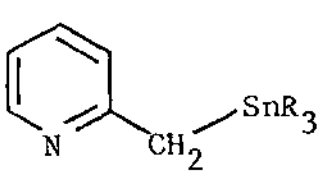
PART -- II

Preparation of picolyltrialkylstannanes and on the mechanism involving ambident nucleophilicity of picolyl anion.

II-1: Introduction

Among the unsymmetrical tetraorganotin compounds of the type R^1SnR_3, vinyl-[1,2] and allylstannanes[2a-c,3] form an increasingly important class of synthetic intermediates owing to their participation in wide range of carbon-carbon bond forming reactions. The reactions of allyltins are usually brought about by heat[4], high-pressure[5], transition metal-catalysis[6] or Lewis acid[7] activation and leading to a high degree of regio- and stereocontrol in the products. Alike allylstannanes(1), in the aromatic system, benzylstannanes(2) too have found applications[8] in organic synthesis taking into consideration that the C=C double bond being a part of the aromatic ring.



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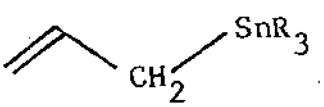
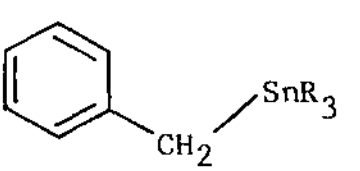


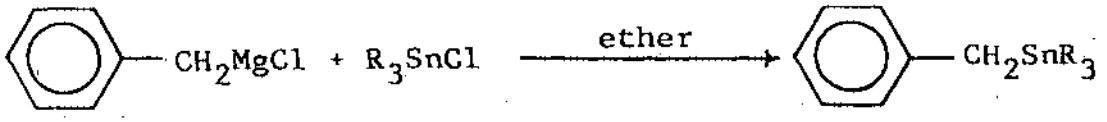
(1)



(2)

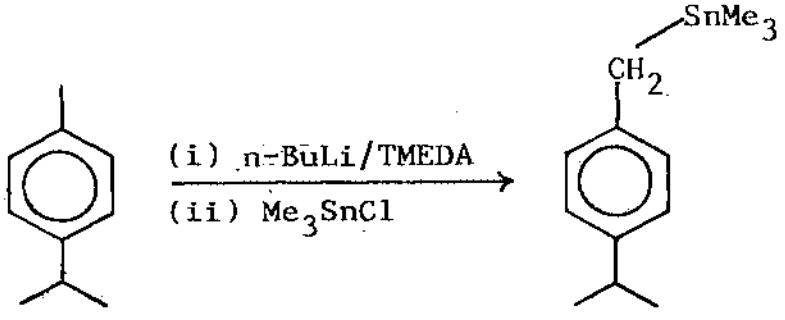
Benzyltrialkyltins(2) may be prepared in several ways:

i) The Grignard reagent(4), prepared from benzyl halide, is being reacted with trialkyltin halides in ether solution[9].



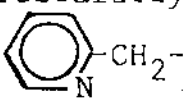
(4) (R=Me,Et,n-Pr,n-Bu) (2)

ii) Generation of benzyl anion by using base followed by quenching with trialkyltin halides[9b]. Recently, Andrianome et al.[8d] prepared the benzyltrimethyltin derivatives in terpenic series following the second procedure. They generated the benzyl anion by using n-butyllithium in tetramethylethylenediamine (n-BuLi/TMEDA) and then quenched with trimethyltin chloride. Their observation was that the introduction of the organometallic group occurred with a high degree of regioselectivity. Thus, p-cymene(5) was treated with n-BuLi/TMEDA and then quenched with Me_3SnCl to afford the benzyltin derivative(6), where the tin substituent appeared at the less substituted carbon atom exclusively.



(5) (6)

II-2: Present work: Objective and planning

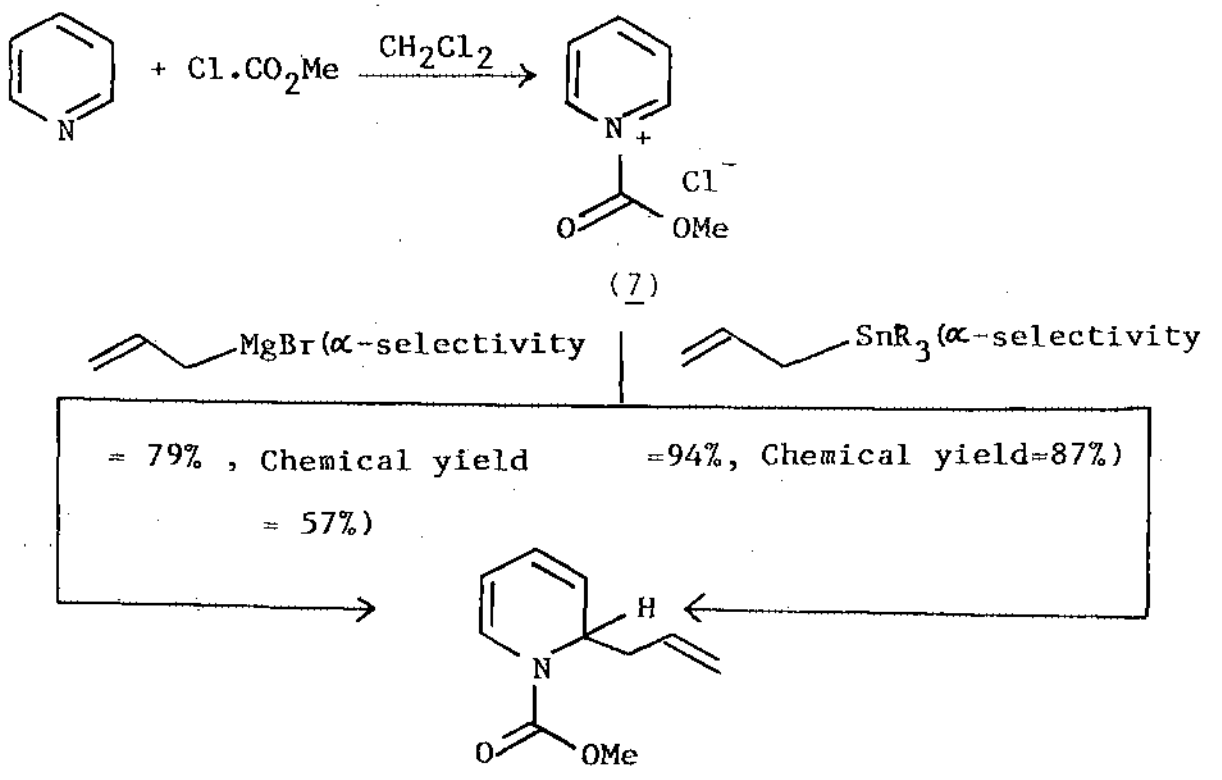
Although benzyltrialkylstannanes have enjoyed widespread applications[8,10] in the domain of synthetic organic chemistry over the last decade, almost no attention has ever been made to the use of benzyltins, where the aromatic ring contains one or more hetero-atom, particularly the nitrogen atom. In the case of pyridine, the  -CH_2- group is called picolyl group and the corresponding tin derivatives may be called as picolyltrialkylstannanes. We envisaged an enormous importance to use picolylstannanes leading to several heterocyclic compounds of great consequences[11] . The six π-electrons delocalisation and aromaticity in pyridine are essentially the same as that of benzene, but the greater electronegativity of nitrogen results in the dipolar resonance structures more important — the negative pole being towards nitrogen. Consequent effects are therefore expected and observed in the 2- and 4- alkyl substituents of the pyridine ring. It was therefore believed that the application of these organometallics in the synthesis of heterocyclic system would encompass a new chapter henceforth.

The plan of our work may be split into two parts, viz., the preparation of picolyltrialkyltins and secondly

their reactions under a variety of conditions, where cleavage of C—Sn bond would occur resulting in the formation of various N-containing substituted heterocyclic systems. In respect of their reactions we planned to carry out mainly two types of reactions.

1. Yamaguchi et al.[12] recently showed that activated pyridine ring(7) reacted with allyltrialkyltins in situ to afford 2-allyl-N-substituted 1,2-dihydropyridine(8) with a high degree of regioselectivity(SCHEME-I). They observed that

SCHEME-I



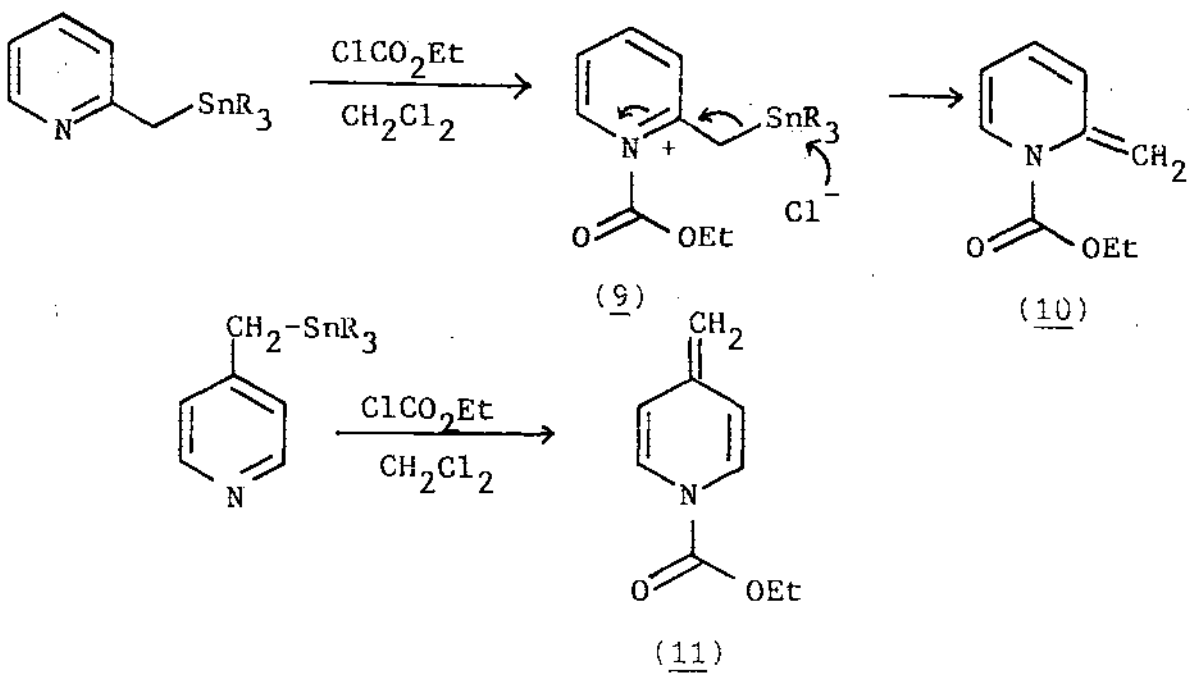
(7)

(8)

the reaction of alkyl magnesium bromide with N-(methoxy carbonyl) pyridinium chloride(7) resulted in rather low α-regioselectivity(79%) and chemical yield(57%) while allyltins gave in situ 94% α-selectivity and 87% chemical yield. It is important to mention that this reactions are believed to take place by S_N2' reaction. Again, allylsilanes, which had been widely used as allylating reagents[13], were found to be less neucleophilic[14] than allylstannanes.

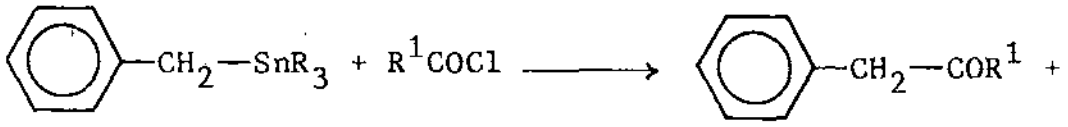
With this view in mind, we reasoned that if these picolyltrialkyltins could be prepared, further activation of the aromatic ring(9) with ethyl chloroformate would lead to N-(ethoxy carbonyl)-1, 2- or N-(ethoxy carbonyl)1,4-pyridine-methenes(10) and (11) respectively as outlined in SCHEME-II.

SCHEME-II



Pyridinemethenes are important intermediates in investigating biochemical mechanism of the toxic action of aldehydes when reacted with nucleotides possessing the dihydropyridine moiety[15,16]. Moreover, this types of pyridinemethene systems have proven to be valuable as synthetic intermediates for a variety of alkaloids[17] as well as NADH mimics[18].

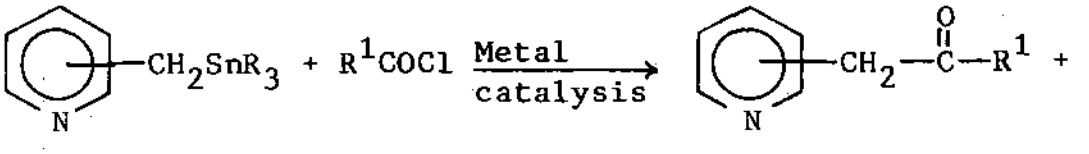
2. Stille et al.[6a,8b] and Mitiga et al.[6b,19] independently showed that benzyltrialkyltins(2) underwent transition metal-catalysed coupling with acid chlorides with the selective transfer of benzyl group thus providing a mild and general method for the synthesis of ketones(12) from acid chlorides.



(2) (12) R_3SnCl

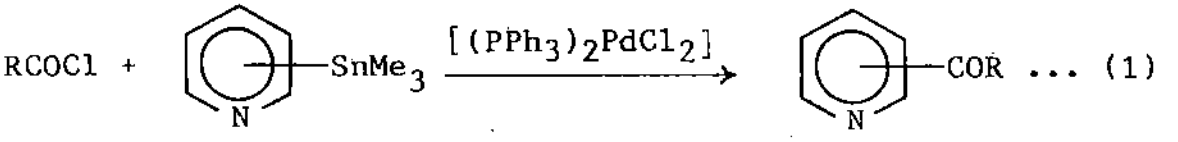
Similar reactions could be studied with picolyltrialkyltins(3) with several acid chlorides resulting in the formation of various picolyl alkyl ketones(13) which are otherwise difficulty accessible(SCHEME-III). Yamamoto et al.[20] showed that trimethyltin derivatives of aromatic

SCHEME-III



(3) (13) R_3SnCl

heterocycles(pyridine, quinoline, isoquinoline) underwent transfer, leading to high yields of aromatic heterocyclic ketones((equation 1).



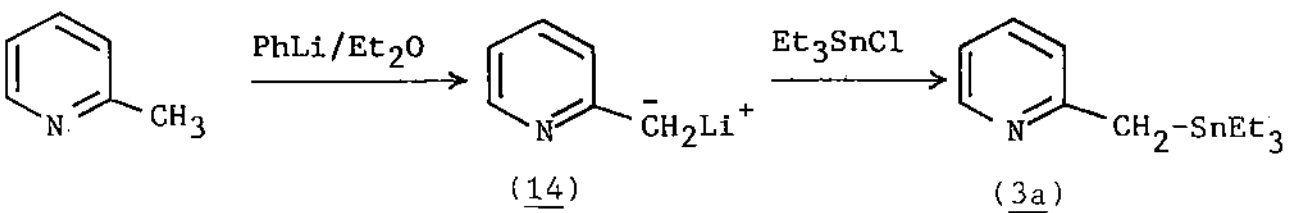
... (1)

II-2.1: Present work: Preparation of Picolyltrialkylstannanes - Results and discussion

The present work described herein is somewhat of exploratory nature. Though the scheme of the total work has been delineated here briefly, in the first phase of this scheme the preparation of picolyltrialkyltins has been realised in poor yield. The problems associated with the reactions to prepare picolylstannanes and the probable mechanistic pathways have been discussed in this Part-II.

Further improvements in terms of yield of the picolyltrialkyl tin compounds and their reactions as proposed are currently underway in this laboratory by other workers.

With a view to prepare the picolyltrialkylstannanes (3), a search in the literature revealed that Zimmer et al.[21] reported the preparation of 2-picolyltriethylstannane (3a) in 1956. Their synthesis of (3a) involved generation of 2-picolyllithium(14) from 2-picoline by treating with phenyllithium in ether and then reaction with triethyltin chloride at refluxing temperature and afforded(3a) in 40% yield. However, while trying this reaction using n-butyl-lithium in hexane to generate 2-picolyllithium(14) in ether



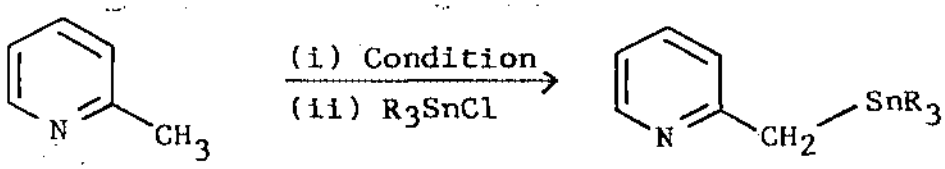
(14) (3a)

followed by quenching of (14) with tri-n-butyltin chloride under similar reaction condition(SCHEME-IV; Type-A), we failed to isolate any desired picolyltri-n-butylstannane(3b) after usual work-up. Triethyltin halides are quite expensive and therefore we used tri-n-butyltin chloride instead. Our failure to prepare the 2-picolyltin derivative(3b) was astounding since our observations throughout the course of

the reaction were as expected. Addition of n-butyllithium to 2-picoline under nitrogen atmosphere developed a dark brown-red colouration of the reaction mixture indicating the formation of picolyl anion(14)[22] which was disappeared after adding tri-n-butyltin chloride in molar proportion. It appeared to us that a smooth reaction had taken place. However, after work-up of the reaction mixture we isolated a small amount of picoline and a fraction, boiled at 165-70°C at 1mm of Hg. The ^{1}H-NMR spectrum of this fraction(liquid) displayed signals corresponding to butyl protons only. The IR spectrum showed a weak ν_{max} at 3440 cm^{-1} and a strong band at 770 cm^{-1}. If this fraction was bis tri-n-butyltin oxide, it should show a ν_{asym} vibration at the range 740-770 cm^{-1}(Sn-O-Sn) and on the other hand, if this was tri-n-butyltin hydroxide, it should display ν_{max} at the range 3610-3630cm^{-1} (-OH). From IR and ^{1}H-NMR spectra, this fraction was assigned as bis tri-n-butyltin oxide.

Addition of organolithium to metalate picolines presents a problem that the organolithium compounds can add to the azomethine bond of the heterocyclic aromatic ring. However, Beumel et al.[23] reported that 2- and 4- picolyllithium could be prepared in quantitative yield by n-butyllithium in hexane if tetrahydrofuran(THF) was present as cosolvent(100 ml per 0.2 moles of picoline). The function of THF was both as solvent for the picolyllithium and as activator

SCHEME-IV



(3b), R=n-Bu

(3c), R=Me

Type — Condition

	R	Base	Solvent	Temperature
A	n-Bu	n-BuLi	Hexane/Et_2O	Reflux
B	n-Bu	n-BuLi	Hexane/ THF	Reflux
C	n-Bu	n-BuLi	Hexane/THF	0°C
D	n-Bu	n-BuLi	Hexane/THF	-10°C
E	n-Bu	n-BuLi	Hexane/THF	-78°C
F	Me	n-BuLi	Hexane/THF	-78°C
G	n-Bu	n-BuLi/ TMEDA	Hexane/THF	0°C
H	n-Bu	$NaNH_2$	Toluene	Reflux

of n-butyllithium[24]. This modified procedure, however, did not improve the attempted metallation of 3-picoline. We,

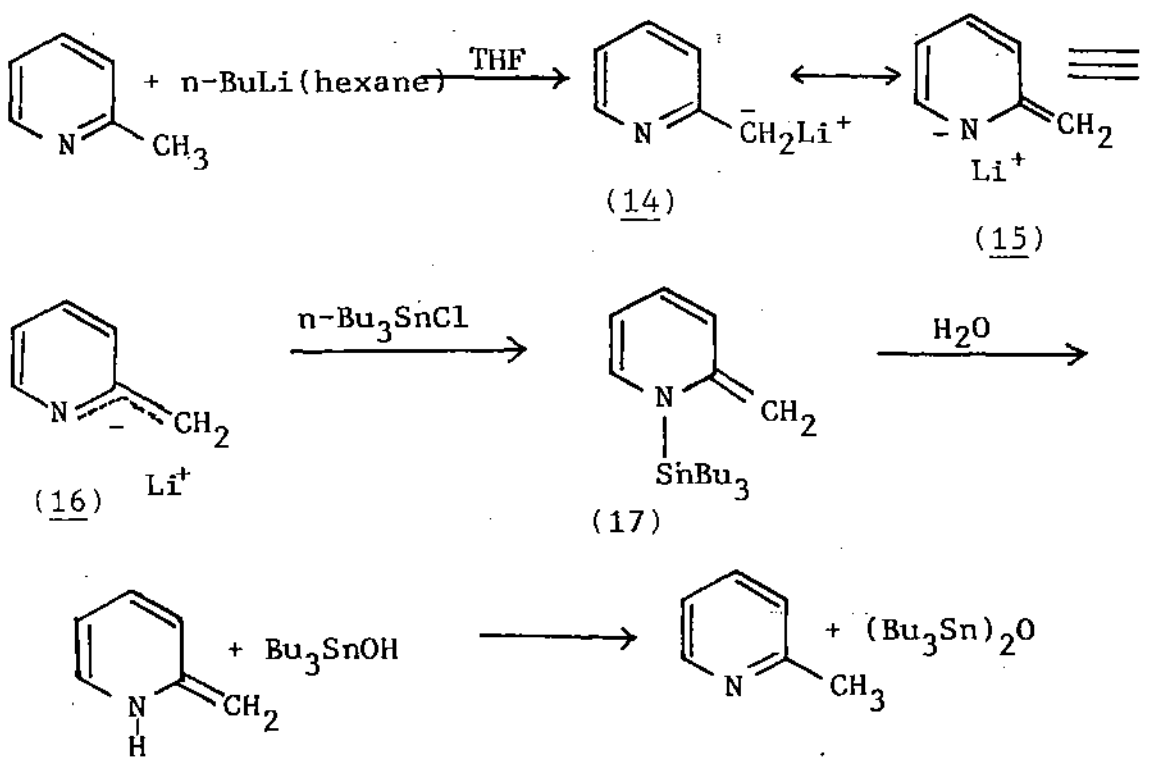
therefore, carried out this reaction using n-butyllithium in hexane and THF as cosolvent at refluxing temperature(SCHEME-IV, Type-B), at 0°C (Type-C), at -10°C(Type-D) and at -78°C (Type-E using Bu_3SnCl and Type-F using Me_3SnCl). In all the cases, a dark brown-red colour was developed while adding n-butyllithium and disappeared after the addition of tin halide. However, the desired picolyltri-n-butylstannane(3b) could not be isolated.

Tetramethylethylenediamine has been used with organolithium to bind the cationic part through chelation[25]. Andrianome et al.[8d] used this reagent for metallation of unsaturated terpenic hydrocarbons. We also tried this condition using n-BuLi/TMEDA at low temperature (Type-G). Final work-up and purification again failed to isolate desired picolyltrialkyltin derivatives(3).

In search of our failure to isolate the picolyltin derivatives, it seemed that though the picolylanion(14) was formed, subsequent stannylation probably did not take place at the carbanion centre. This could be accounted for by assuming the involvement of the anion(15) (SCHEME-V). If the anion(15) participated in the reaction, N-stannylation would take place affording the product(17). However, because of the hydrolytic instability of the N-Sn bond[26], the product(17) might undergo hydrolysis to furnish eventually picoline, and

the resulting tri-n-butyltin hydroxide might be converted into bis tri-n-butyltin oxide during distillation. The probable mechanism has been outlined in SCHEME-V.

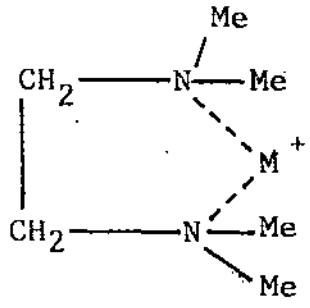
SCHEME-V



(Similar mechanism should be valid for 4-picoline)

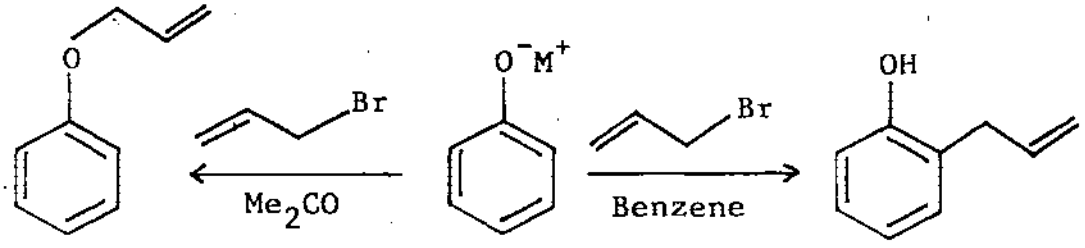
If this mechanistic pathway might be involved, such ambident nucleophiles should attack a given substrate under a given set of conditions[27]. In this case, N-stannylation, leading to product(17), is burdened energetically by the fact that aromaticity is destroyed. However, N-stannylation should be most pronounced when the anion(15) is most free. Since tetrahydrofuran, diethyl ether, though weakly polar solvents,

are known to act as good cation solvators[28], their presence might make the anion(15) free to react with trialkyltin halides(Type A to F). Presence of tetramethylethylenediamine (TMEDA) would bind the alkali metal cation strongly by chelation(18) and thus favouring again N-stannylation (Type-G). We therefore chose to use aprotic non-polar solvent



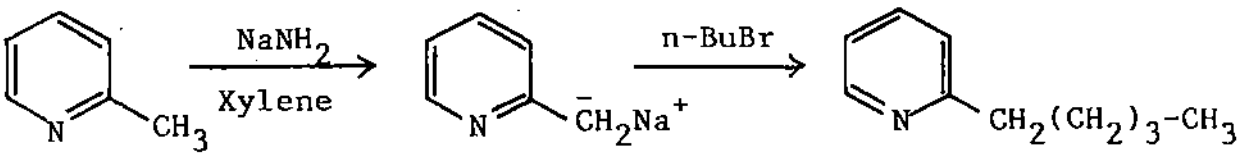
(18)

like benzene, toluene etc. It was known that phenoxide anion(19) reacted with allyl bromide to produce O-allyl ether(20) (O-alkylation) in acetone or ethanol while O-alkyl phenol(21) (C-alkylation) in benzene[29]. In benzene, probably the reaction (C-alkylation) occurred in heterogeneous phase[30].



(20) (19) (21)

Earlier, picoline was heated with sodamide in xylene to produce picolyl anion(22) which was then reacted with n-butylbromide to yield(23) by C-alkylation[31].



(22) (23)

Following similar procedure, we carried out the reaction of 2-picoline with tri-n-butyltin chloride using sodamide in dry toluene (**SCHEME-V, Type-H**). After work-up and chromatography we were able to isola te pure 2-picolyltri-n-butylstannane(3b) in only 10-12% yield alongwith bis tri-n-butyltin oxide. Though in poor yield, the formation of picolyl tri-n-butylstannane(3b) under this condition (Type-H) supported the proposed mechanism that might be involved. In search of better yield of the desired product (C-stannylation) by changing solvent and using smaller cationic part, studies are under active pursuit in this laboratory.

II-2.2: Conclusion

In PART-II of this dissertation, several attempts have been made to synthesise picolyltrialkylstannanes involving generation of picolylanion followed by quenching of

the latter with trialkyltin halides. Based on chemical/ spectral evidence, the involvement of ambident nucleophilicity of the picolyl anion has been suggested. The competition between N-stannylation versus C-stannylation has been considered in terms of role of solvent. Further works to improve the yield of the picolyl stannanes are being undertaken both for substantiating the suggested mechanism and for studying their reactions.

II-3: Experimental

Procedure-I : Attempted preparation of Picolyltri-n-butylstannane(3b) under condition Type-C :

To a magnetically stirred solution of freshly distilled 2-picoline (1.32g, 14.2 mmole) in tetrahydryfuran (7 ml) was added n-butyllithium (1.5 M in hexane, 9.5 ml, 0.912 g, 14.2 mmole) using a 10 ml syringe, dropwise over a period of 30 minutes at 0°C(ice-bath) under a steady flow of nitrogen. The colour of the reaction mixture turned immediately into dark brown-red colour. It was stirred for more 30 minutes at 0°C and then a solution of freshly distilled tri-n-butyltin chloride (4.62 g, 14.2 mmole) in tetrahydrofuran(1 ml) was added slowly at 0°C. The dark colour of the reaction mixture was disappeared at the end of the addition of $n\text{-}Bu_3SnCl$ solution. Stirred the mixture for 2 hours during which the temperature was gradually raised to room temperature. Dissolved the fine solid appeared in the reaction mixture by adding ice-cold water and extracted with ether. The aqueous part was saturated with sodium chloride and then extracted twice with ether. The combined etherial layer was washed with brine solution until the washings were neutral to litmus. The organic phase was dried (Na_2SO_4) and concentrated. TLC of the crude brown-residual liquid was compared with picoline and tri-n-butyltin chloride .No spot

of Bu_3SnCl was obtained in TLC of this brown liquid. The liquid was purified by sublimation and different fractions were collected. (1) A low boiling fraction was obtained in small amount and was characterised as 2-picoline (by IR spectra); (2) Another fraction boiled at 160-165°C/1 mm Hg as colourless liquid (3.3 g). IR and ^{1}H-NMR spectra suggested the liquid as bis tri-n-butyltin oxide. No aromatic protons were found in the ^{1}H-NMR spectrum.

Following the similar procedure, this reaction was carried out under different conditions: [**Type-A** (using anhydrous ether), **Type-B** (reflux after addition of Bu_3SnCl), **Type-D** (at -10°C, using ice-salt bath), **Type-E** (at -78°C, using liquid N_2/acetone bath), Type-F (at -78°C using liquid N_2/acetone bath and adding Me_3SnCl)].

In all the cases (Type **A, B, D. E**),similar observation was found after work-up and sublimation of the crude oily residue.

In the case of **Type-F** condition, Me_3SnCl (2.83 g, 14.2 mmole) was used by dissolving the solid in anhydrous THF (in 3 ml). After work-up, as described, the residue was a semi solid. It was first sublimed at ~60°C/under water suction. A solid compound (1.5 g) was obtained, recrystallised from benzene light petroleum, m.p. 110-112°C. This fraction was assigned as trimethyltin hydroxide (lit.[32]

m.p. 117-118°C). IR : (Nujol) of this solid compound:
ν_{max}: 565(s), 720(m), 770(s)cm^{-1}.
^{1}H-NMR($CDCl_3$) : δ 0.45(br.s, 9H, $-CH_3$), 1.62(br. s, 1H, -OH).

The residual part in sublimation tube was sublimed at 115-120°C/1 mm Hg to afford an oily compound($\sim$ 0.8g). In the ^{1}H-NMR spectra of this oily compound, small aromatic protons were observed alongwith two peaks at δ 2.46 and 2.13. Initially we thought that this could be a mixture of 2-picoline and 2-picolyltrimethylstannane. However, further purification through column chromatography did not afford any pure desired product.

Procedure-II : Attempted preparation of Picolyltri-n-butyl-stannane (3b) under condition Type-G :

The procedure reported by Andrianome et al.[8d] was followed.

To a stirred solution of n-butyllithium (1.5 M, 1.97 g, 6.95 ml, 10.6 mmole) in hexane was added N, N, N', N' - tetramethylethylenediamine(1.24 g, 1.61 ml, 10.6 mmole) under nitrogen atmosphere. During the addition, the temperature was raised to ca. 45°C, cooled down to 25°C, whereupon 2-picoline (2 g, 2.12 ml, 21.4 mmole) was added. After having stirred for 4 hours at room temperature, the pale yellow mixture was cooled to 0°C (ice-bath) and quenched with a solution of

freshly distilled Bu_3SnCl(5.52g, 4.60 ml, 16.9 mmole) in hexane (5 ml). After 4 hours the insoluble salts were removed by filtration. The filtrate solvent was poured into a saturated aqueous ammonium chloride solution to remove excess TMEDA, and extracted with ether (3 x 30 ml). The combined organic layer was washed with water, dried (Na_2SO_4) and evaporated. The residue was sublimed at 155-165°C/1 mm Hg to afford a colourless liquid, characterised as bis tri-n-butyltin oxide.

Procedure-III : Preparation of 2-picolyltri-n-butylstannane (3b) using sodamide in toluene (Type-H) :

In a 50 ml three necked round bottom flask, fitted with a pressure-equualising dropping funnel and a condenser, was taken a fine suspension of sodamide (2.6g, 0.067 mole) in dry toluene(5 ml) and then the set-up was flashed with nitrogen. To this suspension was added 2-picoline (2.5 g, 2.65 ml, 0.0268 mole) and the mixture was magnetically stirred for 1 hour at room temperature. A pale yellow colour was developed during stirring. Then freshly distilled tri-n-butyltin chloride (8.73 g, 7.28 ml, 0.0268 mole) in 5 ml of toluene was added through the dropping funnel over a period of 1 hour at room temperature and the mixture was heated under reflux for 2 hours. After cooling the reaction mixture to 0°C(ice-bath), crushed ice was added to it to dissolve the

excess sodamide and the product was extracted with benzene (3 x 30 ml). The combined organic layer was washed with brine solution repeatedly until the washings were neutral to litmus. The organic phase was dried over anhydrous Na_2SO_4, evaporated under water suction to afford a liquid residue which was distilled under reduced pressure. Two fractions were collected at different boiling points. One fraction (5.1 g) at 145-155°C/1 mm Hg and the other fraction (4.8 g) at 155-165°C/1 mm Hg.

The higher boiling fraction(4.8 g) showed two spots in TLC (elution with benzene, R_f=1 and 0.15). This fraction was chroma tographed over silica-gel(150 g) and elution with light petroleum furnished a fraction (3.1 g), characterised as tri-n-butyltin oxide(3g). The other fraction was eluted with 2% ethylacetate in benzene, 1.1g(11%); TLC single spot (in benzene, R_f=0.16).

IR(neat) of the first fraction from distillation and that of the first fraction from chromatography were identical.

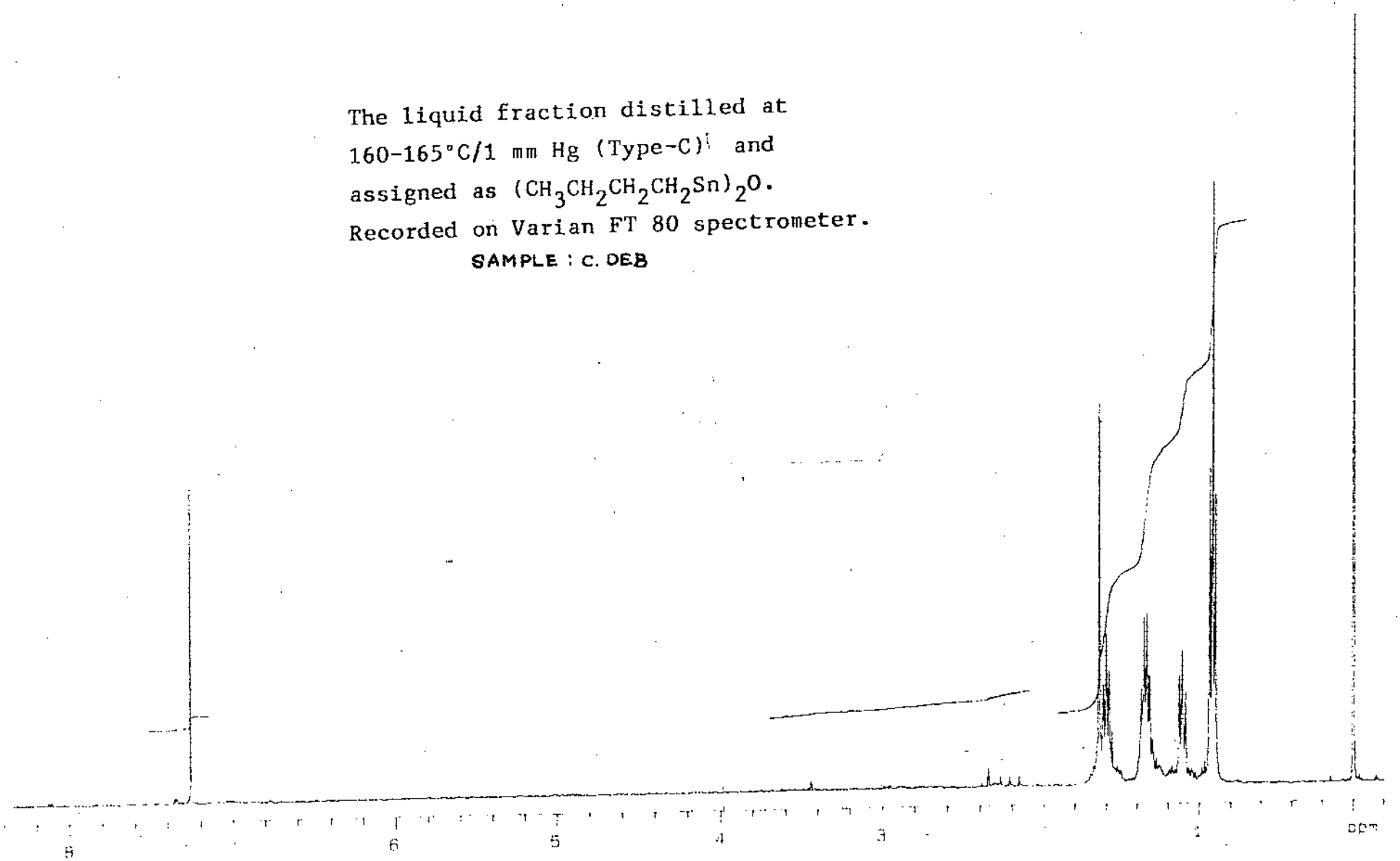
ν_{max}: 770(s, Sn-O-Sn), 1372(s), 1410(w), 1450(s), 3440(w).

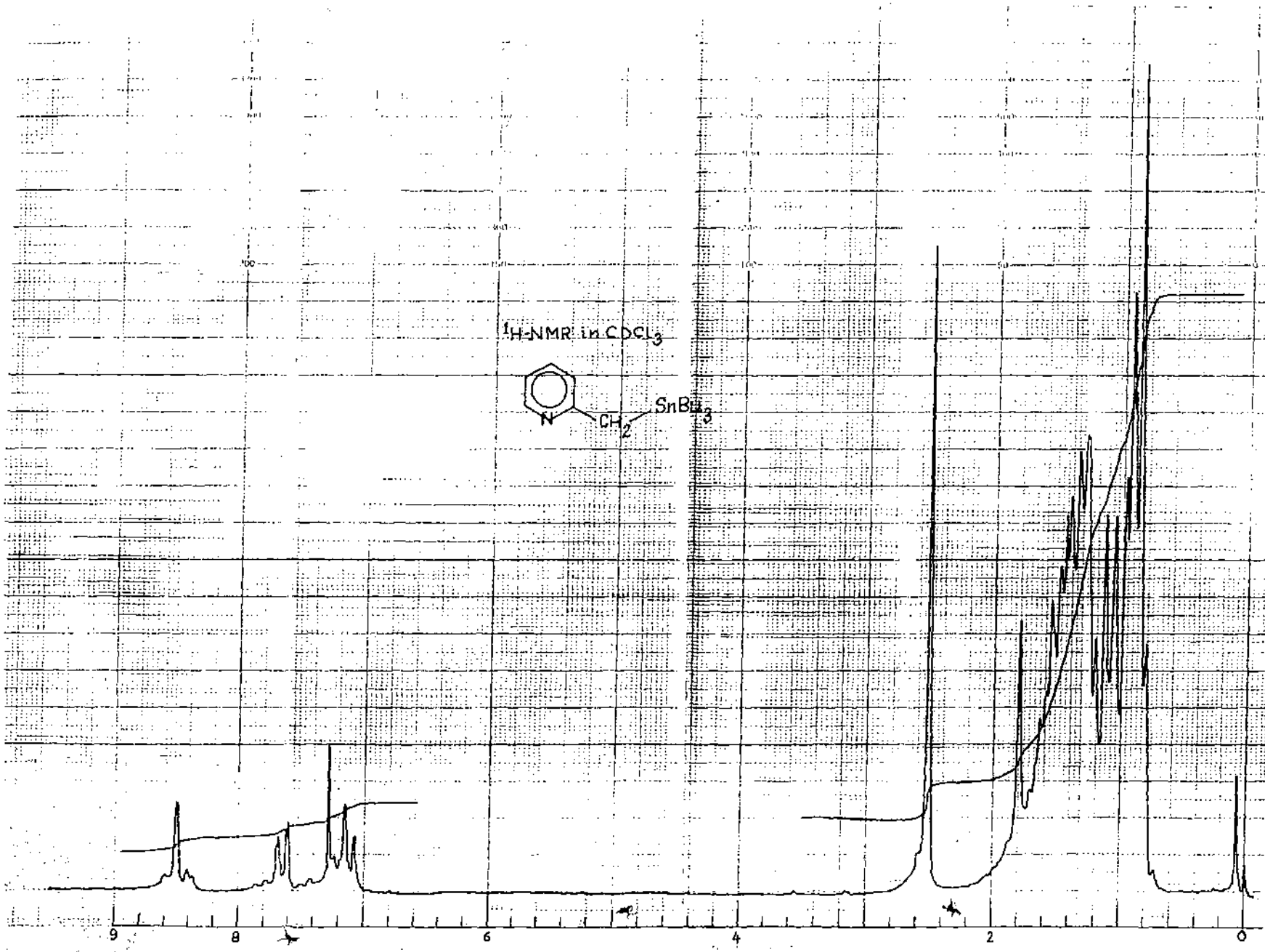
^{1}H-NMR($CDCl_3$) : δ 0.93(t, 18H, $-CH_3$), 1.12(m, centered at, 12H, $-CH_2$), 1.35(m, centered at, 12H, $-CH_2$), 1.60(m, centered at, 12H, $-CH_2$).

IR(Neat) of the second fraction from chromatography: ν_{max}: 1600(s). ^{1}H-NMR($CDCl_3$): δ 0.73-1.77(m, 27H, butyl H), 2.45(s, 2H, Ar-CH_2-Sn), 6.97-7.22(m, 2H, Ar-H), 7.58(dd, 1H, J=8 and 2 Hz, Ar-H), 8.43(m, centered at, 1H, Ar-H).

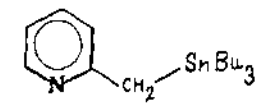
The liquid fraction distilled at
160-165°C/1 mm Hg (Type-C) and
assigned as $(CH_3CH_2CH_2CH_2Sn)_2O$.
Recorded on Varian FT 80 spectrometer.

SAMPLE : C. DEB





SAMPLE : C.DEB



SOLVENT $CDCl_3$

REF TMS

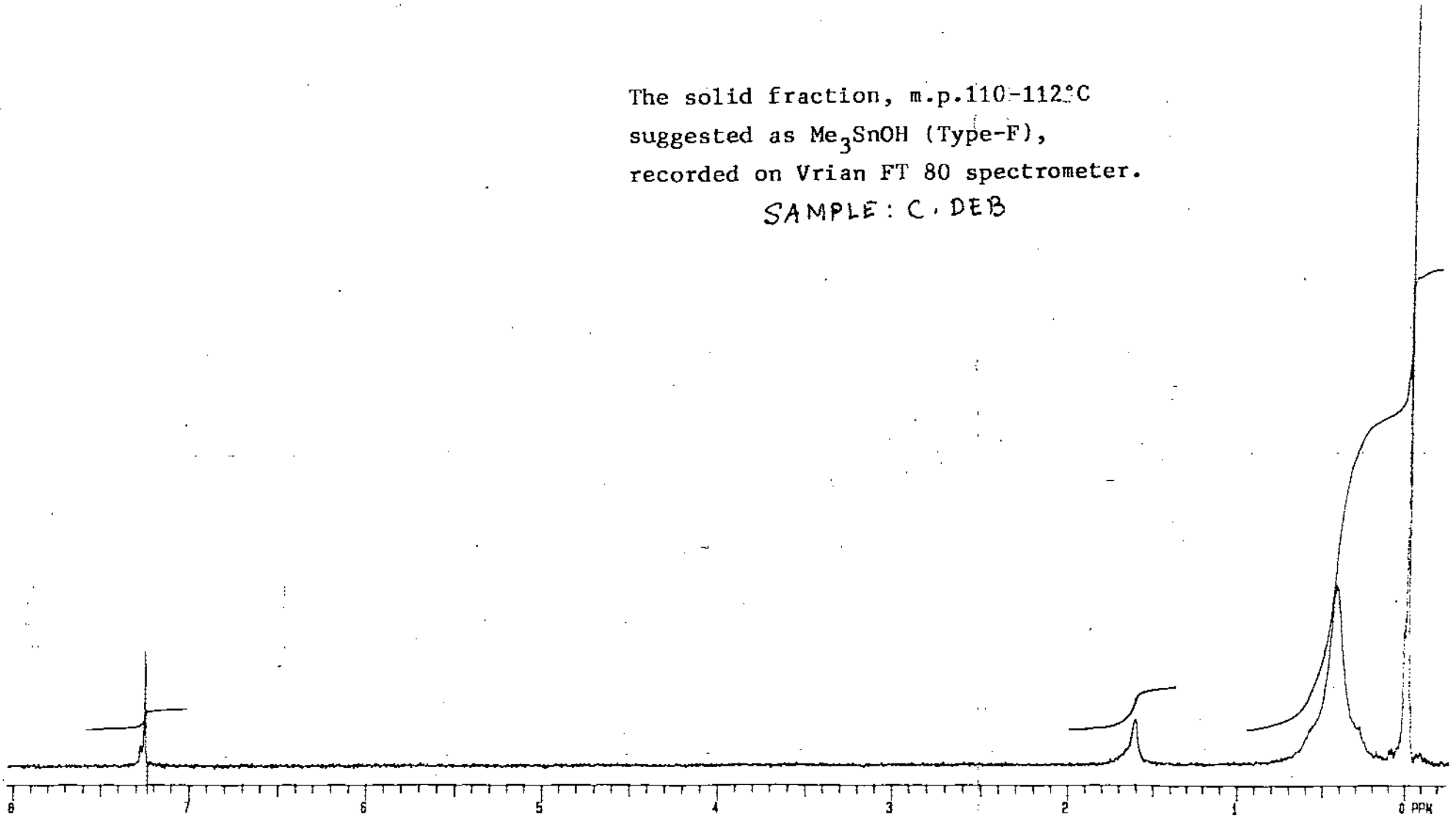
^{1}H

PULSE SINGLE

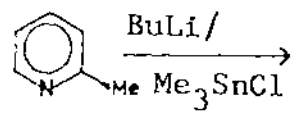
1000

The solid fraction, m.p.110-112°C
suggested as Me_3SnOH (Type-F),
recorded on Vrian FT 80 spectrometer.

SAMPLE : C . DEB

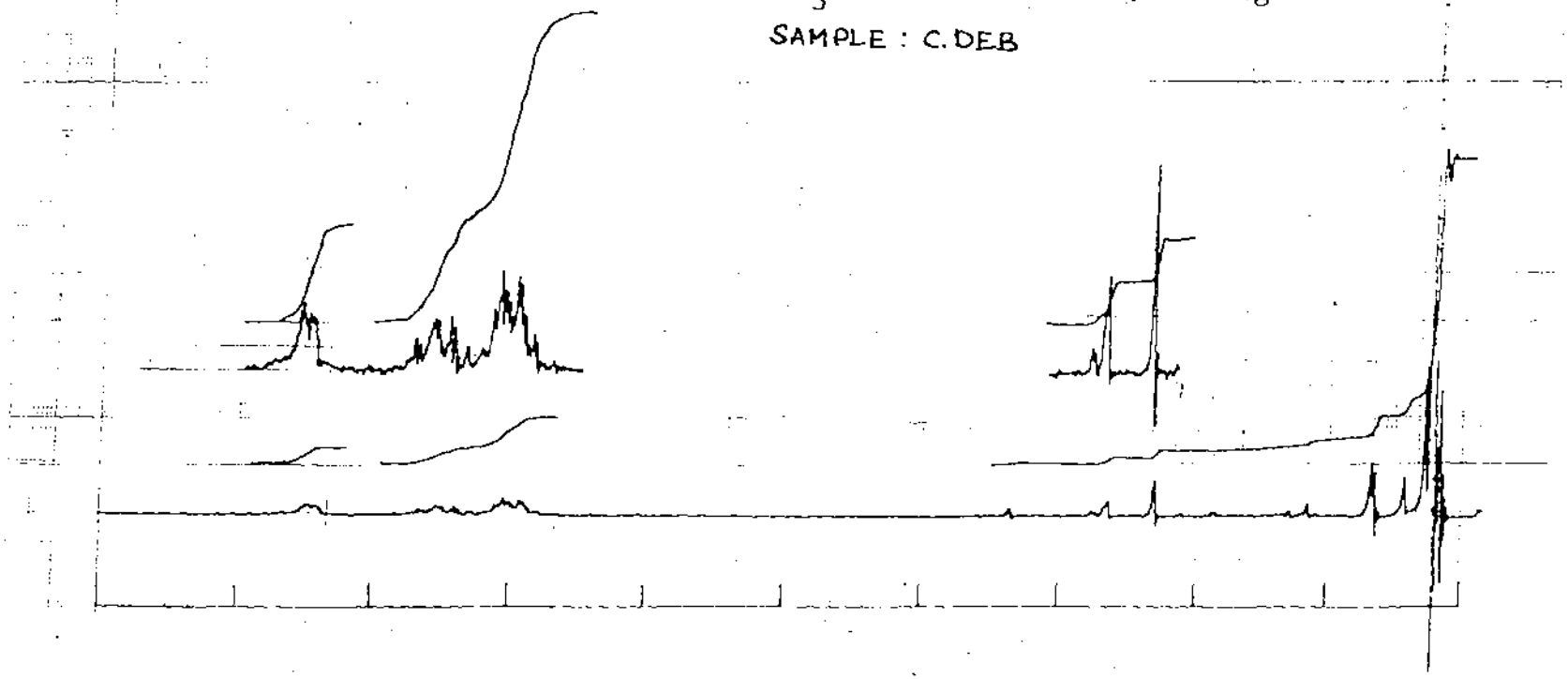


^{1}H-NMR in CCl_4



Me_3SnCl → Liquid fraction boiled at 115-120°C/1 mm Hg

SAMPLE : C.DEB



EM-360 60 MHz NMR SPECTROMETER

Dr. B Bam

60/33/2

11/1/93

DECOUPLE POS.

Cdcl3

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