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],

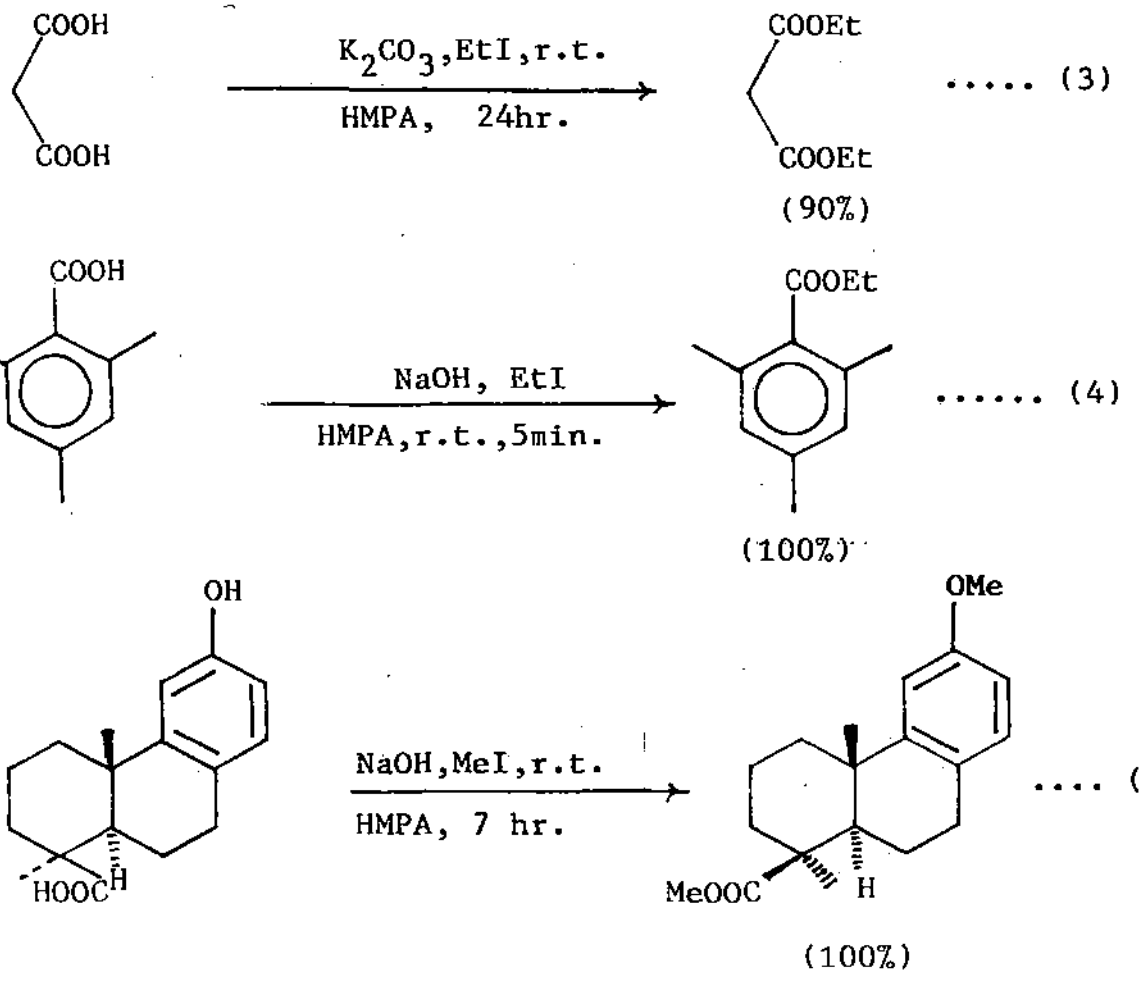
$$R\text{-}COOH + R^1OH \underset{}{\overset{H^+}{\rightleftharpoons}} R\text{-}COOR^1 + H_2O \quad \ldots\ldots\ldots(1)$$

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].

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

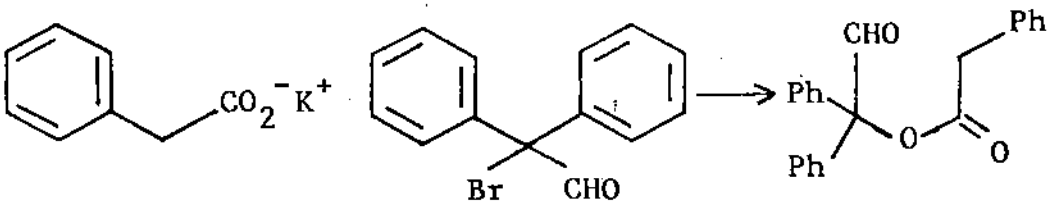
R	X	Time(hr.)	Yield(%)
n-pr	Br	0.5	90
n-pr	Cl	6	50
Ph	Cl	1	100

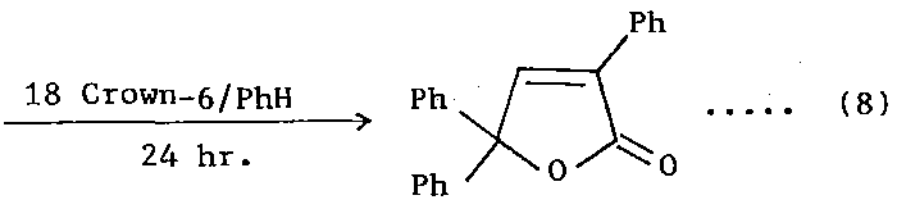
Holmberg and Hansen[14] also noted the formation of methylene diesters while using dichloromethane as solvent and they used this observation as a basis for a synthesis of a variety of methylene diesters (equation 7).

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

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).





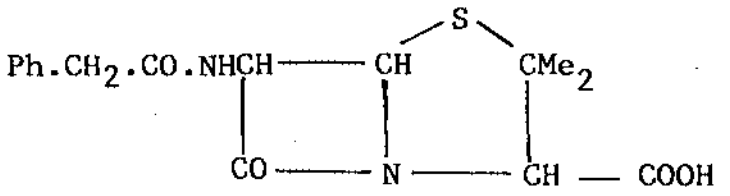
..... (8)

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).

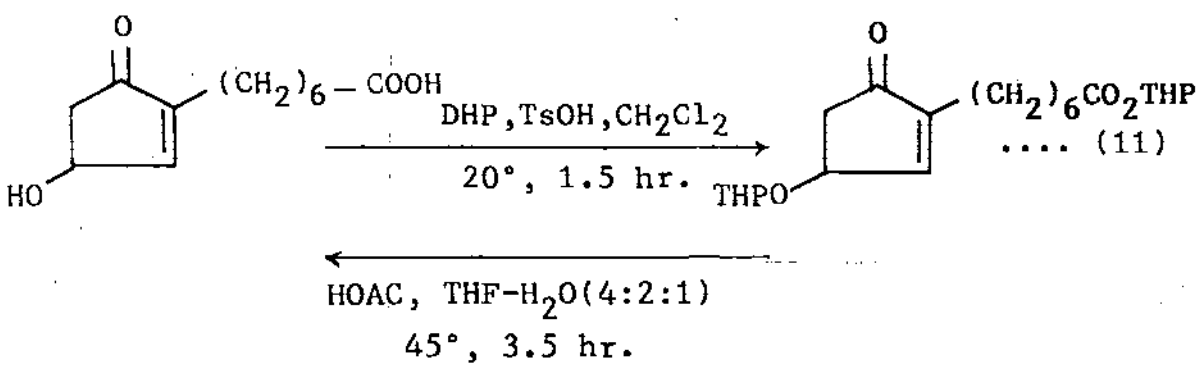
$$RCOOH + [MeO.CH_2.OMe,\ Zn/Br.CH_2.CO_2Et] \xrightarrow{0°} \xrightarrow[0 - 20°C,\ 2\ hr.]{CH_3COCl}$$

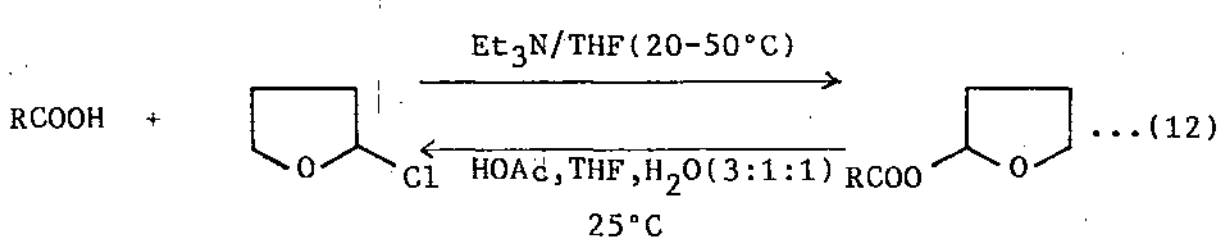
$$R.COOCH_2.OCH_3 \quad ..... \quad (10)$$

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

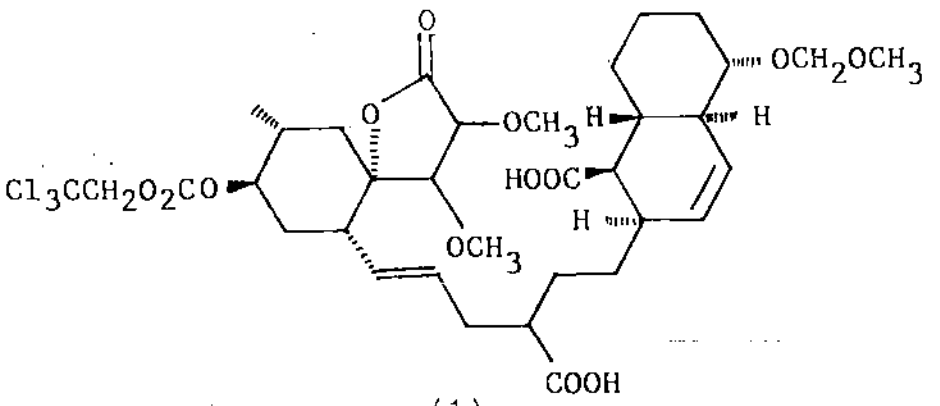
that the methoxymethyl ester was hydrolysed by using R_3SiBr in trace methanol keeping the methoxymethyl ether unreacted.

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).





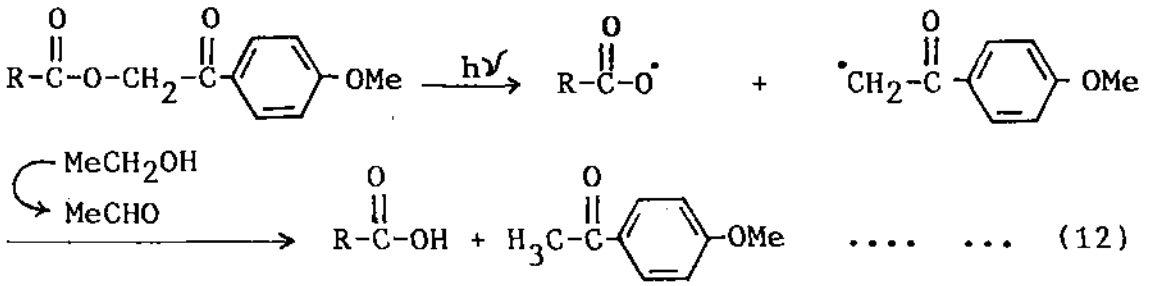
Methoxyethoxymethyl ester (MEM ester) was first prepared by Meyers et al.[29] by the reaction of carboxylic acid with MEM-chloride in presence of i-pr_2NEt at 0°C in good yield. Because of steric reasons, the MEM ester could be prepared selectively of an unhindered -COOH in presence of sterically hindered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



(1)

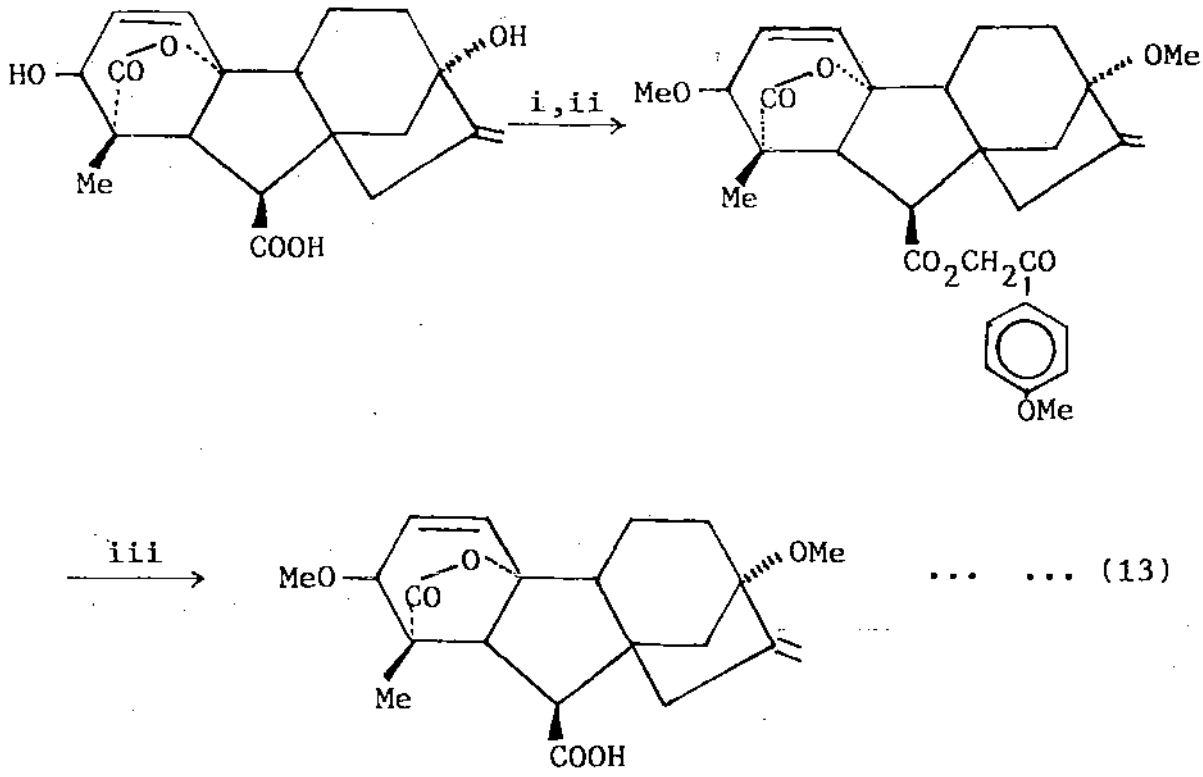
The benzyloxymethyl esters were prepared by P.A.Zoretic et al.[31] by reacting sodium carboxylates with benzyloxymethyl chloride in HMPA at 25°C. Both aromatic and aliphatic carboxylic acids were found to give their corresponding esters under this condition. Their removal, however, could be accomplished 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)

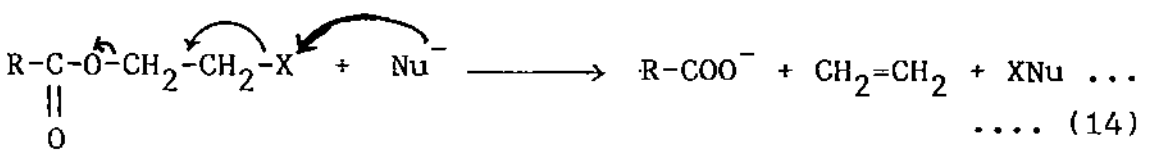
i) Et_3N-MeO-  -$COCH_2Br$-DMF-0°

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).

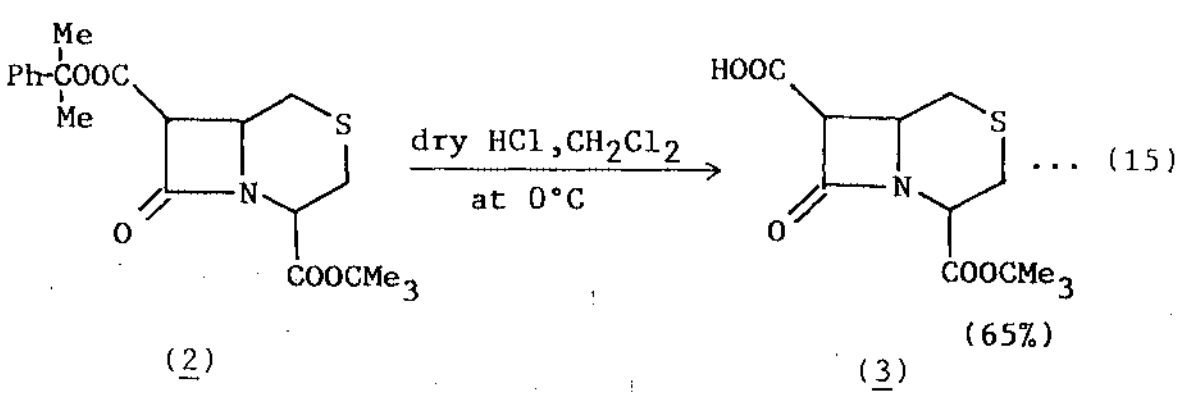


$$R\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}CH_2\text{-}X + Nu^- \longrightarrow R\text{-}COO^- + CH_2{=}CH_2 + XNu \quad \ldots\ldots (14)$$

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.

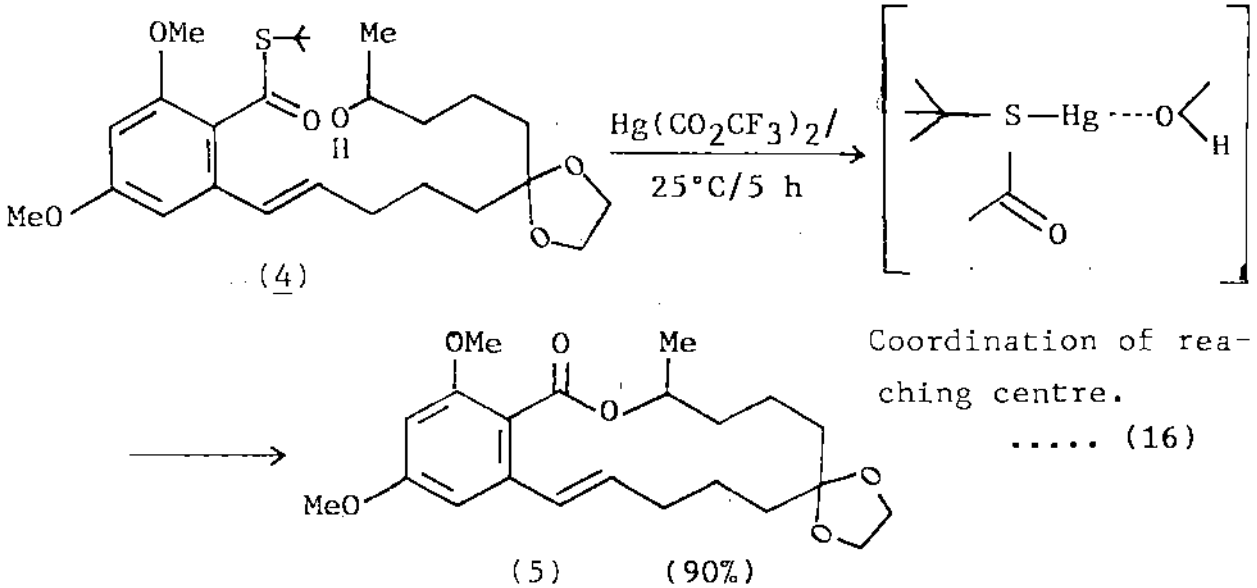
2-(Trimethylsilyl) ethyl carboxylates were prepared from the acid by P.Seiber[43] or from the acid chloride by H.Garlach[44] upon reaction with 2-(trimethylsilyl) ethyl alcohol, $Me_3SiCH_2CH_2OH$ using DCC/py in acetonitrile at 0°C or using pyridine respectively. These esters were found to be deprotected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



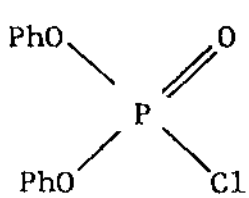
(4)

(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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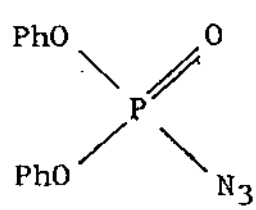

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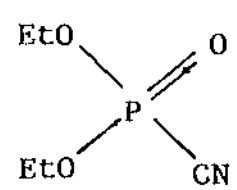

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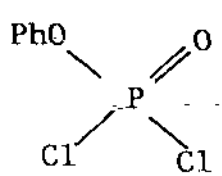

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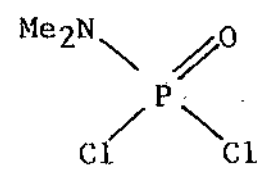
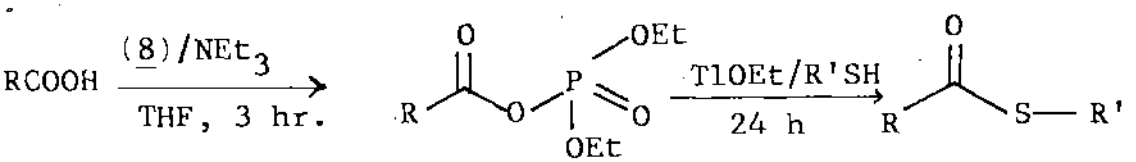


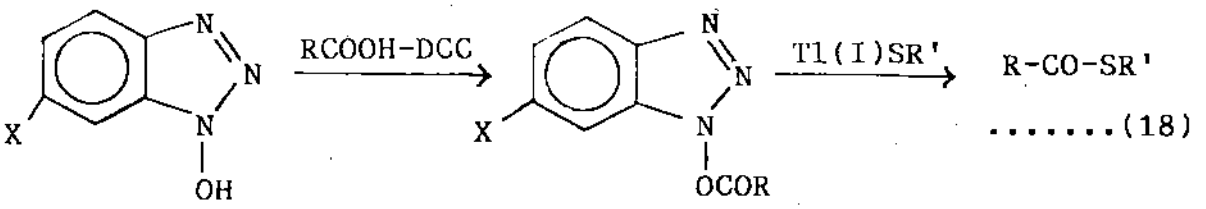
(10)

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).

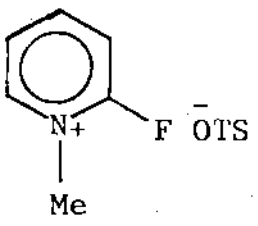


.....(18)

(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).



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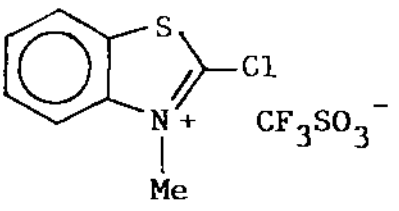

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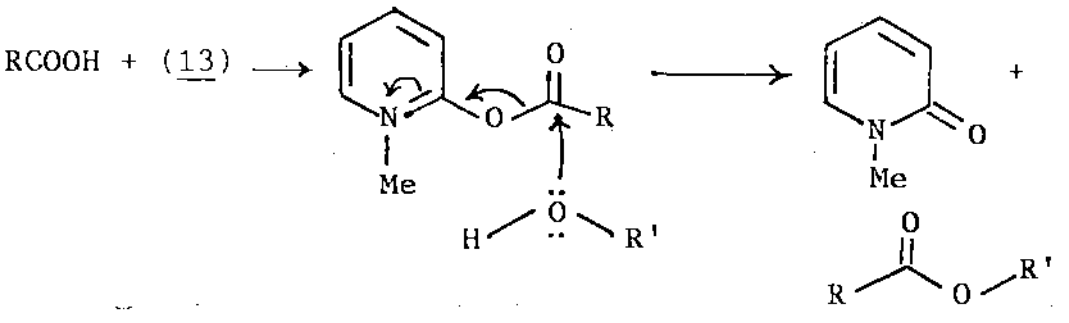
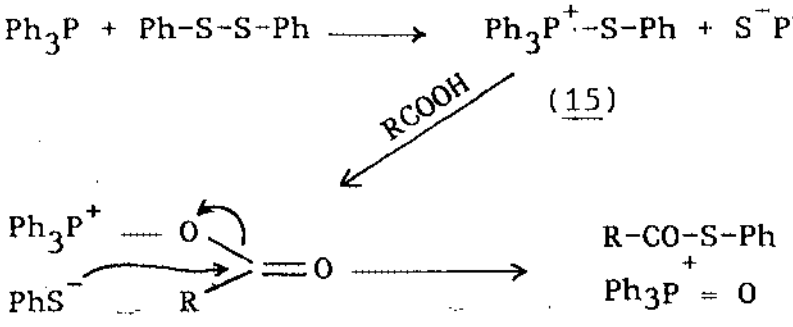


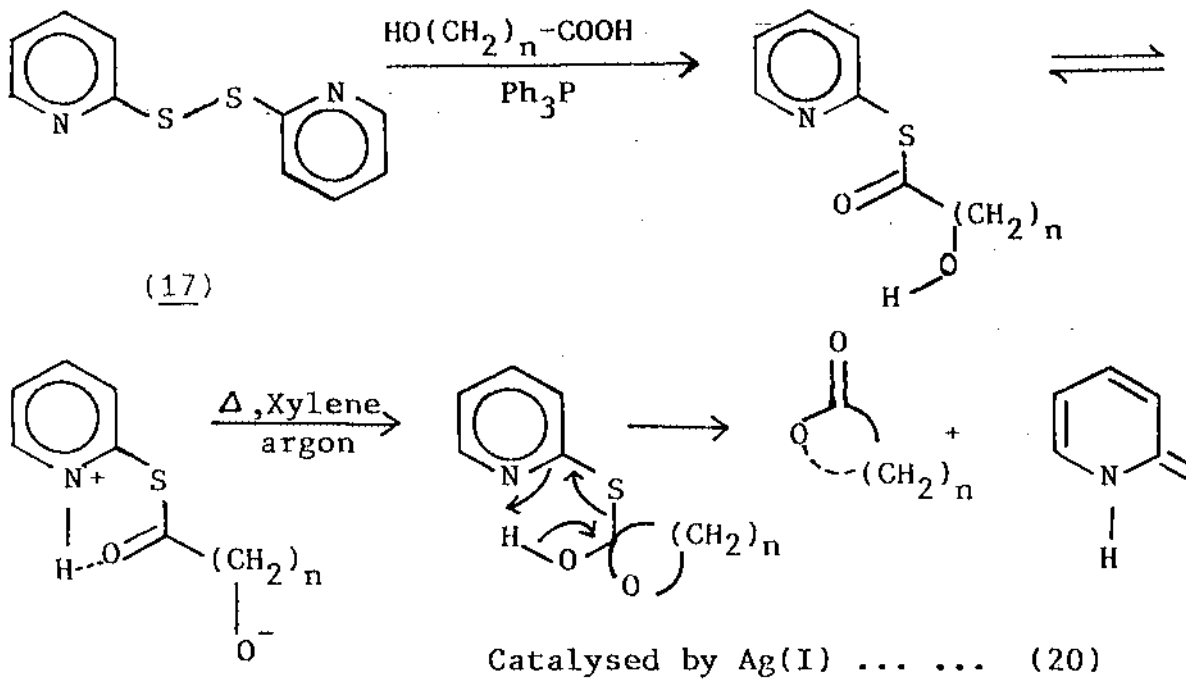
... .. (19)

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).

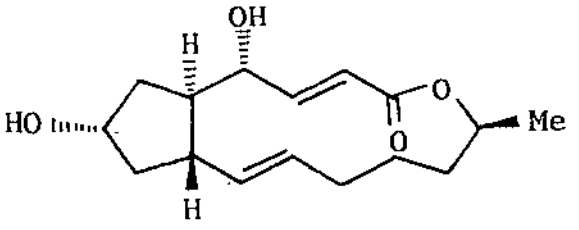


(17)

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).



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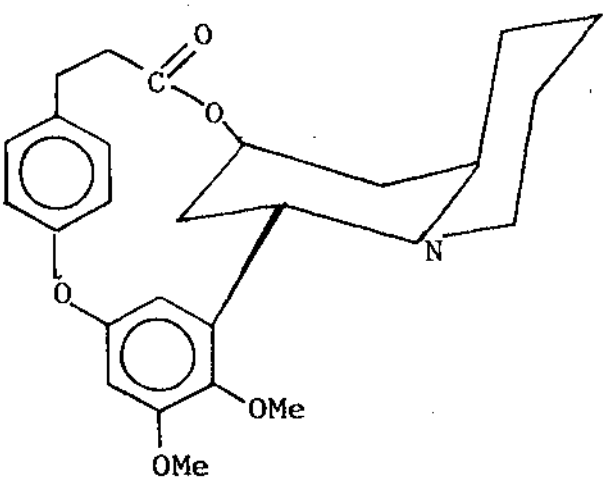
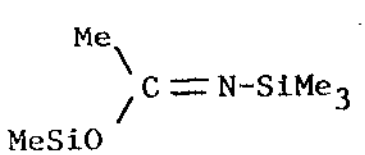
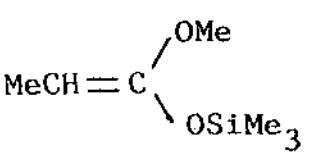


(19)

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;



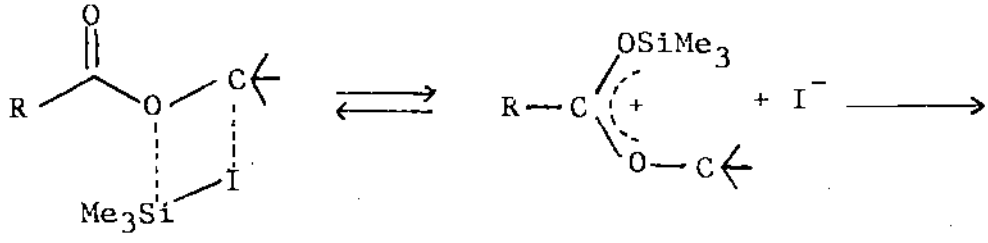
in Ether at 25°C



in CH_2Cl_2 at 15-25°C

$Me_3SiNHSO_2OSiMe_3$ in CH_2Cl_2 at 30°C.

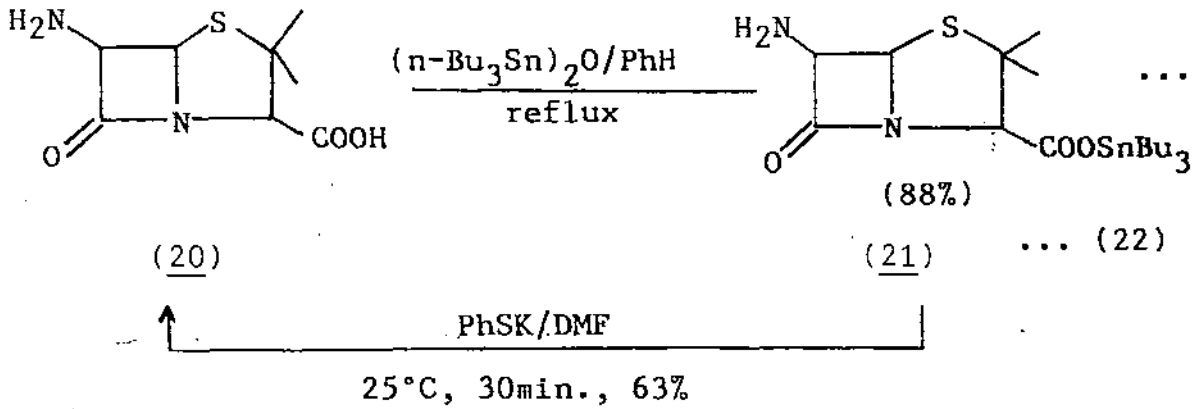
All the methods gave trimethylsilyl esters in nearly quantitative yield. Olah et al.[66] prepared trimethylsilyl esters from the alkyl esters by reacting with trimethylsilyl iodide in neat or in solution. They reported[67] that alkyl esters undergo transesterification to silyl esters in presence of trimethylsilyl 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.

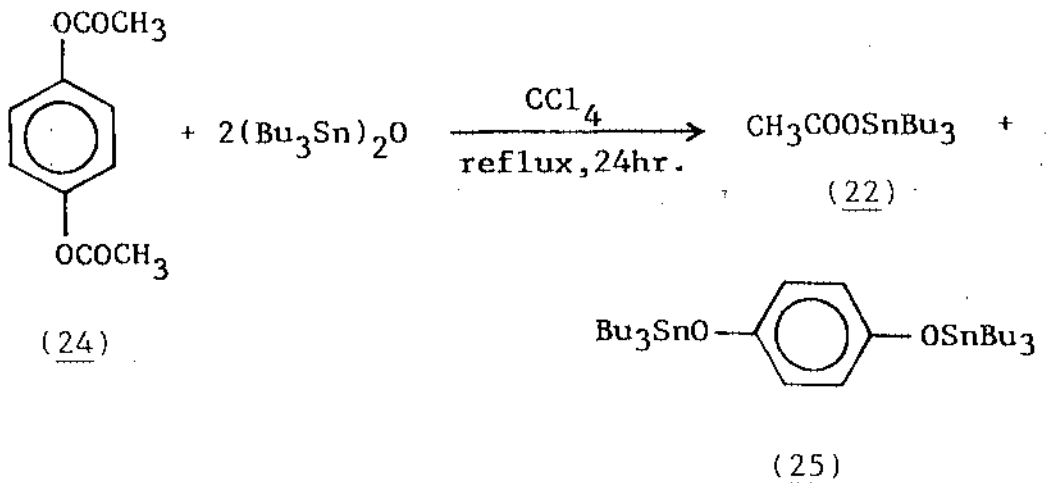
2. Change of R^2; we considered alkyl (Me and Et), benzyl (26) and phenyl (24) functions.

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).

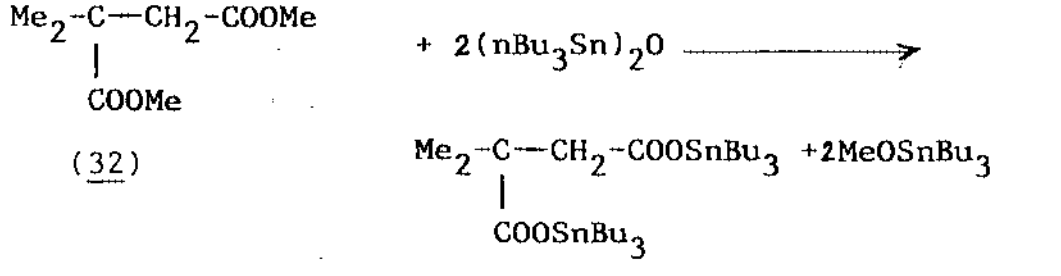
$$R^1\text{-CH=CH-COOR}^2 + R_3Sn\text{-O-}SnR_3 \longrightarrow R^1\text{-CH=CH-COOSn}R_3 + R^2OSnR_3$$

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

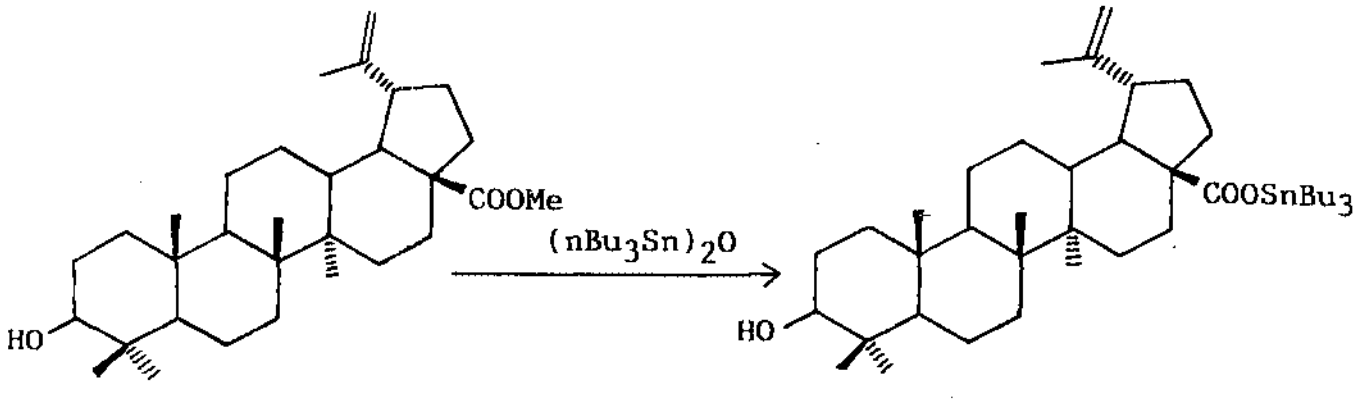
In the case of tri-n-butyltin cinnamate(31), obtained from methyl cinnamate(30), the IR absorption of CO_2 and C=C appeared at 1640(m) and 1538(s)cm^{-1}. In the PMR spectrum, the β-proton showed a doublet at δ 7.61 (J=15.94 Hz). The aromatic protons appeared in the region of δ7.33-7.52. The ^{13}C-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



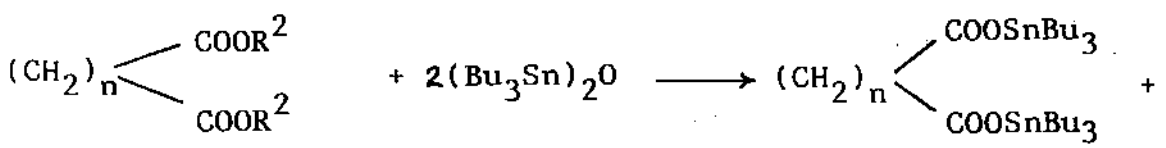
(32) (33)



(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

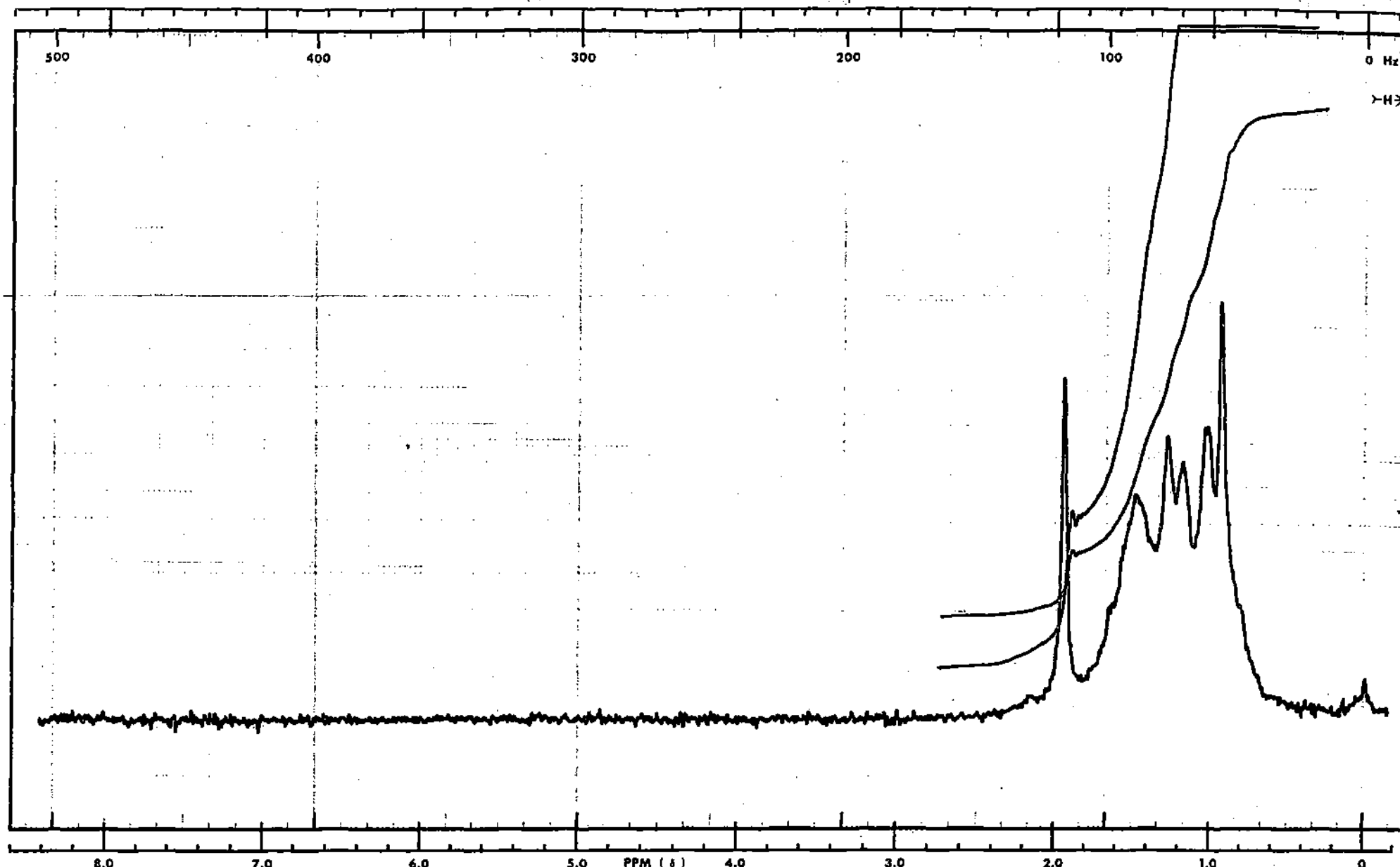
I.B-2.3.2: Hydrolysis of Triorganotin carboxylates (22, 28, 29, 31, 33, 35, 37, 39, 41) into their corresponding Acids

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:

$CH_3COOSnBu_3$

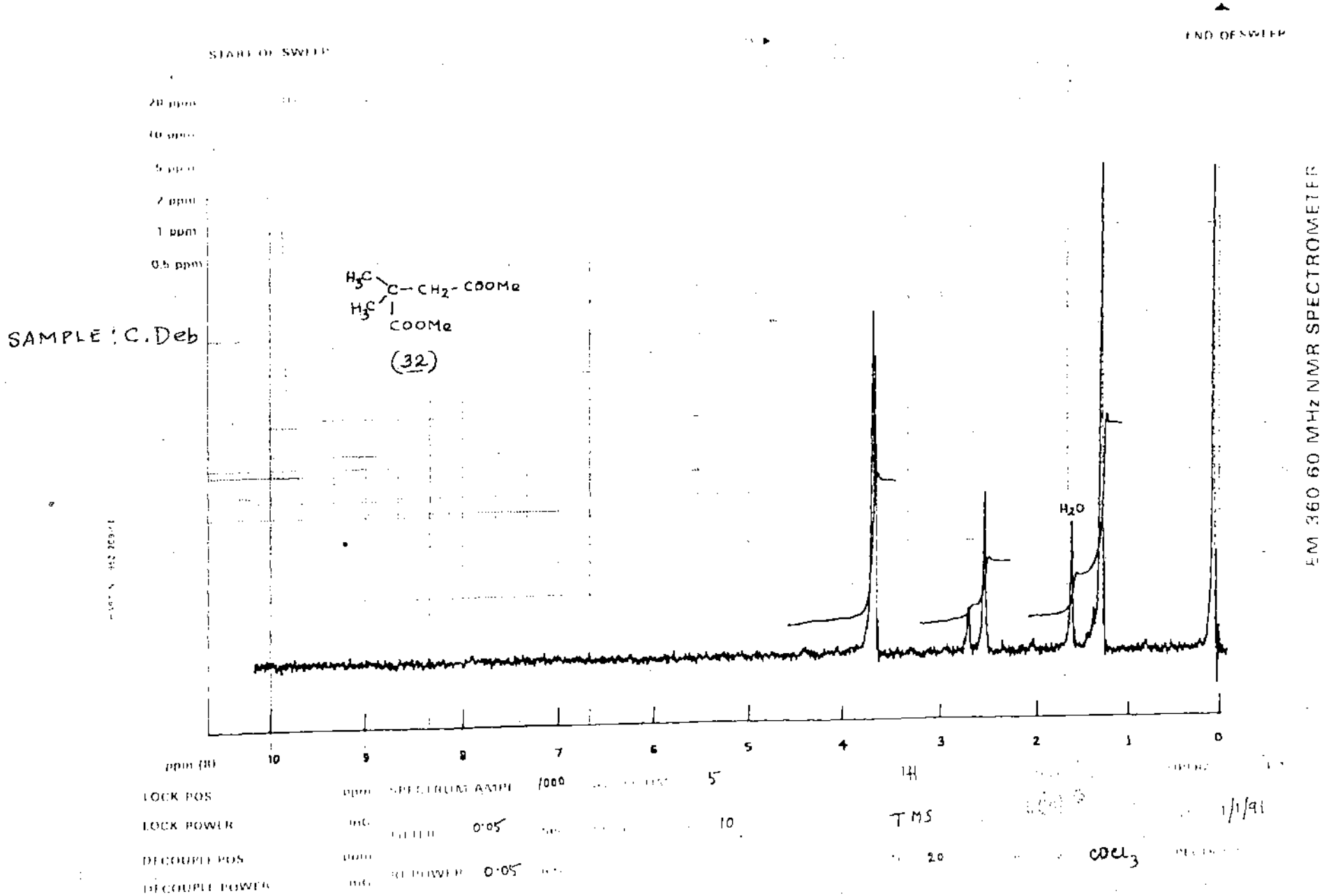
(22)

varian
analytical instrument division

DATE: 08/8/90

OPERATOR:

60 MHz NMR
SPECTRUM NO.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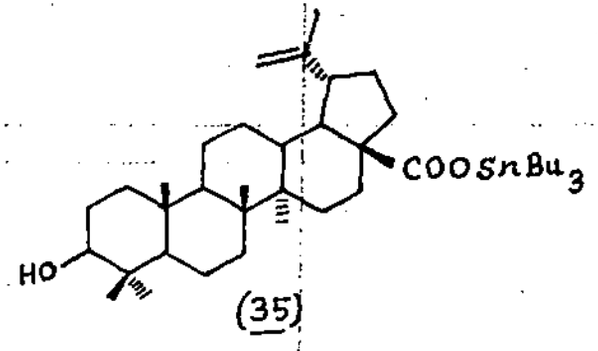
END OF SWEEP
SAMPLE : C. Deb
(32)
H_2O
ppm (δ)
10
9
8
7
6
5
4
3
2
1
0
TMS
$CDCl_3$
1/1/91
LOCK POS
LOCK POWER
DECOUPLE POS
DECOUPLE POWER
0·05
0·05
EM 360 60 MHz NMR SPECTROMETER

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)

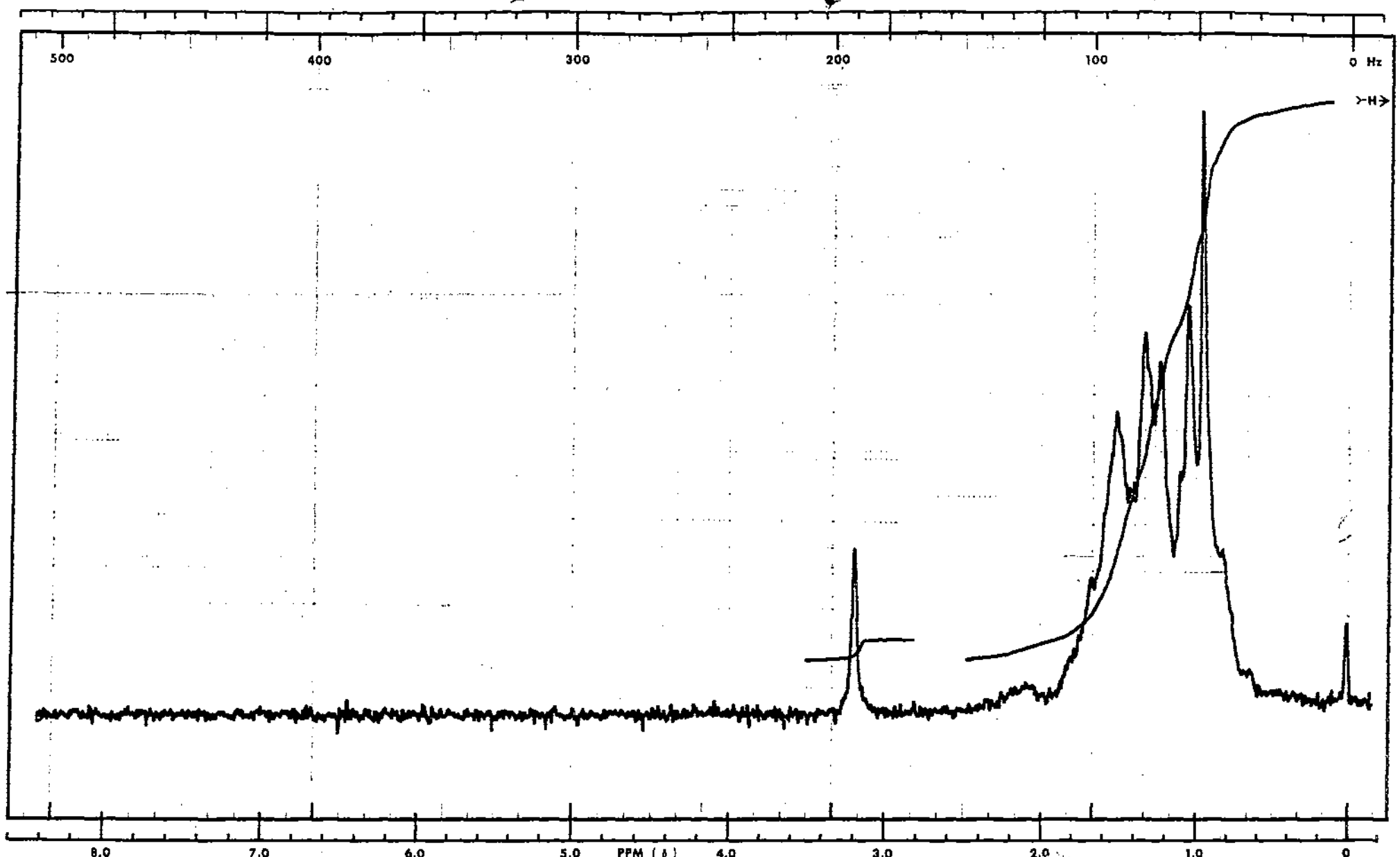
SOLVENT: $CDCl_3$

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$_3$)$_2$

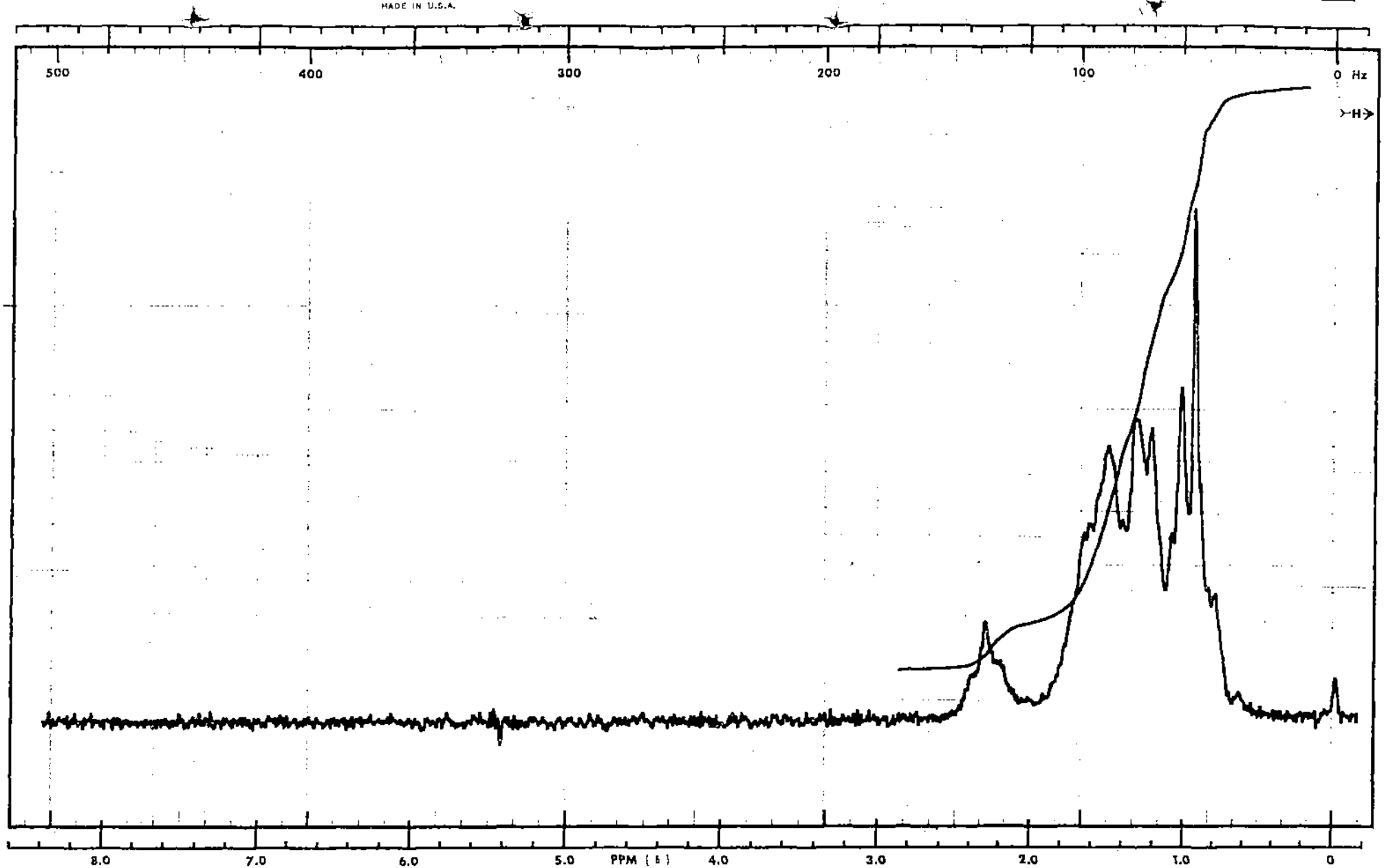
varian
analytical instrument division

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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