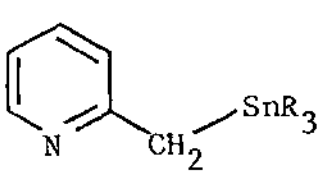
PART -- II

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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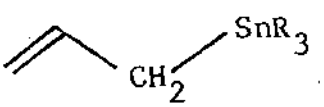

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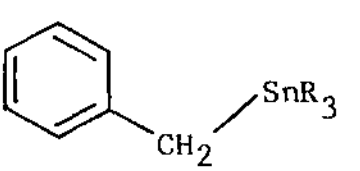
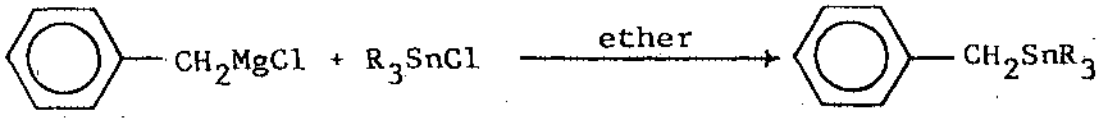


(2)

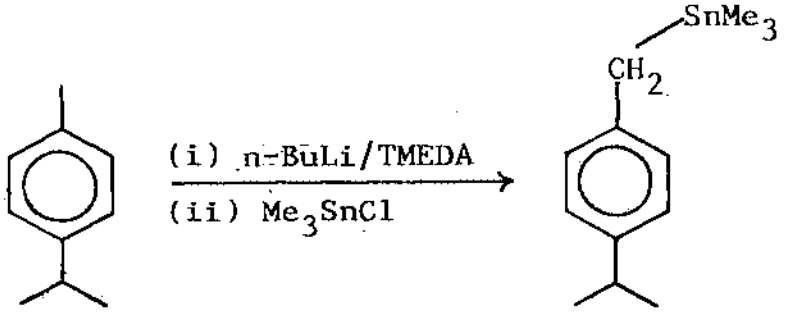
Benzyltrialkyltins(2) may be prepared in several ways:

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



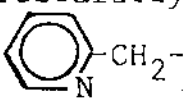
(4) (R=Me,Et,n-Pr,n-Bu) (2)

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

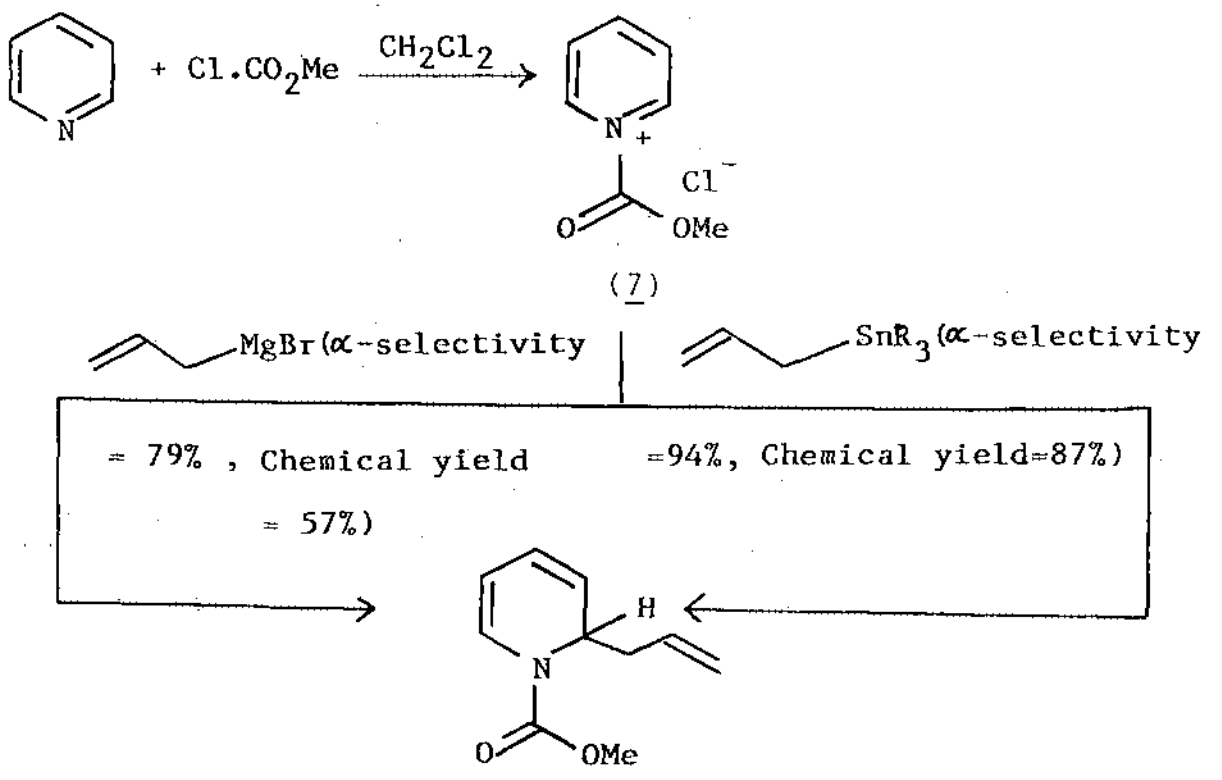
Although benzyltrialkylstannanes have enjoyed widespread applications[8,10] in the domain of synthetic organic chemistry over the last decade, almost no attention has ever been made to the use of benzyltins, where the aromatic ring contains one or more hetero-atom, particularly the nitrogen atom. In 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



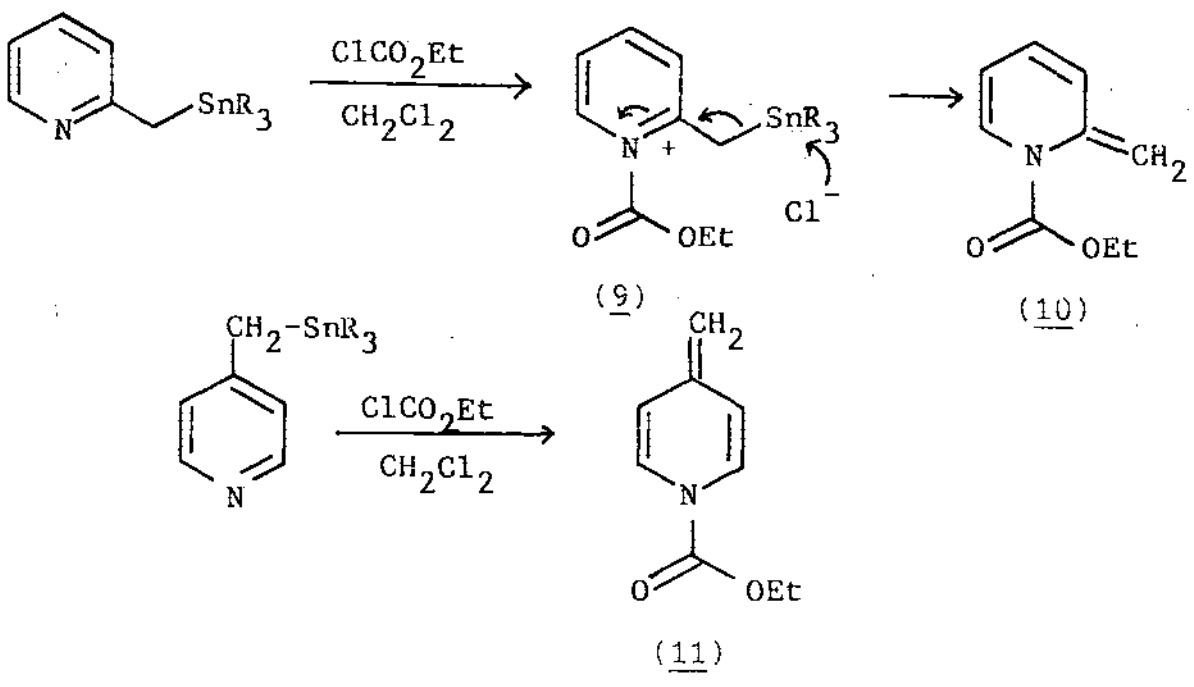
(7)

(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.

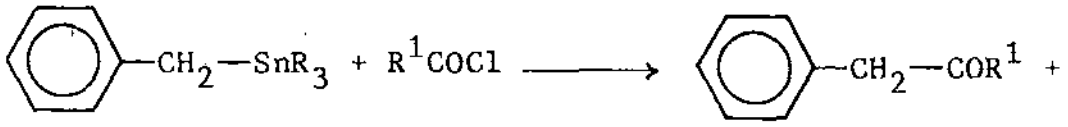
With this view in mind, we reasoned that if these picolyltrialkyltins could be prepared, further activation of the aromatic ring(9) with ethyl chloroformate would lead to N-(ethoxy carbonyl)-1, 2- or N-(ethoxy carbonyl)1,4-pyridine-methenes(10) and (11) respectively as outlined in SCHEME-II.

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].

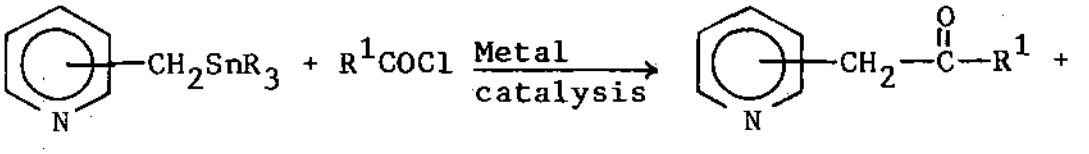
2. Stille et al.[6a,8b] and Mitiga et al.[6b,19] independently showed that benzyltrialkyltins(2) underwent transition metal-catalysed coupling with acid chlorides with the selective transfer of benzyl group thus providing a mild and general method for the synthesis of ketones(12) from acid chlorides.



(2) (12) R_3SnCl

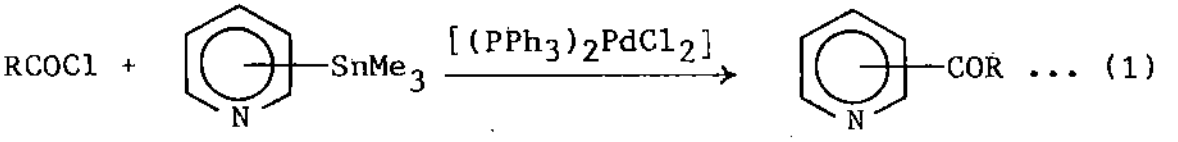
Similar reactions could be studied with picolyltrialkyltins(3) with several acid chlorides resulting in the formation of various picolyl alkyl ketones(13) which are otherwise difficulty accessible(SCHEME-III). Yamamoto et al.[20] showed that trimethyltin derivatives of aromatic

SCHEME-III



(3) (13) R_3SnCl

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



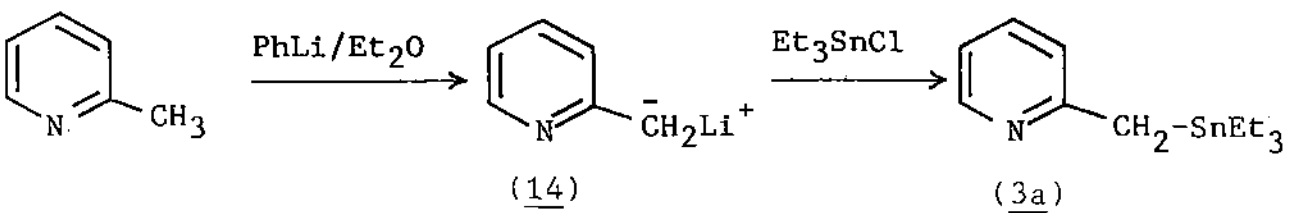
... (1)

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



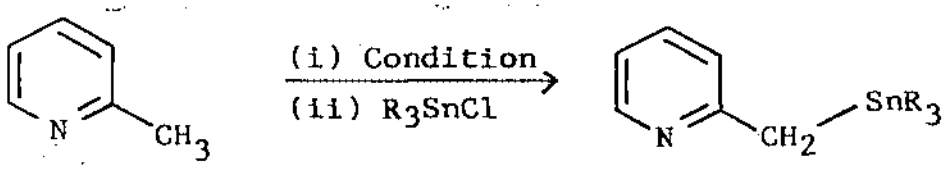
(14) (3a)

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,

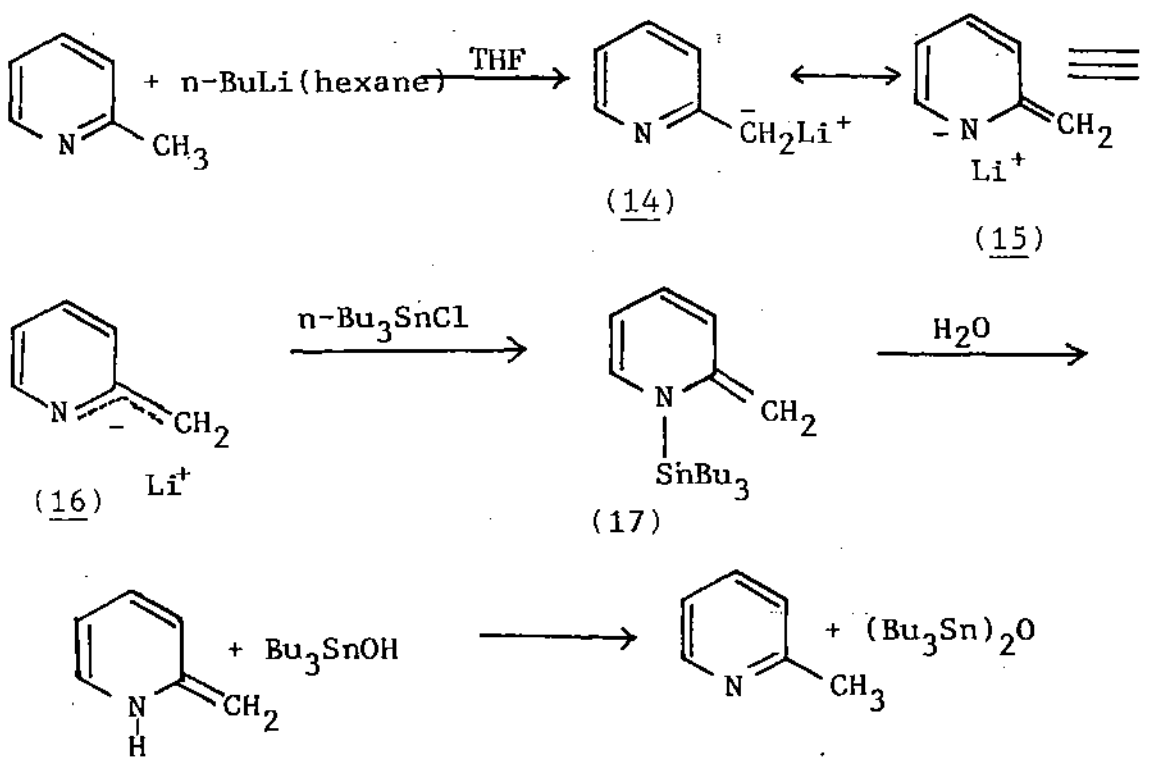
therefore, carried out this reaction using n-butyllithium in hexane and THF as cosolvent at refluxing temperature(SCHEME-IV, Type-B), at 0°C (Type-C), at -10°C(Type-D) and at -78°C (Type-E using Bu_3SnCl and Type-F using Me_3SnCl). In all the cases, a dark brown-red colour was developed while adding 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.

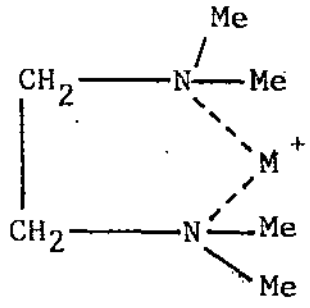
SCHEME-V



(Similar mechanism should be valid for 4-picoline)

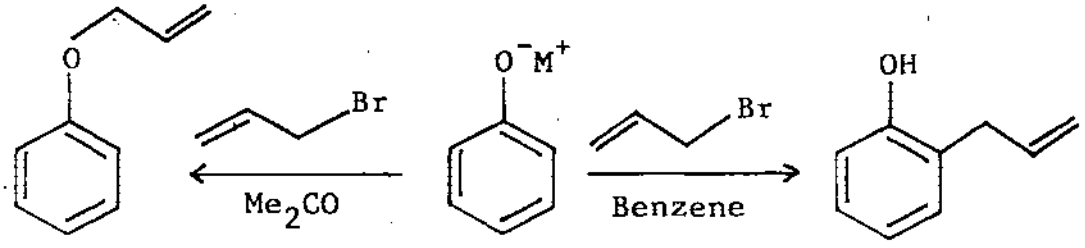
If this mechanistic pathway might be involved, such ambident nucleophiles should attack a given substrate under a given set of conditions[27]. In this case, N-stannylation, leading to product(17), is burdened energetically by the fact that aromaticity is destroyed. However, N-stannylation should be most 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



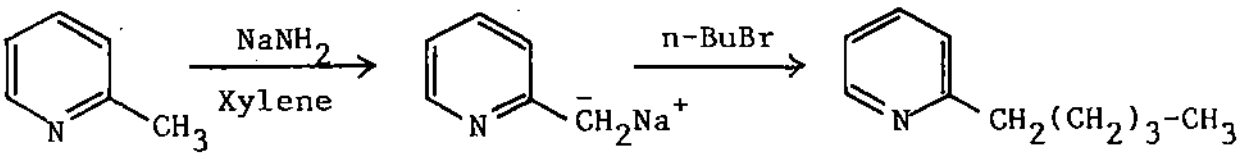
(18)

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.

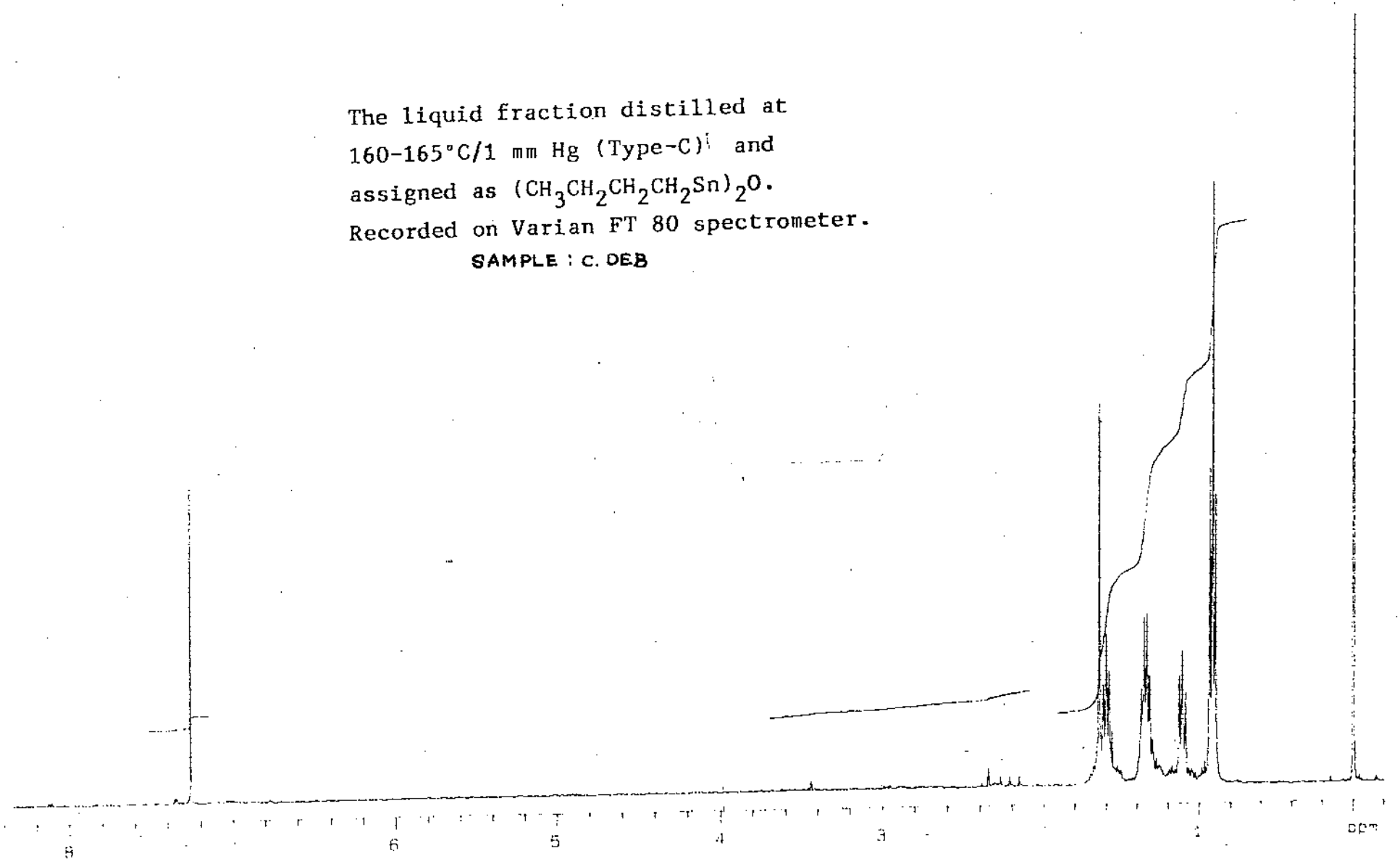
ν_{max}: 770(s, Sn-O-Sn), 1372(s), 1410(w), 1450(s), 3440(w).

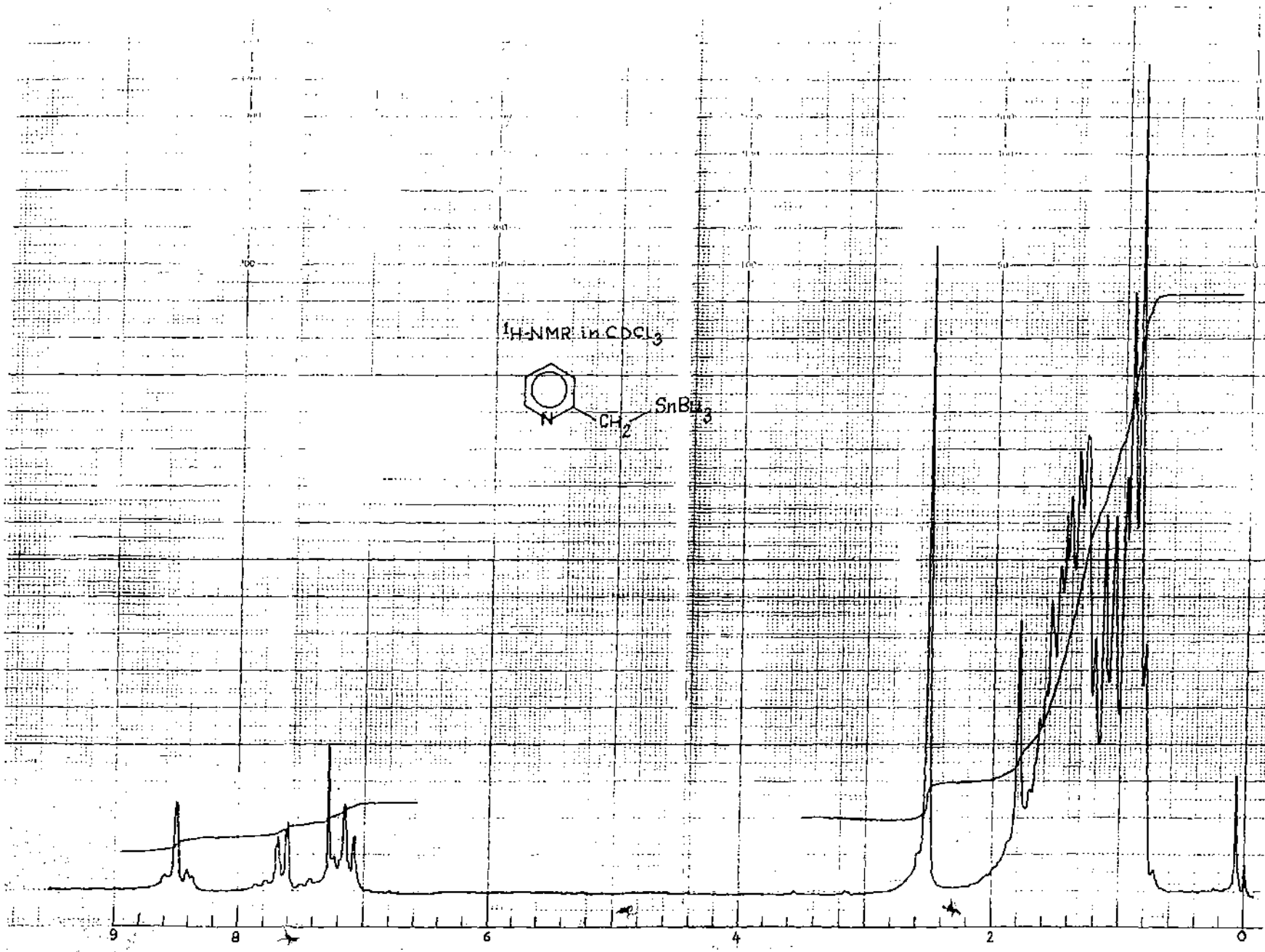
^{1}H-NMR($CDCl_3$) : δ 0.93(t, 18H, $-CH_3$), 1.12(m, centered at, 12H, $-CH_2$), 1.35(m, centered at, 12H, $-CH_2$), 1.60(m, centered at, 12H, $-CH_2$).

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).

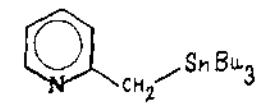
The liquid fraction distilled at
160-165°C/1 mm Hg (Type-C) and
assigned as $(CH_3CH_2CH_2CH_2Sn)_2O$.
Recorded on Varian FT 80 spectrometer.

SAMPLE : C. DEB





SAMPLE : C.DEB



SOLVENT $CDCl_3$

REF TMS

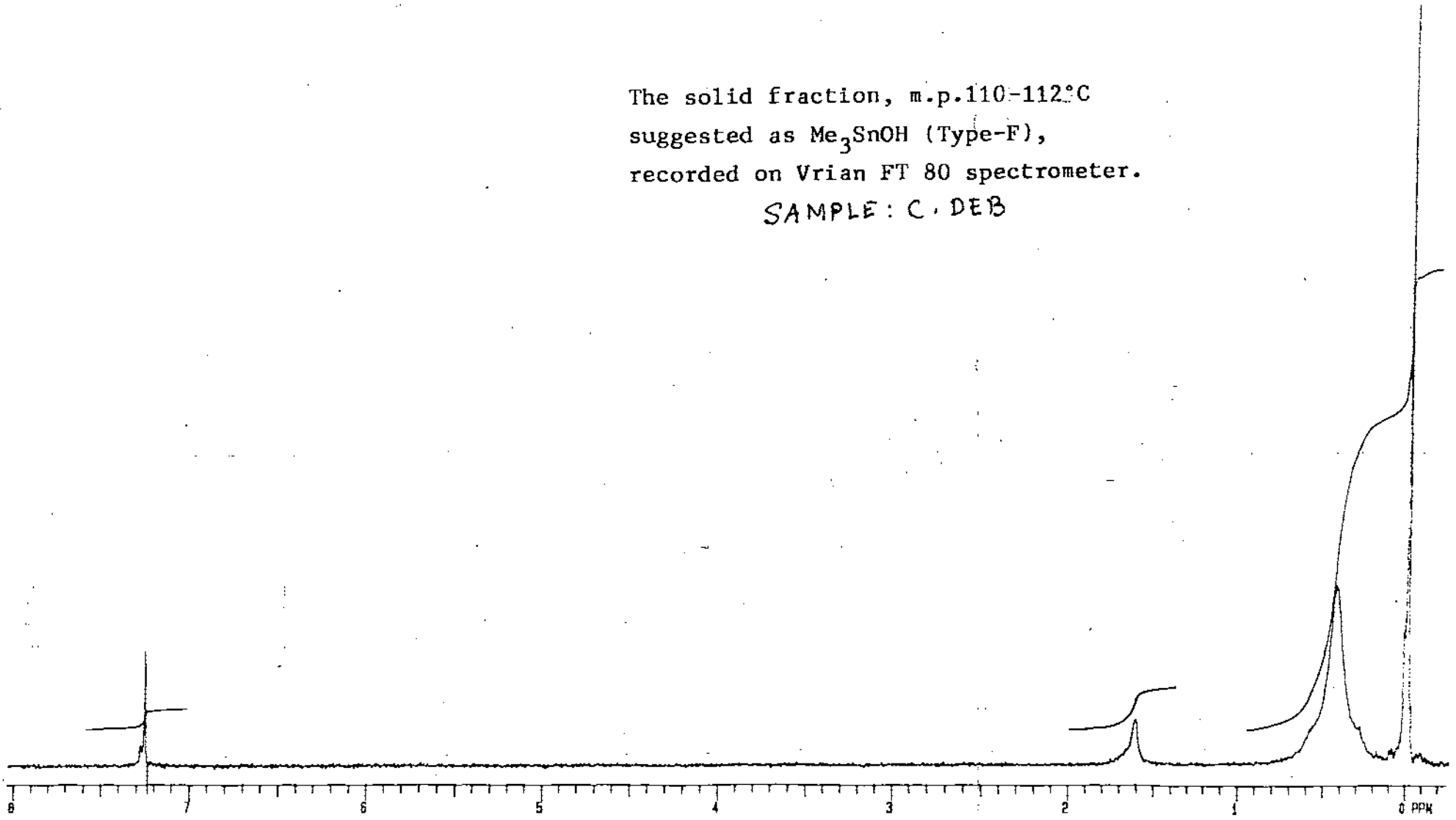
^{1}H

PULSE SINGLE

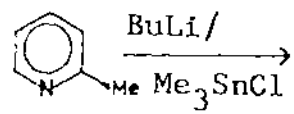
1000

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

SAMPLE : C . DEB

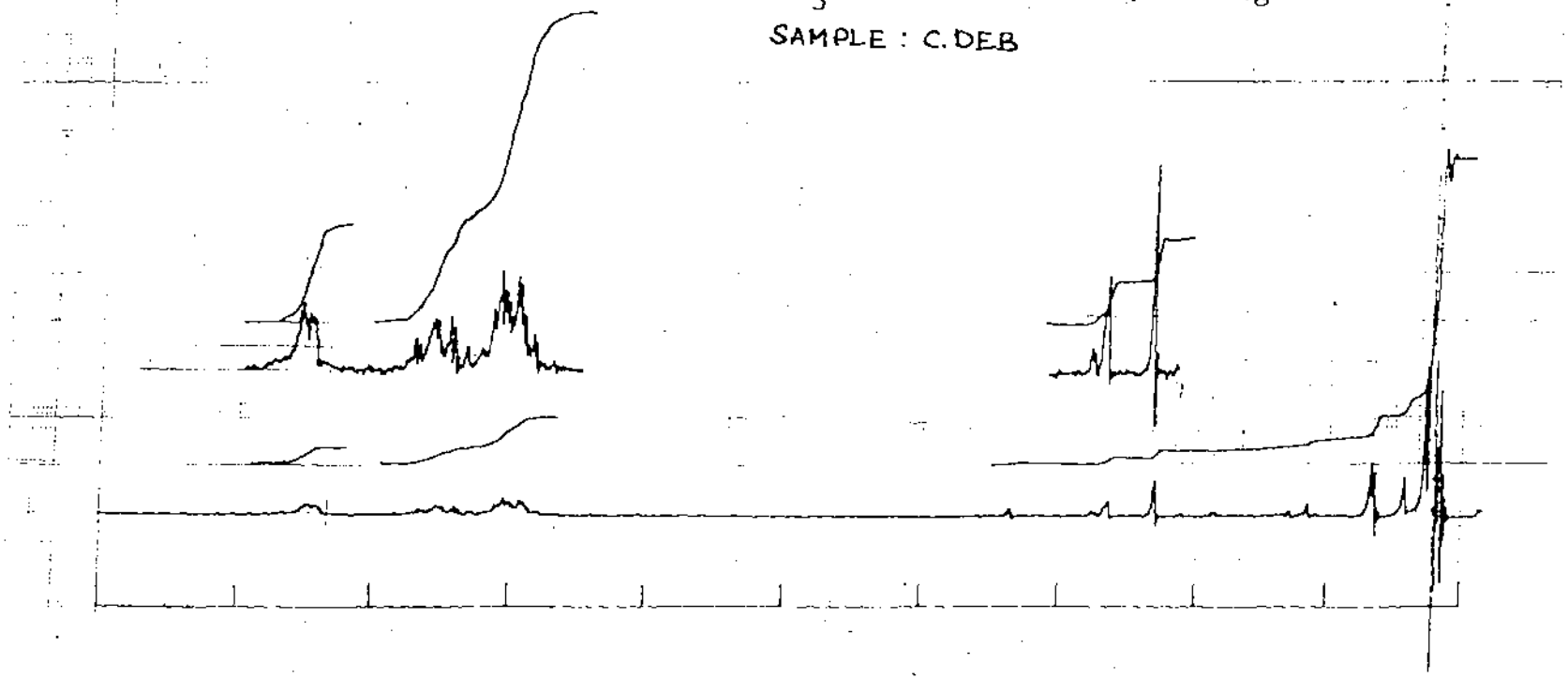


^{1}H-NMR in CCl_4



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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