SYNTHETIC AND MECHANISTIC STUDIES ON THE HYDROBORATION OF OLEFINS WITH VARIOUS BORANE LEWIS BASE COMPLEXES

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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JANUARY 1988

To

my wife

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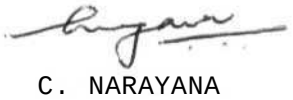
S T A T E M E N T

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of Dr. M. Periasamy.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



C. NARAYANA

C E R T I F I C A T E

Certified that the work contained in this thesis entitled 'SYNTHETIC AND MECHANISTIC STUDIES ON THE HYDROBORATION OF OLEFINS WITH VARIOUS BORANE LEWIS BASE COMPLEXES' has been carried out by Mr. C. Narayana, under my supervision and the same has not been submitted elsewhere for a Degree.

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28.1.88

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(THESIS SUPERVISOR)

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DEAN
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A C K N O W L E D G E M E N T S

It is with great pleasure that I acknowledge my profound gratitude to my research supervisor, Dr. M. Periasamy, for suggesting this research problem and for constantly guiding and encouraging me throughout the course of this work.

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January 1988 **C. NARAYANA**

ABBREVIATIONS

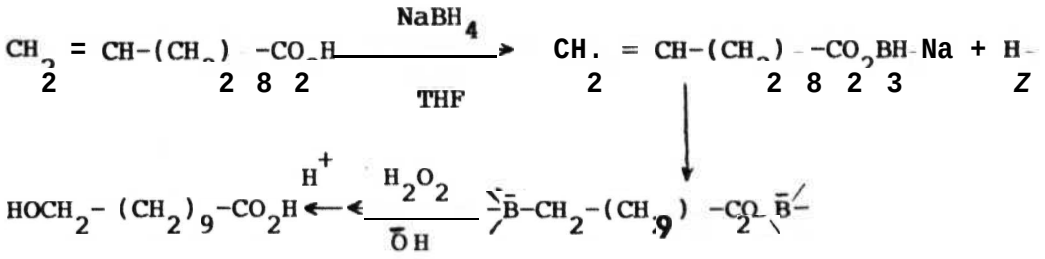
AcOH	acetic acid
Ac_2O	acetic anhydride
9-BBN	9-bora bicyclo[3.3.1]nonane
B_2H_6	diborane
BMS	borane dimethylsulfide complex
n-BuLi	n-butyl lithium
DB	dialkylborane
DCM	dichloromethane
DCME	α,α-dichloromethylmethylether
DG	diglyme
DMF	dimethylformamide
ee	enantiomeric excess
EE	diethyl ether (Et_20)
1PC	isopinocampheyl borane
LIH	lithium hydride
LAH	lithium aluminium hydride
MB	monoalkylborane
MIBDA	mono iodoborane N,N-diethylaniline complex
PDC	pyridinium dichromate
Sia_2BH	disiamylborane
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
Thexyl	2,3-dimethyl-2-butyl
TMS	tetramethylsilane
p-TsCl	p-toluene sulphonyl chloride (tosyl chloride)

ABSTRACT

This thesis deals with synthetic and mechanistic investigations on the hydroboration of olefins with various borane Lewis base complexes. It comprises of three chapters. Each chapter is subdivided into three parts; Introduction, Results and Discussion and Experimental Sections.

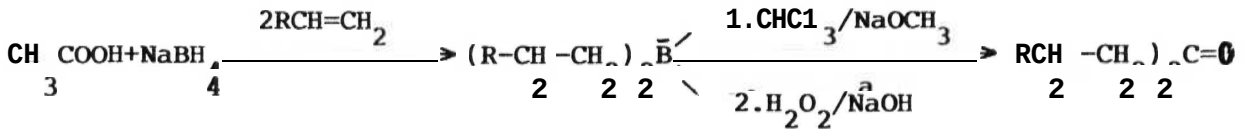
The first chapter describes the studies on the hydroboration of olefins with $Hg(OAc)_2/NaBH_4$ and $RCOOH/NaBH_4$ systems. It was found that $Hg(OAc)_2/NaBH_4$ and $CH_3COOH/NaBH_4$ systems hydroborate olefins. The hydroborations of olefins with these systems are relatively slow and only one equivalent of olefin reacted after 12 h at r.t. Although the hydroboration of olefins with $CH_3COOH/NaBH_4$ system has been reported earlier, the system has not been extensively studied. Utilization of the $CH_3COOH/NaBH_4$ system for selective hydroborations and controlled hydroborations was studied. The slow hydroborating nature of the $CH_3COOH/NaBH_4$ system was exploited in the selective hydroboration of olefins in the presence of other reducible functional groups. Selective hydroboration of olefinic moiety when it is present along with a carboxylic group in a molecule is difficult with $BH_3.THF$ as the reduction of carboxylic group by this reagent is faster than hydroboration. This objective has been achieved in the past by protecting the carboxylic group as an ester or by utilizing two equivalents of hindered disiamylborane as the hydroborating agent. During the present studies, it was observed that the hydroboration of olefinic moiety present in a molecule along with a carboxylic acid group can be readily achieved by adding $NaBH_4$ to the olefinic acid (Scheme 1).

Scheme 1



Hydroboration of olefins with $CH_3COOH/NaBH_4$ system followed by carbenoidation using the simple $CHCl_3$/NaOMe reagent and oxidation with H_2O_2/NaOH give symmetrical dialkylketones (Scheme 2). This transformation was earlier carried out under relatively more exotic reaction conditions. In addition to providing a simple synthetic method for the conversion of olefins to dialkyl ketones, the present transformations also throw some light on the nature of the species involved in the processes.

Scheme 2



Hydroboration of terminal alkenes with $CH_3COOH/NaBH_4$ system followed by oxidation with $Cr^{VI}/(CH_3)_3COH$ reagent give the corresponding carboxylic acids in 30% to 75% yields. Although the yields are very modest in some cases, this method serves as a simple one pot procedure for the conversion of terminal alkenes into the corresponding carboxylic acids.

In the 2nd chapter, the studies on the synthesis and application of borane and iodoborane N,N-dialkylaniline complexes are described. Various methods reported for the generation of diborane were reviewed

in order to select a simple method for the generation of diborane for utilization in the synthesis of amine-borane complexes. The method reported by Freeguard and Long in 1965 involving the utilization of $NaBH_4/I_2$ system in diglyme appeared to be simple (eq.1,2). These authors trapped the liberated diborane in a series of liquid nitrogen traps using vacuum line technique. However, this simple system has not been extensively utilized for diborane generation, despite the facts that the starting materials are relatively simple to handle and the advantage over the diborane generated utilizing $BF_3OEt_2/NaBH_4$ system has been demonstrated.

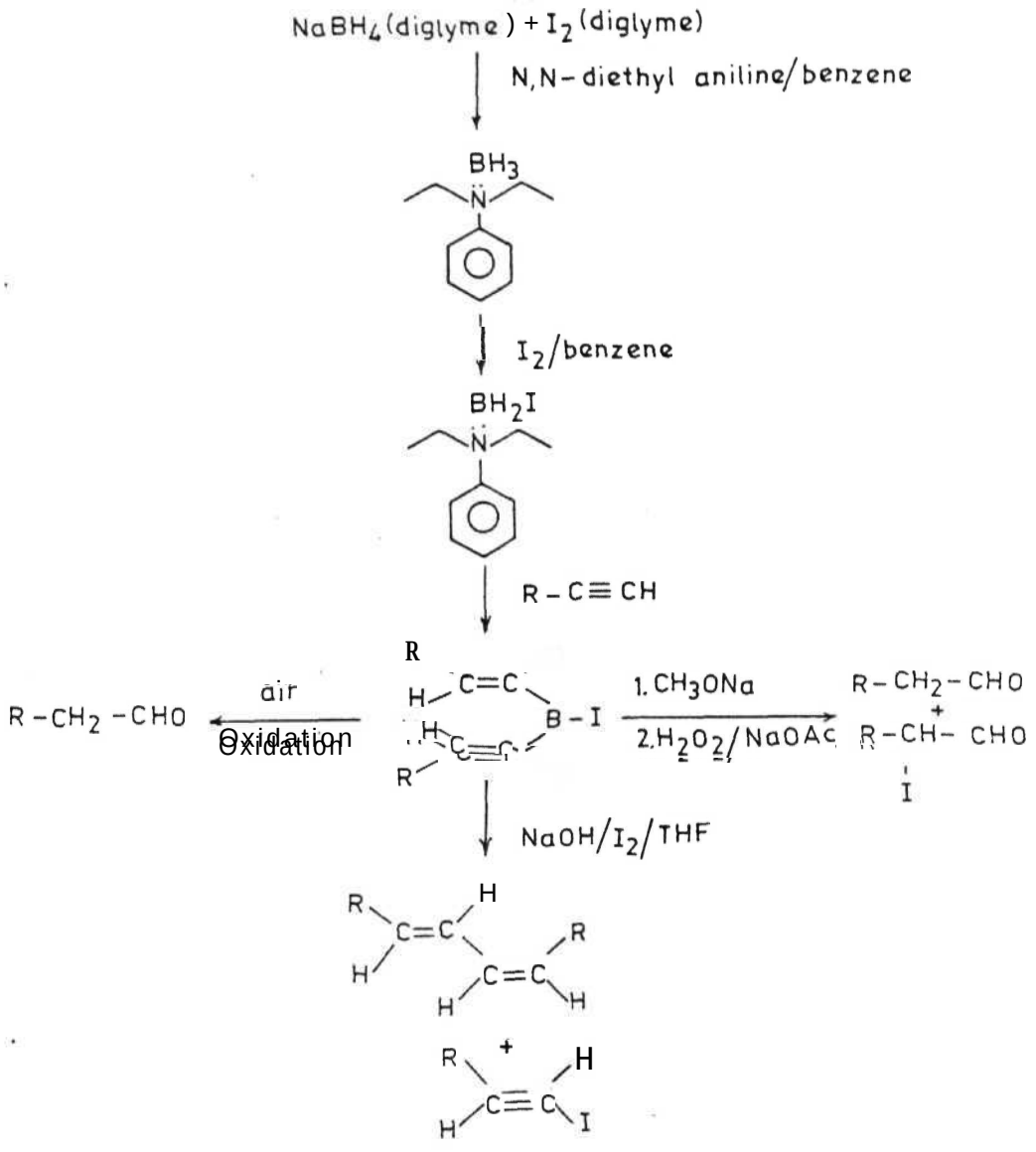
$$2NaBH_4 + Hg_2Cl_2 \xrightarrow[r.t.]{diglyme} 2Hg + 2NaCl + H_2 + B_2H_6 \quad (1)$$

$$2NaBH_4 + I_2 \xrightarrow[r.t.]{diglyme} 2NaI + H_2 + B_2H_6 \quad (2)$$

During the present studies, it has been observed that the diborane can be readily generated utilizing the $NaBH_4/I_2$ system using the equipment similar to that utilized for the $NaBH_4/BF_3.OEt_2$ system. The diborane generated by the above method was utilized for the synthesis of N,N-dialkylaniline borane complexes, for hydroboration of olefins, reduction of amides, imines and carboxylic acid groups. The N,N-diethylaniline borane complex was utilized for symmetrical dialkyl ketone synthesis from olefins via hydroboration-carbenoidation-oxidation and synthesis of unsymmetrical dialkyl ketones via sequential hydroborations of two different olefins was also attempted.

Mono iodoborane-N,N-diethylaniline complex was prepared in benzene by the reaction of I_2 with the corresponding amine borane complex and its synthetic utility was explored (Scheme 3).

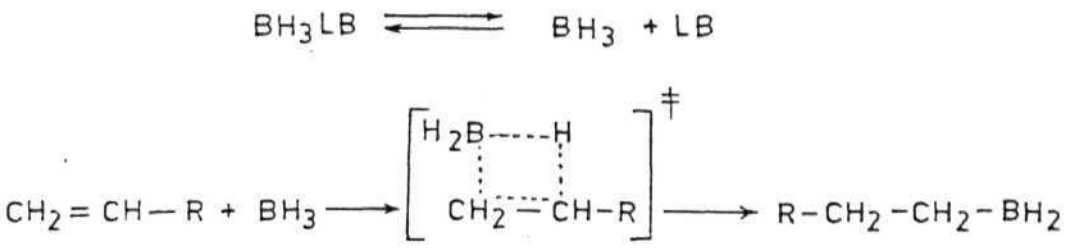
Scheme 3



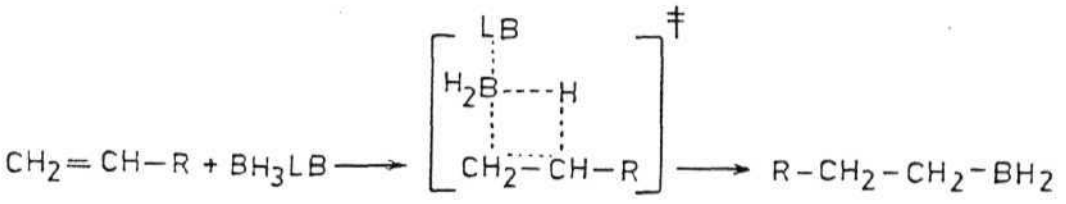
In chapter 3, the mechanistic studies on the hydroboration of prochiral olefins with various borane-chiral Lewis base complexes are described. In the introductory section, contributions by various research groups to the mechanistic studies on the hydroboration reaction are reviewed. Three different mechanistic proposals can be visualised from these reports (Scheme 4).

Scheme 4

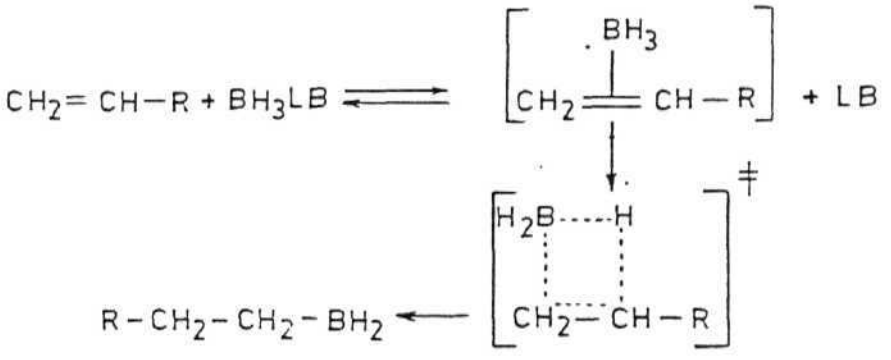
1. S_N1 like mechanism: Involving free 'BH_3' monomer formation in an equilibrium step.



2. S_N2 like mechanism: Without any intermediate.



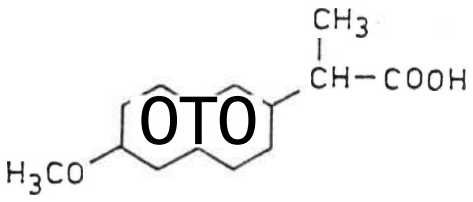
3. Mechanism with π-complex intermediate.



The obvious difference between the S_N1 like mechanism and S_N2 like mechanism is the absence or presence of the Lewis base in the transition state of the >B-H addition to the olefin. Although it is not clear whether the Lewis base will have any influence during >B-H addition in the mechanism involving TT -complex intermediate, the influence (if any)

will be only little since the >B-H addition here is an intramolecular rearrangement. Accordingly, it was thought that the problem (i.e. whether the Lewis base is present or absent in the transition state) can be examined by utilizing BH_3-chiral Lewis base complexes for the hydroboration of prochiral olefins.

The chiral Lewis base auxiliaries (2,3,4,5) were synthesized following modified literature procedures. The commercially available acid **(1)** was also utilized.



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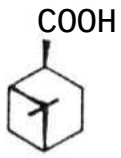

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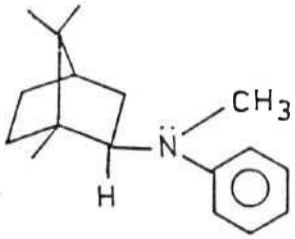

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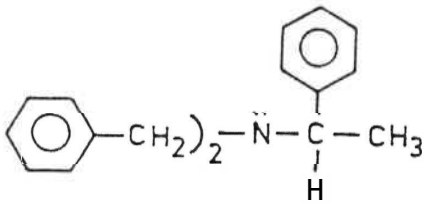

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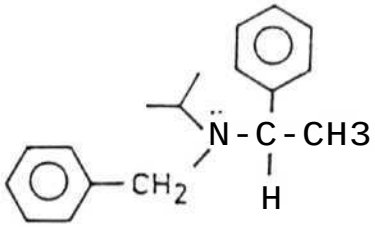

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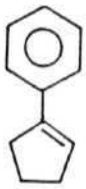

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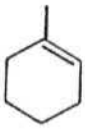

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Hydroboration of prochiral olefins (6 to 9) were carried out with these chiral $RCOOH/NaBH_4$ systems and chiral amine borane complexes. The corresponding alcohols with optical inductions 0.3%ee to 19.2%ee were isolated after oxidation of the resulting organoborane with H_2O_2/ NaOH. These results were considered in the context of mechanisms (Scheme 4) proposed by various workers for the hydroboration reaction. The present results along with the existing data in the literature indicate that

there is a spectrum of mechanisms possible for the hydroboration reaction, depending on the reactivity of the substrates. The results are discussed by taking into account of the frontier orbital interactions and steric factors involved.

GENERAL INTRODUCTION

Diborane was isolated and characterised as early as in 1912.[1] The observation that it slowly reacts with ethylenc at 100°C in the gas phase to give triethyl borane was made in 1948.[2] However, the observation that the addition of the >B-H bond in diborane to olefins is facile in ether solvents was made only in 1956.[3,4,5] The historical account reveals that this discovery of the powerful catalysis by ether solvents was delayed as diborane was not generated in ether solvents in the presence of olefins prior to 1956. It is now well established that the diborane reacts with Lewis bases (eg, ether solvents, dimethyl sulfide, amines, etc.) to give the corresponding BH_3-Lewis base complexes which hydroborate olefins more readily than the parent diborane. Many such BH_3-Lewis base complexes are now commercially available (eq.1).

$$B_2H_6 + : LB \longrightarrow 2BH_3:LB \qquad (1)$$

LB = THF, Me_2S, R_3N(R=H or alkyl) etc.

Our preliminary experiments revealed that the $Hg(OOCCH_3)_2/NaBH_4$ system or the $CH_3COOH/NaBH_4$ system in THF hydroborates olefins at room temperature. The reaction is relatively slow compared to BH_3.THF and only one equivalent of 1-alkene reacts in 12 h at room temperature. Many literature reports indicate that the stronger the Lewis-base borane

complex, the slower is the hydroboration. In some instances, the stronger complexing ability of Lewis bases can be utilized for achieving controlled hydroboration. For example, $ClBH_2 .OEt_2$ gives the corresponding dialkyl chloroborane with 1-butene in diethylether but in the presence of 1 to 2 equivalents of THF the hydroboration can be stopped at the monoalkyl-chloroborane stage[7] (eq.2,3).

$$ClBH_2OEt \xrightarrow[Et_2O]{C_2H_5CH=CH_2} (C_2H_5CH_2CH_2)_2BCl \qquad (2)$$

$$ClBH_2OEt \xrightarrow[\text{1 to 2 eq.THF}]{C_2H_5CH=CH_2} C_2H_5CH_2CH_2BHCl \qquad (3)$$

It has been suggested that stronger complexation by THF prevents further hydroboration.[7] It was of interest to investigate the utilization of the $RCOOH/NaBH_4$ system for selective and controlled hydroborations.

As mentioned above, diborane reacts with ether solvents and other Lewis bases to form BH_3 Lewis base complexes which then hydroborate olefins. The reactivity is dependent on the stability of such complexes. However, the mechanism of this important reaction and the role of the Lewis base in the transition state of the reaction are not clearly understood and differences of opinion exist. It was also of interest to investigate this problem.

Since several monographs[5,8-11] and detailed reviews[12-14] have been published covering hydroboration and other reactions of BH_3-Lewis base complexes and also the reactions of organoboranes, only the reports

closely related to the present investigations will be discussed under the 'introduction and results and discussion' sections in Chapters 1-3.

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CHAPTER 1

Studies on the hydroboration of olefins with $Hg(OAc)_2/NaBH_4$ and $RCOOH/NaBH_4$ systems

INTRODUCTION

An excellent review on the nature of the species produced in the reaction of RCOOH with $NaBH_4$ and their reactions towards various organic functional groups has been published recently.[1] However, it is helpful to briefly survey various original reports published in this area before and during the course of the present studies.

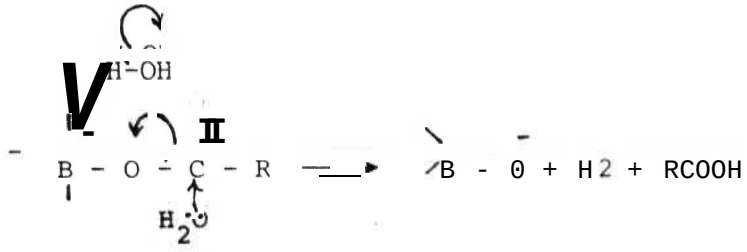
Whereas aqueous acids completely hydrolyse $NaBH_4$, pure mineral acids give diborane. Treatment of $NaBH_4$ with neat carboxylic acids gives hydrogen and acyloxyborohydride species. Even in neat carboxylic acids, the triacyloxyborohydride $Na(RCOO)_3BH$ is relatively stable and the last hydride is lost only upon heating or prolonged exposure to RCOOH.[1] The sodium triacyloxyborohydride has been characterised by IR studies.[2,3] The mono and diacyloxyborohydrides will be expected utilising requisite amount of the RCOOH (eq.1).

$$NaBH_4 + x\ RCOOH \longrightarrow NaBH_{4-x}(OOCR)_x + xH_2 \qquad (1)$$

$x = 1$ to 3

Originally it was observed that upon reaction of $NaBH_4$ (eq.1) with CH_3COOH (1 eq) a material analysed for '$NaBH_3OAc$' crystallizes out of THF.[4] The reaction of this material with H_2O liberates three

moles of hydrogen (H_2) (eq.2).



(2)

No diborane was detected on heating this material at 55°C for 10 minutes. However, the material gives $(RO)_3PBH_3$ in good yields on treatment with trialkylphosphites.[4] Accordingly, even if the material at hand is not exactly '$NaBH_3OAc$', it is able to supply 'BH_3' moiety on reaction with trialkylphosphites.

The related propionic acid derivative was reported to have been formed from the reaction of $NaBH_4$ in diglyme with an equivalent of propionic acid and also by the reaction of sodium propionate with diborane.[5] However no evidence was presented to support its structure.

Later, it has been observed that the reaction of isobutric acid (1 eq) and $NaBH_4$ (1 eq) in THF actually gives a suspension in which $NaBH_4$ is in equilibrium with the mono-, di-, tri and tetra-acyloxyborohydride species.

$$NaBH_4 \rightleftharpoons NaBH_3OAc \rightleftharpoons NaBH_2(OAc)_2 \rightleftharpoons NaBH(OAc)_3 \rightleftharpoons NaB(OAc)_4$$

Very recently it has been reported[7] that the solution obtained from the $LiBH_4$(1 eq)/CH_3COOH (1 eq) system in THF, $NaBH_4$ (1 eq)/CH_3COOH (1 eq) system in diglyme, BH_3.THF(1 eq)/$Na(OAc)_4$ (1 eq) system

in diglyme at 25°C give ^{11}B-NMR signals corresponding to the presence of only MBH_4 and $MB(OAc)_4$. It has been concluded that either the reaction of alkali metal borohydrides with an equivalent of acetic acid does not produce monoacetoxyborohydrides or the monoacetoxyborohydrides, if first produced, are very labile in solution and undergo rapid disproportionation to give a mixture of borohydride and tetra acetoxyborohydride[7] (eq.3,4).

$$CH_3COOH + MBH_4 \longrightarrow [MBH_3OAc] + H_2 \quad (3)$$

$$4\ MBH_3OAc \rightleftharpoons 3\ MBH_4 + MB(OAc)_4 \quad (4)$$

It has been observed that the reaction of $LiBH_4$ and an equivalent of CH_3COOH in diethylether gives diborane and H_2.[7] The diborane can be trapped as BH_3-SMe_2 complex if the reaction is carried out in the presence of Me_2S (eq.5).

$$CH_3COOH + LiBH_4 \begin{cases} \xrightarrow{Et_2O} 1/2\ B_2H_6 + H_2 + LiOAc \\ \xrightarrow[Et_2O + Me_2S]{} BH_3:SMe_2 + LiOAc \end{cases} \quad (5)$$

On the basis of these observations, the reaction in the case of $LiBH_4$ may be represented as follows (eq.6,7).

$$4\ LiBH_4 + 4\ HOAc \xrightarrow{LB} 4\ BH_3.LB + 4\ LiOAc + 4\ H_2 \quad (6)$$

$$4\ BH_3.LB + 4\ LiOAc \longrightarrow 3\ LiBH_4 + LiB(OAc)_4 \quad (7)$$

LB = Solvent

In non-coordinating solvents such as Et_2O, the intermediate $BH_3.OEt_2$ will not be stable and decomposes to B_2H_6 as the LiOAc precipitates out of the solution. In THF, the reaction gives only the $LiBH_4$ and $LiB(OAc)_4$. However, the mixture of $LiBH_4$ and $LiB(OAc)_4$ obtained from $LiBH_4$ and an equivalent of acetic acid was found to hydroborate olefins.[7] Since the $LiBH_4$ itself does not hydroborate olefins, the hydroborating species must be produced in situ from this on reaction with $LiB(OAc)_4$.

The ^{11}B-NMR studies[1] were carried out in solvents where both the MBH_4 and $MB(OAc)_4$ are soluble and it is not clear what will be the species formed in the reaction of $NaBH_4$ with an equivalent of CH_3COOH in THF from which the $NaBH_3OAc$ species has been reported to have crystallized out.[4]

Among various acyloxyborohydride species that will be expected to be formed by the reaction of RCOOH with $NaBH_4$, the following hydride delivering ability order was suggested.[1]

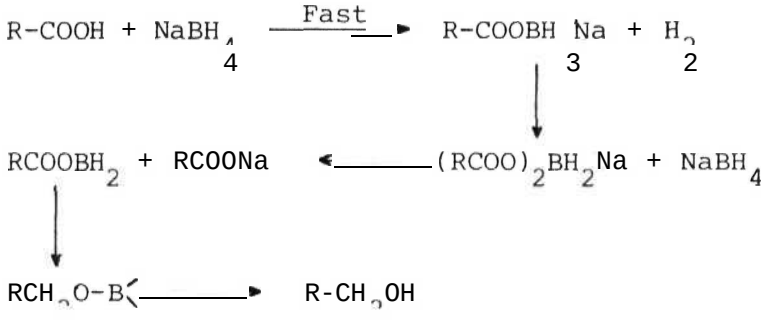
$$\bar{B}H_3OCOR > \bar{B}H_2(OCOR)_2 > \bar{B}H(OCOR)_3$$

It was noted that under the conditions where the triacyloxyborohydride will be formed using 3 equivalents of RCOOH, no hydroboration was observed.[1]

Formation of gaseous acetaldehyde was observed in the reaction

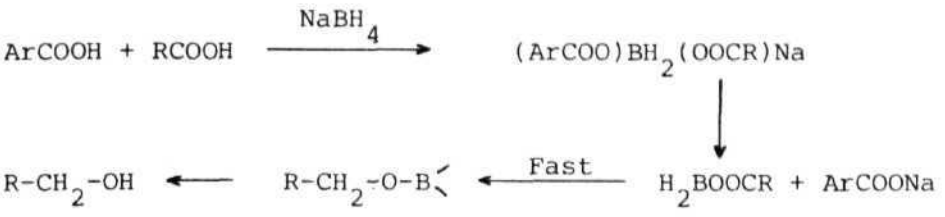
of $NaBH_4$[g] with excess acetic acid. The reagents obtained by the reaction of $NaBH_4$ and an equivalent of RCOOH or two equivalents of RCOOH in THF were found to be stable at r.t. and the acyloxy group was not reduced even after 24 h.[9] The reagent prepared using $LiBH_4$ (1 eq) and caproic acid (1 eq) is not stable and the acyloxy group is reduced in 24 h at room temperature in diethyl ether solvent to give n-hexanol in 60% yield.[10] However, the $NaBH_4$/RCOOH system in THF also gives the corresponding RCH_2-OH in 50% yield along with 50% of the unreacted RCOOH after refluxing the reaction mixture for several hours.[9] This observation was explained by the mechanism involving the formation of $RCOOBH_2$[2] intermediate which has been reported to undergo reduction even at -80°C. (Scheme 1).

Scheme 1



The reaction was exploited for the selective reduction of aliphatic acids in the presence of aromatic acids by utilizing $NaBH_4$ and one equivalent each of aliphatic acid and aromatic acid in THF and refluxing the mixture for 3 to 6 h[9] (Scheme 2).

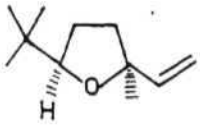
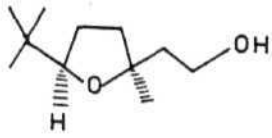
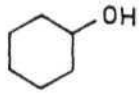
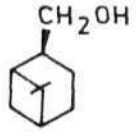
Scheme 2



The $RCOOH/NaBH_4$ system prepared in neat carboxylic acids or in solvents such as benzene, THF, dioxane, DMF, dichloroethane, dichloromethane, etc. have been utilized for several useful synthetic transformations and an excellent review has appeared recently.[1] The reagent system has been utilized for reduction of enamines,[2,12-15] and related substrates,[16-23] reductions of imines,[2] indole[24] and substituted indoles,[24-29] N-alkylation of amines,[2,30-37] reductive N-alkylation of nitrogen heterocycles,[2,34,38-42] reductive N-alkylation of oximes[43-45] and related substrates, reduction of hydrazones,[46] nitriles,[47] amides,[47] and carbamates,[36,48] reduction of alkenes,[49-53] alcohols[49] and ketones[54-56] which give stable carbonium ions in acid media, acylation of alcohols, phenols and amines,[2,57] selective reduction of aldehydes[58,59] in the presence of ketones,[60-62] asymmetric reduction of ketones,[63-66] reductive cleavage of acetals, ketals and ethers[67] and for many other applications.

Hydroboration of alkenes by the $RCOOH/NaBH_4$ system was first reported in 1963.[70] Although this method has not been extensively utilized several examples are known (Table 1).

Table 1 : Hydroboration of Alkenes

Substrate	Product	Condition	Yield
		1. $NaBH_4$/HOAc 2. H_2O_2/OH	75%
		1. $NaBH_4$/HOAc 2. H_2O_2/OH	79%
 (others)		1. $NaBH_4$/HOAc 10-20°C 2. H_2O_2/OH	85%
 (others)		1. $NaBH_4$/HOAc, 20° 2. H_2O_2/OH	73%
		1. $LiBH_4$/HOAc 2. H_2O_2/OH	95%

The conditions for the hydroboration were optimised in 1974.[71,72] It was observed that 3 equivalents of 1-alkenes or 2 equivalents of internal alkenes react when they were taken in THF along with $NaBH_4$ (1 eq) and CH_3COOH (1 eq) was added slowly at 0°C, and stirred further for 2 h at r.t. The yields of the alcohols obtained after oxidation with H_2O_2/NaOH indicate the formation of trialkylborane from 1-alkenes and dialkylborane from internal alkenes. These observations indicate that the reactivity of the species generated in situ is similar to BH_3.THF

as the latter also gives dialkylborane from internal alkenes such as cyclohexene and trialkylborane from 1-alkenes.

We became interested in studying the utilization of this simple $RCOOH/NaBH_4$ reagent system for selective and controlled hydroborations.

RESULTS AND DISCUSSION

Hydroboration of alkenes with $Hg(OAc)_2/NaBH_4$ and $RCOOH/NaBH_4$ system

In continuation with our previous studies on the carbonylation of radicals produced in the reaction of organomercurials with $NaBH_4$ in THF,[73] we became interested in the reaction of $Hg(OAc)_2/NaBH_4$ system. We have observed that the reaction of $Hg(OAc)_2$ with two equivalents of $NaBH_4$ in THF at 0°C gives a gas and elemental mercury. The contents hydroborates olefins. The reaction is slow and only one equivalent of 1-decene reacts in 12 h at room temperature. Several other olefins were hydroborated by this system and the results are summarized in Table 2.

It was reported[74] in 1965 that Hg_2Cl_2 and $HgCl_2$ liberate diborane on treatment with $NaBH_4$ in diglyme at room temperature (eq.8).

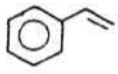
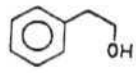
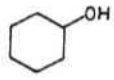
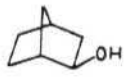
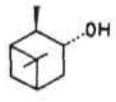
$$Hg_2Cl_2 + 2NaBH_4 \xrightarrow[r.t.]{\text{diglyme}} 2NaCl + 2Hg + B_2H_6 + H_2 \qquad (8)$$

Comparison of the present $Hg(OAc)_2/NaBH_4$ system with the above reaction would suggest the following stoichiometry (eq.9).

$$Hg(OAc)_2 + 2NaBH_4 \xrightarrow[r.t.]{THF} 2NaBH_3OAc + H_2 + Hg \qquad (9)$$

Table 2

Hydroboration-Oxidation of alkenes with $Hg(OAc)_2/NaBH_4$ system.

Substrate	Product	Yield[a] (%)	m.p./b.p. (lit. m.p/b.p)[b] [°C or °C/mm Hg]
$CH_3(CH_2)_7-CH=CH_2$	$CH_3(CH_2)_8-CH_2OH$	70[c]	107/7 (231/760)[75]
		82[d]	98/20 (219-220/760)[75]
		80	60/20 (160/760)[75]
		79[e]	125 (126)[76]
		70	98/10 (217/760)[76]

a) Yields are of isolated and distilled products. The products were identified by spectral data (IR, NMR) and comparison with the data reported in the literature. The spectral data are given in the experimental section.

b) Literature m.p/b.p. are given in parentheses along with the corresponding literature reference.

c) Signals corresponding to the isomeric secondary alcohol is not present in the ^{13}C-NMR spectrum of the alcohol. However, chromic acid oxidation of the organoborane gives 3% of 2-decanone (see later in the text). This indicates that the secondary alkyl boron species is present at least to the extent of 3%.

d) The isomeric 1-phenylethanol is present to the extent of 8% (^1H NMR).

e) Isolated by column chromatography using hexane/chloroform (50 v/v) as eluent.

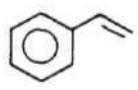
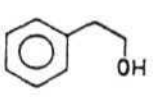
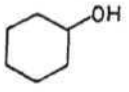
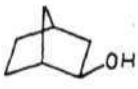
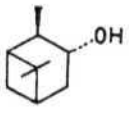
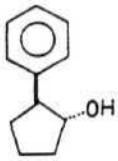
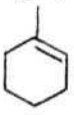
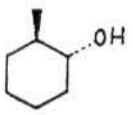
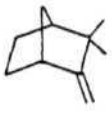
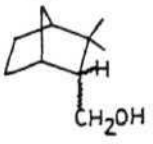
Treatment of Ph_3P with the contents of this reaction mixture gave Ph_3PBH_3 complex in quantitative yield confirming the stoichiometry.

As mentioned previously, several reports[1-4] indicate the formation of '$NaBH_3OOCR$' species in the reaction of $NaBH_4$ with an equivalent of RCOOH although more recent studies showed that these species undergoes disproportionation in solution.[6,7] In order to compare the reactivities of the $Hg(OAc)_2/NaBH_4$ and $RCOOH/NaBH_4$ systems, we have carried out the reaction of $NaBH_4$ with an equivalent of CH_3COOH in THF at 0°C, stirred the reaction mixture for 1 h and then carried out the hydroboration with 1-decene. We have observed that in this case also the reaction is slow and only one equivalent of 1-decene reacts in 12 h at room temperature indicating that the hydroborating species obtained in both the cases are same. The hydroboration was carried out with several other olefins and the results are summarized in Table.3.

As outlined earlier, it was reported[71] in 1974 that when the 1-alkene (3 eq) was taken in THF along with $NaBH_4$ and an equivalent of acetic acid was added at 0°C and further stirred for 2 h, all the three equivalents of olefin reacted. We have also reproduced this observation by taking 1-decene (3 eq) along with $NaBH_4$ and then carrying out the reaction as reported.[71] Apparently, the reaction of RCOOH with $NaBH_4$ in THF gives more reactive species which can be successfully trapped by the olefin if it is present. Otherwise, the species is converted into less reactive species with time.

Table 3

Hydroboration-Oxidation of alkenes with $CH_3COOH/NaBH_4$ system.

Substrate	Product	Yield[a] (%)	m.p./b.p. (lit.m.p/b.p)[f] [°C or °C/mm Hg]
$CH_3(CH_2)_7CH=CH_2$	$CH_3(CH_2)_8-CH_2OH$	76[b]	106/7 (231/760)[75]
$CH_3(CH_2)_3CH=CH_2$	$CH_3(CH_2)_4-CH_2OH$	80	155/760 (157/760)[75]
		89[c]	98/20 (219-220/760)[75]
		85	60/20 (160/760)[75]
		84[d]	125 (126)[76]
		72	98/10 (217/760)[77,76]
		80	88-90/2 (65-67/0.2)[76,77]
$CH_2=CH-(CH_2)_8-COOCH_3$	$HOCH_2CH_2(CH_2)_8CO_2CH_3$	73[e]	122/0.5 (156/4.5)[78]
		85	75/0.5 (129-131/6)[76]
		83	78/20 (166/760)[76]
		84	95/10 (213/760)[79]

a) Yields are of isolated and distilled products. The products were identified by physical constants and spectral data (IR, NMR) and comparison with the data reported in the literature. The spectral data are given in the experimental section.

b) Signals corresponding to the isomeric secondary alcohol is not present in the ^{13}C-NMR spectrum of the alcohol. However, chromic acid oxidation of the organoborane gives 4% 2-decanone indicating the formation of secondary alkyl boron at least to the extent of 4%.

c) The isomeric 1-phenylethanol is present to the extent of 8% (^{1}H NMR).

d) Isolated by column chromatography using hexane/chloroform (50 v/v) as eluent.

e) Oxidation with H_2O_2/NaOAc.

f. literature m.p/b.p are given in parentheses along with the corresponding literature reference.

As described in the introductory section,[7] recent studies indicate the following stages in the reaction of CH_3COOH with MBH_4 when both these reagents are soluble in the solvent (diglyme or THF) utilized.

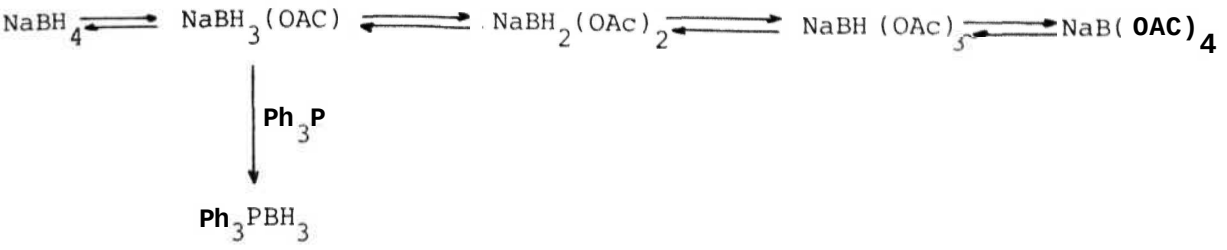
$$CH_3COOH + MBH_4 \longrightarrow CH_3COOM + BH_3{:}S + H_2 \quad (10)$$

$$MOOCCH_3 + BH_3{:}S \longrightarrow MBH_4 + MB(OOCCH_3)_4 \quad (11)$$

S = THF or diglyme

The greater reactivity (i.e. reaction of 3 eq. of 1-decene) can be readily explained by considering the above sequences since the 1-decene would react in a fast manner if it is present when the BH_3.THF is generated.

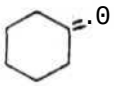
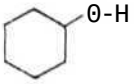
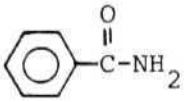
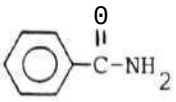
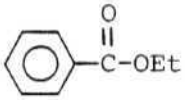
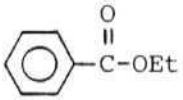
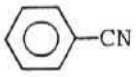
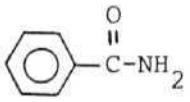
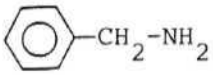
When the CH_3COOH and $NaBH_4$ reagents are mixed and stirred for 1 h at r.t. only a suspension is obtained after the reaction. It has been reported[6] that in the case of $NaBH_4$/isobutric acid in THF the precipitate corresponds to the presence of $NaBH_4$ and $NaBH_3$ (OOCR) as major components and the solution contains the $NaBH_2(OOCR)_2$ and $NaBH(OOCR)_3$ species as major components. In the present case also the suspension in THF will most probably contain similar species. However, the suspension on treatment with Ph_3P gives Ph_3PBH_3 in essentially quantitative yield indicating the ability of the system to supply 'BH_3' moiety. The following equilibria may operate.



Similar equilibria had been suggested for the $NaBH_4$/isobutric acid system in THF.[6]

As indicated by the present results, the reactivity of the CH_3COOH/$NaBH_4$ system towards olefins is lowered by stirring the system for 1 h after mixing the components in THF. It was of interest to examine the hydroboration of olefins in the presence of functional groups utilizing the $CH_3COOH/NaBH_4$ system. We have carried out the hydroboration of 1-decene (1 eq) with the $CH_3COOH/NaBH_4$ system for 12 h at room temperature in the presence of an equivalent amount of cyclohexanone, benzonitrile, ethyl benzoate and benzamide in individual runs. The results are summarised in Table 4. The results indicate that hydroboration of 1-decene takes place without the reduction of ethylbenzoate and benzamide. Cyclohexanone is completely reduced to cyclohexanol and benzonitrile is partly reduced to benzylamine along with complete hydroboration of 1-decene. We have also observed that methyl-10-undecenoate gives methyl 11-hydroxyundecanoate after oxidation with CH_3COONa/H_2O_2 and the corresponding 1,11-diol is not formed.

Table 4 : Selective hydroboration of 1-decene with $CH_3COOH/NaBH_4$ system in the presence of other reducible functional groups.[a]

Substrate	Product(s)	Yield (%)
$n\text{-}C_8H_{17}CH{=}CH_2$	$n\text{-}C_8H_{17}CH_2\text{-}CH_2OH$	80
		95[c]
$n\text{-}C_8H_{17}CH{=}CH_2$	$n\text{-}C_8H_{17}CH_2\text{-}CH_2OH$	79
		85[d]
$n\text{-}C_8H_{17}CH{=}CH_2$	$n\text{-}C_8H_{17}CH_2\text{-}CH_2OH$	80
		87[d]
$n\text{-}C_8H_{17}CH{=}CH_2$	$n\text{-}C_8H_{17}CH_2\text{-}CH_2OH$	78
		46[d]
		45

a) In each run 10 mmol of $CH_3COOH/NaBH_4$ was utilized along with 10 mmol of 1-decene and 10 mmol of other substrate containing reducible functional group. The reactions were carried out for 12 h at room temperature.

b) Yields are of the products isolated and separated by distillation or chromatography on a silica gel column.

c) Oxidation with $H_2O_2/NaOH$.

d) Oxidation with $H_2O_2/NaOAc$.

Similar reactivites have been also observed with BH_3.THF. The results indicate that the simple $CH_3COOH/NaBH_4$ system which utilizes very simple bench top chemicals for hydroboration should be a good reagent for organic syntheses where hydroboration oxidation is desired.

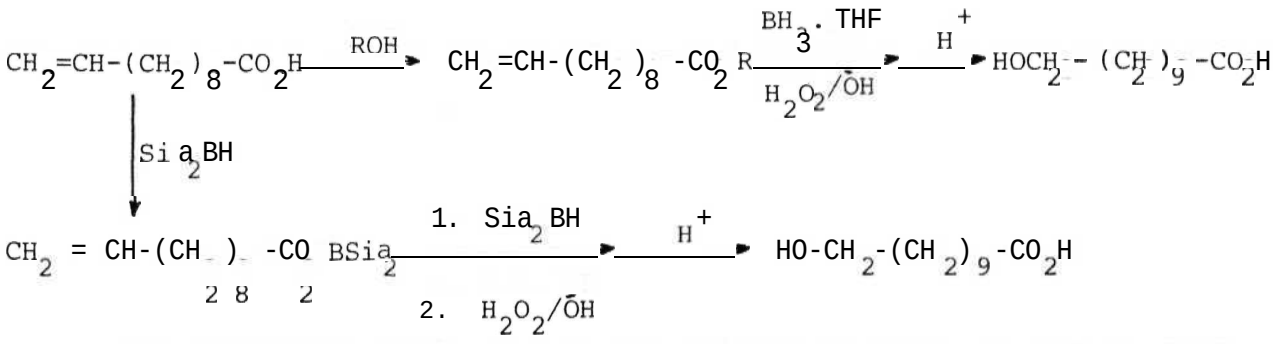
The BH_3.THF reagent has the following reactivity order :[81]

RCOOH > $R-CH=CH_2$ > R-C-R > R-CN > $R-C\equiv C-R_2$ > R-COOR > R-COCl and no reaction with $RCOO^-$.

If the olefinic moiety is present in the same molecule along with a carboxylic acid group (eg. 10-undecenoic acid), the selective hydroboration of the olefinic group with BH_3.THF can be achieved only after protecting the carboxylic group by esterification[77] (Scheme 3).

The alternate method[82] recommended for the direct selective hydroboration of olefinic moiety in the presence of carboxylic acid requires two equivalents of disiamylborane which serves as both the protecting and hydroborating agent because of steric hindrance (Scheme 3).

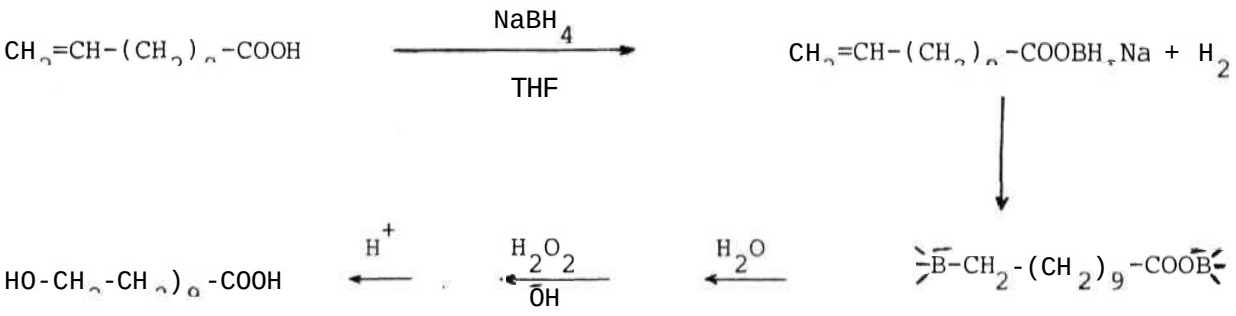
Scheme 3



The carboxylic acids do not get reduced by $NaBH_4$ in THF at room temperature even after 24 h although reduction occurs at **refluxing conditions.**[9] Also, $RCOO^-$ species **has** been **reported** to **coordinate with** BH_3.THF **without any reduction of the carboxylic group.**[5] **However, the** $RCOOH/NaBH_4$

system hydroborates olefins at room temperature as indicated by the present observations and previous findings by others.[71,72] Accordingly, it should be possible to achieve hydroboration of the olefinic moiety in 10-undecenoic acid utilizing $NaBH_4$ in THF without the reduction of the carboxylic group as envisioned in Scheme 4.

Scheme 4



It was observed that addition of 10-undecenoic acid to an equivalent of $NaBH_4$ in THF at 0°C for 1 h and further stirring the reaction mixture for 12 h followed by oxidation with H_2O_2/NaOH and neutralization with 2N HC1 gave 11-hydroxy undecanoic acid in 85% yield and the corresponding diol was not formed. This is an interesting observation as it simplifies the problems involved in the hydroboration of olefinic moiety in the presence of a carboxylic acid group.

Synthesis of Dialkylketones **via Hydroboration with $CH_3COOH/NaBH_4$ system and Carbenoidation with $NaOCH_3/CHCl_3$ system**

As outlined in the introductory section, even if the CH_3COOBH_3 species is formed from $RCOOH/NaBH_4$, it disproportionates into the borohy-

dride and various acyloxyborate species.[6,7] However, it has been found that the combination of MBH_4 and $MB(OAc)_4$ also hydroborates olefins.[6] Since MBH_4 itself does not hydroborate olefins, the hydroborating species must be produced from the reaction of MBH_4 and $MB(OAc)_4$. We have observed that both the $RCOOH/NaBH_4$ and $Hg(OAc)_2/NaBH_4$ systems in THF on reaction with Ph_3P give Ph_3PBH_3 adduct in quantitative yield. Clearly, these systems are able to give species containing 'BH_3' moiety which can be trapped as unreactive Ph_3PBH_3 complex. As mentioned earlier, the $CH_3COOH/NaBH_4$ system may give mono, di-, tri-, tetra-acetoxyborohydride in equilibria with $NaBH_4$. The slow hydroboration of the system may be due to the heterogenous nature of the reagent system. In addition, complexation of the BH_3 with the acetate anion also would reduce the hydroborating ability of the system.

In order to examine whether the $CH_3COOH/NaBH_4$ system gives trialkylborane species, we carried out an experiment with 3 equivalents of 1-decene at 50-55°C (bath temperature) for 3 h. It was observed that 1 equivalent of 1-decene remained unreacted. Increasing the reaction time or temperature did not increase the olefin uptake.

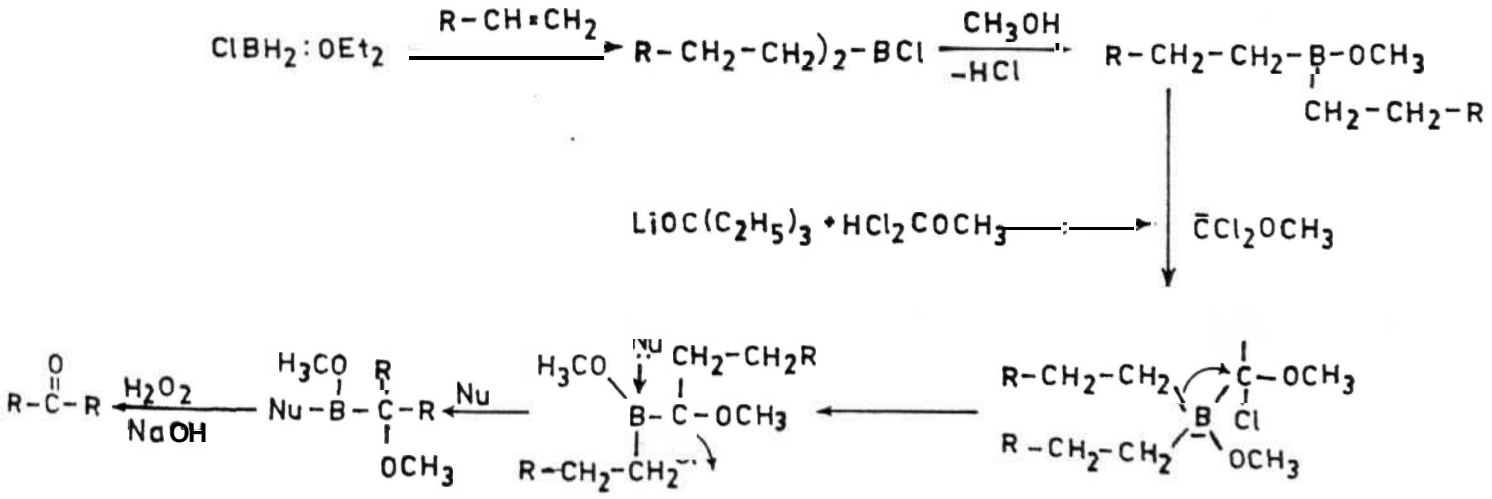
In order to examine the fate of the remaining hydride, we carried out an experiment with $NaBH_4$ and 1-decanoic acid in THF and cyclohexene (2 equivalents) at 50-55°C. Oxidation of the reaction mixture with H_2O_2/NaOH and acidification with 2N HCl gave 1-decanol (10%) besides cyclohexanol (85%) and 1-decanoic acid (90%). Consequently, at least 20% of the hydride has been utilized for the reduction of the carboxylic group. Similar concomitant reduction during hydroboration utilising $CH_3COOH/NaBH_4$

system at 50-55°C would account for the failure of the system to react with 3 equivalents of 1-decene.

The observation that the $CH_3COOH/NaBH_4$ system has difficulty in forming trialkylborane species is interesting as it indicates that the species formed may be dialkylborane species.

Dialkylborane species such as R_2BOMe prepared by hydroboration of alkenes with chloroborane followed by reaction with methanol react with the carbenoid reagent prepared from dichloromethylmethylether and lithium triethylcarboxide to give the corresponding dialkylketone after oxidation.[83] The following mechanism has been proposed (Scheme 5).

Scheme 5



The above reaction, which is generally referred to as the 'DCME' reaction gives trialkylcarbinol from trialkylborane after oxidation[83,84] (eq.12).

$$R_3B \xrightarrow[0^\circ C \text{ to } r.t.]{CH_3OCHCl_2/LiOC(C_2H_5)_3} R-\underset{R}{\overset{R}{C}}-B \xrightarrow[OH]{H_2O_2} R-\underset{R}{\overset{R}{C}}-H \qquad (12)$$

The DCME reaction conditions were originally standardised for the reaction with R_3B.[84] The reaction works under mild conditions and gives the tertiary alcohols in yields in the range of 80-85%. The reaction gives poor results when less hindered alkoxide bases such as potassium t-butoxide (30% carbinol) is utilised.[84] It was suggested that a sterically hindered base like lithium triethylcarboxide is necessary since the use of less hindered base would lead to complexation of the R_3B by the Lewis base itself and hence would make the reaction less efficient[83,84] since the free uncomplexed R_3B is the species required for the reaction.

$$R_3B \xrightarrow{\bar{C}Cl_2OCH_3} R_3\bar{B}-CCl_2OCH_3 \longrightarrow \longrightarrow R-\underset{}{\overset{R}{C}}-B \qquad (13)$$

(uncomplexed)

The 'DCME' reaction condition utilizing dichloromethylmethyl ether and lithium triethylcarboxide was latter found to give good yields of dialkylketone with R_2B-OCH_3 obtained from the hydroboration of alkenes with $ClBH_2OEt_2$ followed by methanolysis.[83]

If the hydroboration of 1-decene (2 eq) with $NaBH_4$ (1 eq) and CH_3COOH (1 eq) in THF gives dialkylboron species, carbenoidation and oxidation of this species will also give the corresponding dialkylketones.

It was of interest to us to examine whether relatively simple carbenoid reagents can be utilized for this transformation. We first attempted the carbenoidation of the organoboron species obtained in the hydroboration of 1-decene (2 eq) with $NaBH_4$ (1 eq) and CH_3COOH (1 eq) in THF, utilizing aq.NaOH and $CHCl_3$ under several conditions of time and temperature. However, in all cases only small amount (maximum 5%) of di-1-decyl ketone was obtained, besides 1-decanol arising from oxidation of unreacted boron compound. It was thought that the CCl_3 anion or the $:CCl_2$ species produced may not be stable enough to react with the organoboron compound at hand under aqueous conditions.

We have found that carbenoidation experiments utilizing 10 mL of $CHCl_3$ and 40 mmol of CH_3ONa gave dialkyl ketones in good yields. The reaction was also performed utilizing various acids and it was found that CH_3COOH gives good results (Table 5).

Table 5

Effect of acid on hydroboration-carbenoidation reaction.

RCOOH/$NaBH_4$[a]	Olefinic substrate[b]	Yield di-n-hexyl ketone (%)	1-hexanol (%)
R = CH_3-	1-hexene	70	20
CF_3-	1-hexene	60	35
Ph-	1-hexene	10	60
H_3C-C(CH_3)$_2$-	1-hexene	20	50

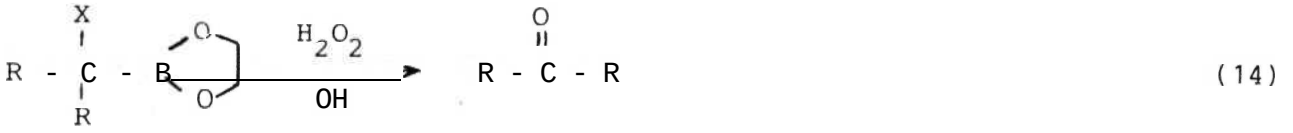
a) The hydroborating species was prepared by adding 10 mmol of RCOOH in THF to 10 mmol of $NaBH_4$ in THF at 0°C and further stirring it for 1 h at ambient temperature.

b) Hydroboration was carried out with 20 mmol of olefin and for carbenoidation 125 mmol of $CHCl_3$ and 40 mmol of $NaOCH_3$ were utilized.

c) Yields **are** of the isolated and distilled **products**

Hydroboration-carbenoidation of 1-decene gave di-1-decylketone in 80% yield. The reaction conditions tolerate the presence of an ester group in the substrate as indicated by the conversion of methyl-10-undecenoate to the corresponding diketone (Table 6).

In the case of norbornene, ethylene glycol (1 eq) was added prior to oxidation step. Otherwise, the yield of the bis-exo-norbornyl ketone **was** less (only 40%) and a product mixture containing boron was also obtained. Presumably, ethylene glycol facilitates the oxidation of the organoborane intermediate by forming the corresponding cyclic boronate.[80]



(14)

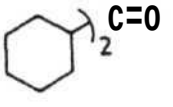
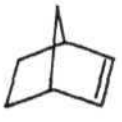
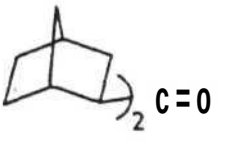
X = OCH_3 or OAc

Although 5-10% of alcohols were also formed, the desired dialkyl-ketones can be readily isolated by crystallization, distillation or chromatography.

The dialkylborane species formed in the present case may be $R_2\bar{B}(OAc)_2$ or $R_2\bar{B}(OC_2H_5)(0Ac)$ - [OC_2H_5, moiety formed by reduction of the acetoxy group] or $R_2\bar{B}H(OAc)$ species. Assuming that the methanolysis of $R_2\bar{B}HOAc$ may be required before carbenoidation, in our preliminary experiments, we methanolysed the hydroboration product. Later, we found that the methanolysis is not necessary. Perhaps, methanol produced in the reaction of $NaOCH_3$ and $CHC1_3$ is sufficient for methanolysis even if this is required. There is also a possibility that the $R_2\bar{B}H$ OAc species may disproportionate

Table 6

Conversion of alkenes to symmetrical dialkylketones.[a]

Substrate	Product	Yield[b] ketone	Yield[b] alcohol	mp/b.p. [°C or °C/mmHg][c]
$C_8H_{17}CH=CH_2$	$C_8H_{17}CH_2-CH_2)_2C=O$	80	8	64 (62)[75]
$C_4H_9CH=CH_2$	$C_4H_9CH_2-CH_2)C=O$	70[d]	8	125/10 (261/760)[75]
		67[d]	10	64/0.4 (96/1.2)[85]
		59[e,f]	6	53 (53-54)[85]
$H_3CO_2C(CH_2)_8CH=CH_2$	$H_3O_2C(CH_2)_8-CH_2CH_2)_2C=O$	78[e,g]	5	72

a) The reactions were carried out using 20 mmol of alkene, 10 mmol of $NaBH_4$, 10 mmol of CH_3COOH, 10 ml of $CHCl_3$ and 40 mmol of $NaOCH_3$. The reaction time and temperature for all the substrates for hydroboration and carbenoidation are the same as the time and temperature given in the representative procedure (See Experimental section).

b) Yields are of isolated products after distillation or recrystallization and are based on the amount of the alkene utilized.

c) Literature m.p/b.p. of ketones are given in parentheses along with the corresponding literature reference.

d) Products isolated by distillation.

e) Products isolated by chromatography on silica gel column using chloroform/hexane (1:9) as eluent.

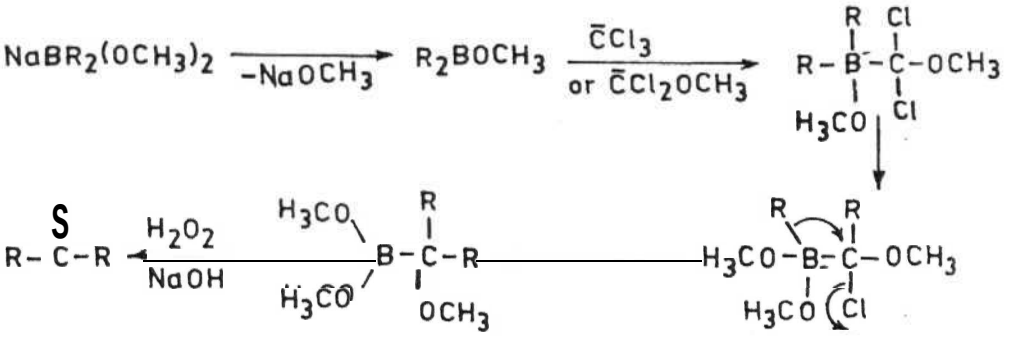
f) Ethylene glycol (10 mmol) was added and the contents were stirred at r.t. for 30 minutes before oxidation.

g) Oxidation with $H_2O_2/NaOOCCH_3$.

to $NaBH_4$ and $R_2\bar{B}(OAc)_2$. The $NaBH_4$ thus produced may not affect the carbenoidation reaction or may get methanolysed by the methanol produced in the reaction as it readily reacts with methanol. The ultimate dialkylboron species present after the reaction with $NaOCH_3$ will be most probably the $NaBR_2(OCH_3)_2$ species since the $NaOCH_3$ can readily displace OAc from boron.

Assuming that the carbenoid reagent ($\bar{C}Cl_3$ or $\bar{C}Cl_2OCH_3$ formed by reaction of $:CCl_2$ generated with $NaOCH_3$) requires trivalent boron species such as R_2BOCH_3, the reaction can be tentatively visualized by postulating disproportionation of the $NaBR_2(OCH_3)_2$ into R_2BOCH_3 (Scheme 6). Disproportionation of $LiBR_2(OC_2H_5)_2$ to $(OC_2H_5)BR_2$ in ether has been postulated previously.[87]

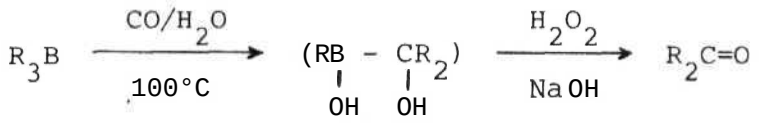
Scheme 6



An alternate possibility is the insertion of the dichlorocarbene, generated in situ, into the $>B-R$ bond of the $NaBR_2(OCH_3)$ or R_2BOCH_3 species followed by further reactions. It should be pointed out that the $:CCl_2$ species generated in the absence of alkoxy bases using $PhHgCCl_2Br$ reagent does react with R_3B through insertion into $>B-R$ bonds.[88]

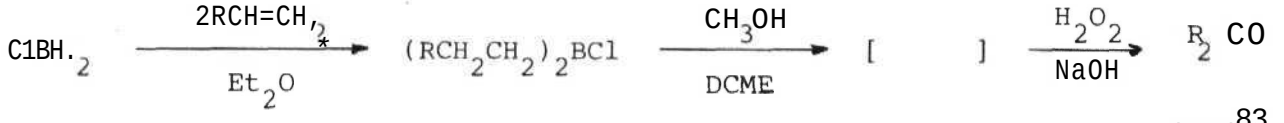
Although the nature of the dialkylboron species and the mechanism

of the carbenoid reaction are not clearly understood, the present method serves as a simple alternate method to the methods available in the literature for the conversion of alkenes into symmetrical ketones via hydroboration (equation 15-19).



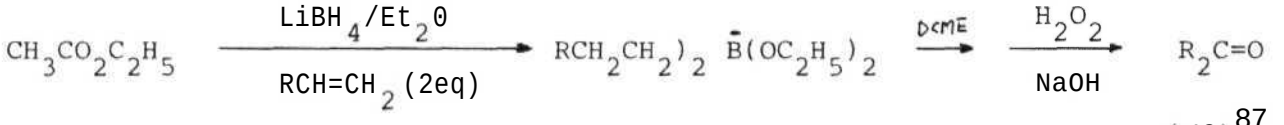
(15)[89]

(16)[90]



(17)[83]

(18)[91]

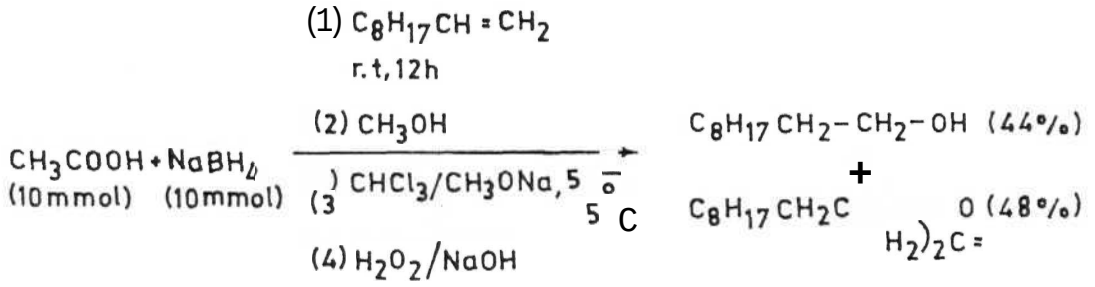


(19)[87]

It is known that the simple boronic esters such as $R\text{-}B(OCH_3)_2$ do not react with carbenoid reagents such as $\bar{C}Cl_3$ or $\bar{C}Cl_2OCH_3$.[80,86] As outlined previously, hydroboration of alkenes with the $CH_3COOH/NaBH_4$ system is relatively slow and one equivalent of 1-decene takes 12 h for hydroboration at r.t. It was of interest to know whether the system gives the monoalkylborane species cleanly. In order to examine this,

we carried out the reaction of 1-decene (1 eq) with the $CH_3COOH/NaBH_4$ system for 12 h. Methanolysis and carbenoidation with $CHCl_3/NaOCH_3$ followed by oxidation with $H_2O_2/NaOH$ gave 48% of di-1-decylketone besides 44% of 1-decanol. This indicates that the reaction utilising one equivalent of 1-decene also gives dialkylborane to some extent. Presumably, there is not much difference in reactivity between the complexed BH_3 and RBH_2 species under the present reaction conditions (Scheme 7).

Scheme 7

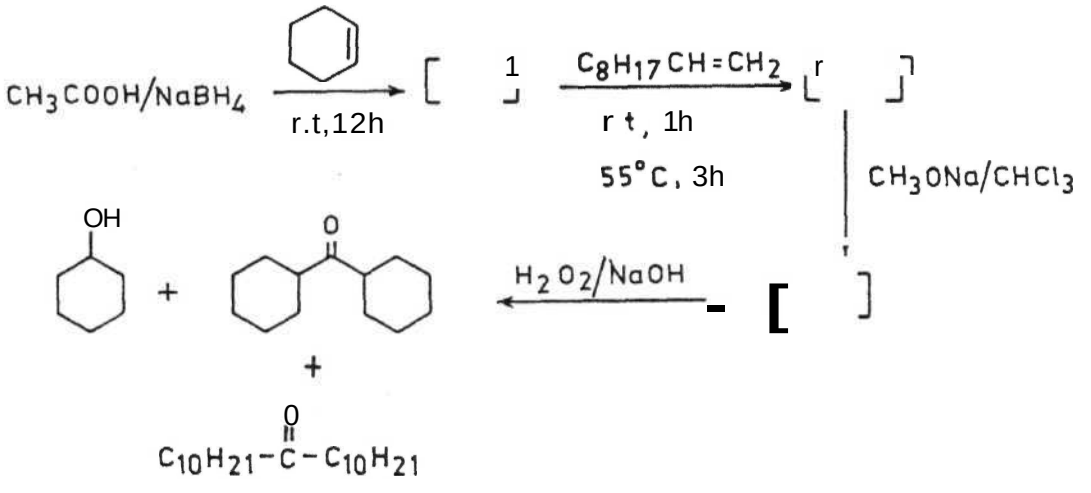


It is known that the hydroboration of cyclohexene (2 eq) with BH_3.THF can be controlled to give dialkylborane.[77,80] It was of interest to examine the reactivity of the species formed in the reaction of cyclohexene (1 eq) with CH_3COOH(1 eq)/$NaBH_4$(1 eq) at room temperature. If this leads to the formation of monocyclohexylboron species, the reagent system can be utilized for further hydroboration of 1-decene to synthesize mixed dialkylborane which can be converted into mixed dialkylketone.

In order to examine this possibility, we have carried out an experiment involving hydroboration of 1-decene (1 eq) by the organoborane species prepared by the reaction of cyclohexene (1 eq) with $CH_3COOH/NaBH_4$ (1:1) in THF. The reaction mixture was stirred further for 1 h at r.t.

and 3 h at 50-55°C. Carbenoidation with $CHCl_3$/NaOMe system followed by oxidation with H_2O_2/NaOH gave dicyclohexylketone and di-1-decylketone and no cyclohexyldecylketone was obtained (Scheme 8).

Scheme 8

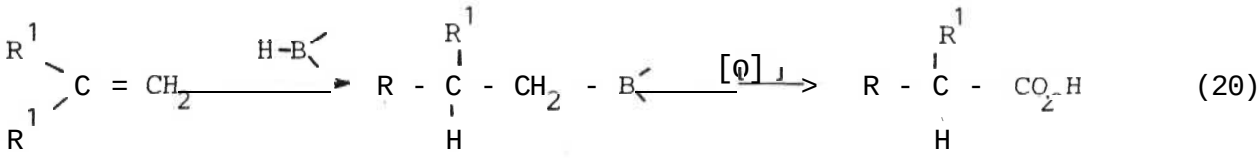


The signals corresponding to cyclohexyldecylketone are not found in the ^{13}C-NMR spectrum of the mixture of ketones. Presumably, the reaction utilizing one equivalent of cyclohexene yields mainly dicyclohexylboron species and the remaining unreacted hydroborating species on addition of 1-decene (1 eq) gives the didecylboron species as indicated in the formation of only these diketones.

Conversion of Terminal Alkenes into carboxylic acids via Hydroboration with $CH_3COOH/NaBH_4$ system

In connection with our studies on the hydroboration of olefins with chiral Lewis base-borane complexes, we required an optically active carboxylic acid. It was thought that the hydroboration of commercially available optically active β-pinene followed by oxidation of the resulting

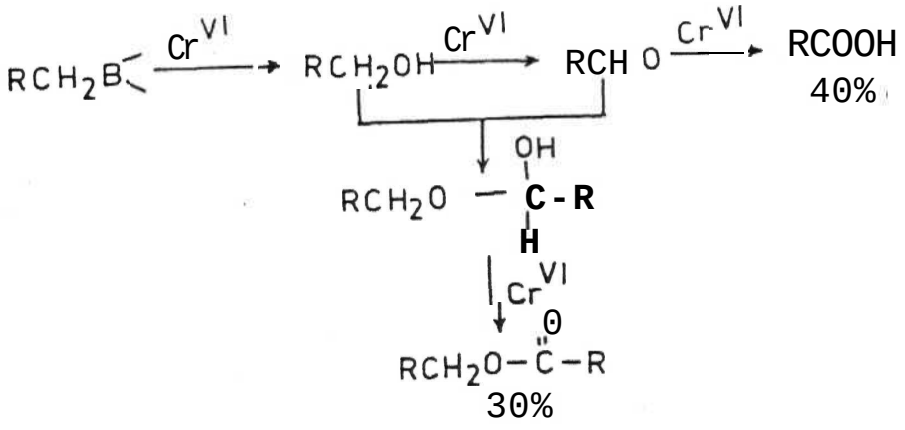
organoborane will provide, in principle the desired transformation in a single pot operation.



(20)

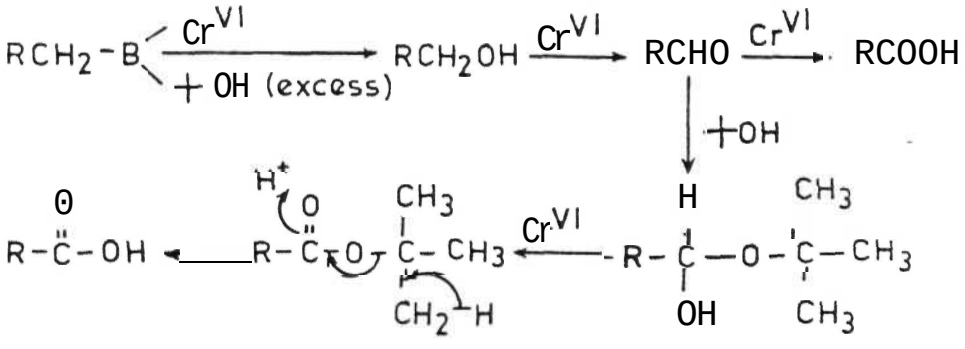
A survey of the literature indicated that several reagents are available for the conversion of alkenes into alcohols,[77,92,93] aldehydes[94] and ketones[95] via hydroboration but no method is available for the direct conversion of alkenes into the corresponding carboxylic acids via hydroboration. It was mentioned that the conversion of primary alkylborane into the corresponding aldehyde was not successful using aqueous chromic acid reagent.[94] Since the aldehydes are readily oxidised in the acid medium by Cr^{VI} reagent, oxidation of the primary alkylboranes with aqueous chromic acid would most probably result in the formation of the corresponding carboxylic acids. We have observed that the hydroboration of 1-decene in THF using the $CH_3COOH/NaBH_4$ system followed by hydrolysis, removal of the THF and oxidation of the residue using the $Na_2Cr_2O_7$/dil H_2SO_4/Et_2O reagent give n-decyl decanoate (30%) besides the desired 1-decanoic acid (40%). The ester is formed via condensation of the starting alcohol with the aldehyde intermediate produced in the course of the oxidation (Scheme 9).

Scheme 9



It was thought that the formation of the ester can be suppressed by carrying out the oxidation in the presence of excess t-butanol which would minimise the formation of the hemiacetal derived from the primary alcohol. Since the t-butyl ester group would readily undergo elimination in acid medium the final product would be the desired carboxylic acid (Scheme 10).

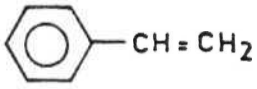
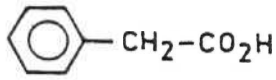
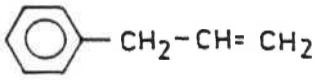
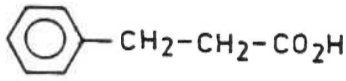
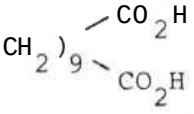
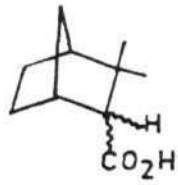
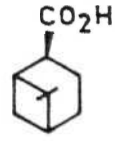
Scheme 10



We have observed that the hydroboration of terminal alkenes using the $CH_3COOH/NaBH_4$ reagent system in THF followed by oxidation with $H_2Cr_2O_7$/ dil. H_2SO_4/acetone **in** the presence of excess t-butanol give the corresponding carboxylic acids in moderate to good yields (Table 7). The acids **can** be **readily isolated since all** the side products are neutral **in nature.**

Table 7

Conversion of alkenes into carboxylic acids.[a]

Substrate	Product	Yield[b]	b.p/m.p.(lit.b.p/m.p)[g] °C or °C/mm Hg
$C_8H_7CH=CH_2$	$C_8H_{17}CH_2CO_2H$	60[c]	170/10 (268/760)[76]
$C_4H_9CH=CH_2$	$C_4H_9CH_2CO_2H$	58[c]	180/20 (205/760)[75]
		55[c]	104-105/1.5 (266/760)[75]
		59[c]	136/2.5 (285/760)[75]
$CH_2=CH-(CH_2)_8-CO_2H$		75[d,e]	101-102 (111-112)[76]
		50[d,f]	65-68"
		30[d]	109-110 (111-112)[85]

a) The reactions were carried out using 20 mmol of $NaBH_4$ 20 mmol of CH_3COOH and 20 mmol of alkenes in THF (70 mL). The oxidations were carried out under the same conditions as given in the representative procedure (see Experimental section). Hydroboration conditions are given in the foot notes (c) and (d).

b) Yields are of the products isolated by distillation or recrystallization.

c) Hydroboration conditions: After the addition of the alkene 2 h at r.t. and 2 h at 50°C.

d) Hydroboration conditions: After the addition of the alkene, 2 h at r.t. and 4 h at 50-55°C.

e) The hydroboration was carried out without using CH_3COOH. The lower melting point may be due to the presence of the corresponding 10-keto-undecanoic acid resulting from the secondary alkylborane. However, the ^{13}C NMR spectrum do not show signals due to any minor product. Accordingly, the keto acid (if any) cannot be present in more than 5%.

f) The product is a 4:1 mixture of the endo and exo acids. The mixture was converted into the exo acid (m.p.114°C) by treatment with p-toluene sulfonic acid following a literature procedure.[79]

g) Literature m.p/b.p. are given in parentheses along with the corresponding literature reference.

In these experiments, we utilized acetone since it has been reported that the oxidation of primary alcohol to carboxylic acids by Cr^{VI} reagents under Jones oxidation conditions[96] gave best results in which acetone was used as solvent. Later, we have found that similar results (yields within ± 5%) can be also obtained without the addition of acetone.

In order to examine the neutral products formed in the reaction, we separated the neutral product mixture by column chromatography in a run with 1-decene. The products were identified as n-decane (7%) formed from the protonolysis of organoborane under acidic conditions,[98] 2-decanone (3%) formed from the oxidation of the secondary alkylborane formed in the hydroboration step and n-decyl decanoate (5%) formed by the reaction between the intermediate aldehyde and the starting decanol. The yields of the acids isolated following the present method are comparable with

the yields of the ketone products (65-85%) realised in the oxidation of the secondary alkylboranes using aqueous chromic acid reagent system.[95] Unfortunately, the myrtanic acid which we required for our mechanistic studies (Chapter 3) was obtained only in 30% yield. This may be due to problem in the oxidation step as we have isolated 80% of the cis-myrtanol in the hydroboration of β-pinene followed by H_2O_2/OH oxidation. The neutral product in this case was found to be a complex mixture (several spots in TLC/silica gel). cis-Myrtanol itself on oxidation under Jones conditions gave only low yields (20%) of cis-myrtanic acid beside a mixture of neutral side products. Presumably, the myrtanyl substrate is too labile under the present oxidation conditions.

SUMMARY

The reagent generated by the reaction of CH_3COOH (1 eq) and $NaBH_4$ (1 eq) was utilized for hydroboration of olefins. The utility of the reagent system for selective hydroboration of olefins in the presence of other reducible functional groups was explored. It was demonstrated that the selective hydroboration of olefinic moiety in 11-undecenoic acid can be readily achieved by the addition of $NaBH_4$ to the acid in THF. It has been observed that hydroboration of olefins (2 eq) with $CH_3COOH/NaBH_4$ system followed by carbenoidation using very simple bench top chemicals such as $CHCl_3/NaOCH_3$ give symmetrical dialkyl ketones in good yields. Conditions were standardised for the conversion of terminal olefins into carboxylic acid via hydroboration with $CH_3COOH/NaBH_4$ system followed by oxidation with chromic acid in the presence of t-butanol.

EXPERIMENTAL

General Information

Melting points reported in this thesis are uncorrected and were determined using a Buchi 510 capillary point apparatus. Infrared spectra were recorded on Perkin-Elmer Model 1310 or 297 Spectrophotometers. All the spectra were calibrated against polystyrene absorption at 1601 cm^{-1}. Protonmagnetic spectra (100 MHz) and Carbon-13-magnetic resonance spectra (25.0 MHz) were run on JEOL-FX-100 Spectrometer. Spectra for all the samples were measured in chloroform-d solution with tetramethyl-silane (8 = o ppm) as internal standard unless otherwise stated.

Optical rotations were measured with an Autopol II-automatic polarimeter at 20°C. Elemental analysis were performed on a Perkin Elmer Elemental analyser Model 240C. Catalytic hydrogenations were carried out on Parr hydrogenation apparatus in 250 mL pressure bottle. Gas chro-matography analysis was carried out on a Packard Model-42 instrument equipped with a flame ionization detector on an SE-30 or Carbowax column using nitrogen as carrier gas. Analytical thin layer chromatographic tests were carried out on glass plates (3x10 cm) coated with (250 mμ) **Acme's** silica gel G or GF 254 containing 13% calcium Sulfate as binder. The spots **were visualized by short exposure** to Iodine vapour or UV light. **Column chromatography was carried o.ut using Acme's silica** gel **(100-200 mesh).**

All the glasswares were predried at 140°C for at least 4 h, assembled hot and cooled under a stream of prepurified dry nitrogen. Unless otherwise mentioned all the operations/transformations of organoborane reagents/ reactions were carried out using standard syringe, septum techniques as recommended for handling organoboranes.[77]

In all the hydroboration experiments, unless-otherwise mentioned, a 250 mL RB flask with a side arm and a side septum, a magnetic stirring bar, a condensor and a connecting tube attached to a mercury bubbler were used. All dry solvents were distilled from appropriate drying agents just before use. Hexane refers to the fraction boiling between 60-80°C. As a routine, all organic extracts were washed with saturated sodium chloride solution (brine) and dried over anhydrous $MgSO_4$ and concentrated on a Buchi-EL rotary evaporator (at reduced pressure). All yields reported are isolated yields of material judged homogeneous by TLC and IR, NMR spectroscopy.

Benzene, toluene, THF and diglyme were distilled over benzophenone-sodium. Sodiumborohydride (97%) 100 g samples supplied by LOBA-Chemie India and Fluka Switzerland were utilised and were kept under N_2 in a dessicator after opening of the bottles. $Hg(OAc)_2$ used was of Reagent Grade. Acetic acid was distilled after adding calculated amount of acetic-anhydride to remove water traces. A standard solution of acetic acid was made in dry THF in a standard flask (50 mL) and kept under nitrogen atmosphere for utilization. The olefins **utilised were commercial samples supplied by Fluka, Switzerland except** 1-phenyl-1-cyclopentene **which was prepared following a literature procedure.**[99] 1-Methyl-1-cyclohexene

utilised in most of the experiments was a commercial sample. Whenever necessary it was also prepared following a literature procedure.[103]

Hydroboration-oxidation of olefins with $Hg(OAc)/NaBH_4$ system

The procedure for the hydroboration-oxidation of 1-decene is representative. To a stirred slurry of $NaBH_4$ (0.8 g, 20 mmol) in dry THF (60 mL) was added $Hg(OAc)_2$ (3.19 g, 10 mmol) at 0°C, over a period of 1 h from a solid addition flask.[77] It was further stirred for 1 h at room temperature and 1-decene (2.8 g, 20 mmol) was added. The contents were stirred for 12 h at r.t. and the excess hydride was carefully destroyed with water (2 mL) while cooling the flask externally with cold water. The oxidation was carried out by the addition of 3N NaOH (15 mL) followed by dropwise addition of H_2O_2 (25 mL, 16%). The reaction mixture was stirred further at r.t. for 2 h and at 35-40°C for 1 h. It was cooled to room temperature. The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic layer was washed with brine, dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Distillation of the residue under reduced pressure yielded 1-decanol (2.2 g, 70%, b.p. 107°C/7 mm Hg. lit.[75] b.p. 231°C/760 mm Hg). The IR spectrum was superimposable with reported spectrum.[100]

^{13}C NMR (25.0 MHz, $CDCl_3$) : 6 ppm 62.4 (C-OH), 32.8, 31.8, 29.6, 29.4, 29.2, 25.7, 22.6, 13.9.

The above procedure utilizing the $Hg(OAc)_2/NaBH_4$ system for hydroboration was followed for the conversion of **several other** olefins into

the corresponding alcohols and the results are presented below and also in Table 2.

Cyclohexene ——► cyclohexanol

Yield: 1.6 g, 80%.

B.p: 60°C/20 mm, lit b.p. 160°C/760 mm"[75]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 70.2, 35.5, 25.7, 243.3.

Norbornene ——► Exo-norborneol

Yield: 1.77 g, 79%

M.p: 125°C, lit. mp. 126°C[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 74.2, 43.7, 41.7, 35.8, 34.2, 28.1, 24.3

Styrene ——► 2-phenylethanol

Yield: 2 g, 22%

B.p: 98°C/20 mm. lit. b.p. 219°C/760 mm.[75]

^{1}H NMR (100 MH_2, $CDCl_3$) : 6 ppm 2.72(t,2H), 3.08(S,1H), 3.68(t,3H), 7.16 (m,5H).

α-Pinene ——► Isopinocampheol

Yield: 2.16 g, 70%B.p: 98°C/10 mm . lit. b.p. 217°C/760 mm[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 71.5, 47.9, 47.7, 41.8, 39.0, 38.2, 34.3,27.7,23.7,20.8.

Hydroboration-oxidation of olefins (20 mmol) with $CH_3COOH/NaBH_4$ (20 mmol each) system

To a slurry of $NaBH_4$ (0.8 g, 20 mmol) in dry THF (60 mL) at 0°C, under nitrogen atmosphere, acetic acid (20 mmol) in THF (10 mL) was

added during 15 minutes. The contents of the flask wore stirred for further 1 h at r.t. until the evolution of the gases (H_2) had ceased. 1-Decene (2.8 g, 20 mmol) was added and the contents were stirred for 12 h at r.t. The excess hydride was carefully destroyed with H_2O (2 mL) and the organoborane species was oxidised with H_2O_2 (25 mL, 16%) and 3N NaOH (15 mL), following the procedure recommended for oxidation of organoboranes.[77] The organic layer was separated and the aqueous layer was extracted with ether (3x30 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and the residue remained after evoporation of the solvent on distillation under reduced pressure afforded 1-decanol, 2.4 g, 76%, bp.108°C/7 mm Hg. IR and ^{13}C NMR spectra of the 1-decanol were identical with that of the alcohol obtained using the $Hg(OAc)_2/NaBH_4$ system for hydroboration.

Several other olefins were also converted into the corresponding alcohols through hydroboration with the $CH_3COOH/NaBH_4$ system. The results are summarized below and also in Table 3.

1-hexene ——► 1-hexanol

Yield: 1.63 g, 80%

B.p: 155°C/760 mm, lit bp. 157°/760 mm[75]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 62.4, 32.6, 31.6, 25.7, 22.7, 14.0.

Cyclohexene ——► cyclohexanol

Yield: 1.7 g, 85%

B.p: 60°C/20 mm, lit bp. 160°C/760 mm[75]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 70.1, 35.5, 25.7, 24.3

Norbornene ——→ exonorborneol

Yield: 1.9 g, 84%

M.p: 125°C, lit. mp. 126°C[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 74.2, 43.7, 41.7, 35.8, 34.2, 28.1, 24.3.

α-Pinene ——→ isopinocampheol

Yield: 2.2 g, 72%

B.p: 98°C/10 mm, lit bp. 217/760 mm[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 71.5, 45.9, 47.7, 41.8, 39.0, 38.2, 34.3, 27.7, 23.7, 20.8.

3-Pinene ——→ cis-myrtanol

Yield: 2.46 g, 80%

B.p: 88-90°C/2 mm, lit bp. 65°C/0.2 mm[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 66.1, 43.7, 42.3, 41.1, 38.1, 32.8, 27.7, 25.8, 22.9, 18.5.

Methyl-10-undecenoate ——→ methyl 11-hydroxyundecanoate

Yield: 3.15 g, 73%

B.p: 122°C/0.5 mm, lit. bp. 156°C/4.5 mm[78]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 173.8, 62.1, 50.8i, 33.6, 32.3, 29.1, 28.8, 25.5, 24.5.

1-Phenyl-cyclopentene ——→ 2-phenylcyclopentanol

Yield: 2.5 g, 85%

B.p: 75°C/0.5 mm, lit bp. 129°C/6 mm[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 142.5, 128.3, 127.3, 126.1, 80.1, 54.1, 33.9.

1-Methylcyclohexene ⟶ trans-2-methyl cyclohexanol

yield: 1.89 g, 83%

B.p: 78°C/20 mm, lit bp. 166°C/760 mm

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 76.2, 40.2, 35.1, 33.7, 25.7, 25.2, 18.6.

Camphene ⟶ Campheol

Yield: 2.59 g, 84%

B.p: 95°C/10 mm, lit. bp. 213°C/760 mm[79]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 61.1, 57.2, 49.2, 39.8, 37.2, 36.9, 32.7, 24.7, 20.6, 20.4.

Examination of the $NaBH_4/CH_3COOH$ system to release 'BH_3' moiety: Trapping of the 'BH_3' as Ph_3PBH_3

To freshly prepared acetoxyborohydride species from $NaBH_4$ (10 mmol) and CH_3COOH (10 mmol) in THF (50 mL) was added triphenylphosphine (2.62 g, 10 mmol) and the mixture was stirred for 12 h at r.t. Water (10 mL) was added and the mixture was extracted with ether (2x20 mL). The combined organic layer was washed with $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and the residue obtained after removing the solvent was subjected to column chromatography (Hexane/chloroform as eluent) to afford pure triphenylphosphine-borane 2.59 g, 94%, mp. 185°C, lit. mp. 188°C.[102]

IR (KBr) V_{max}: 3350 (broad), 1490, 1450, 1120, 1060, 740, 700 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 133.5, 133.2, 131.5, 129.1, 128.7.

Selective hydroboration of 1-decene with $CH_3COOH/NaBH_4$ system in the presence of other functional groups

The procedure for the hydroboration oxidation of 1-decene in the presence of cyclohexanone is representative.

To a suspension of acetoxyborohydride prepared using 10 mmol of $NaBH_4$ and 10 mmol of CH_3COOH in THF 10 mmol each of 1-decene (1.40 g) and cyclohexanone (0.98 g) were added and stirred at r.t. for 12 h. The flask was cooled and 2N HCl (5 mL) was carefully added and stirred for 1 h at r.t. It was neutralized with 3N NaOH and oxidised by $H_2O_2/NaOH$. The organic layer was separated and aqueous layer was extracted with ether (3x30 mL). The combined organic layer was washed with brine, dried ($MgSO_4$), evaporated on a rotary evaporator and the residue was distilled. The fraction distilled at 60°C/20 mmHg was identified as cyclohexanol (0.95 g, 95%) and the fraction distilled at 107°C/7 mmHg was identified as 1-decanol (1.26 g, 80%) by comparison with IR spectra and GC r.f. values of the authentic samples.

Similar experiments were carried out by taking 1-decene along with benzamide, ethyl benzoate and benzonitrile and the results are summarised in Table 4.

Selective hydroboration of olefinic moiety in the presence of carboxylic acid group: Hydroboration oxidation of 10-undecenoic acid with $NaBH_4$

To a stirred suspension of $NaBH_4$ (0.4 g, 10 mmol) in dry THF (60 mL) at 0°C, 10-undecenoic acid (1.843 g, 10 mmol) in THF (10 mL)

was added during 30 minutes under nitrogen atmosphere. It was stirred at r.t. for 12 h, cooled and 2N HCl (5 mL) was carefully added to destroy the excess hydride. After the evolution of the gases had ceased, the reaction mixture was neutralised with 3N NaOH using pheno]phthalein as indicator. The organoborane was oxidised with H_2O_2/NaOH. The contents were acidified with 2N HCl and extracted with ether (3x40 ml). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and the solvent was removed. The crude product was recrystallized from acetonitrile to yield 11-hydroxyundecanoic acid, 1.7 g, 85%, mp.65°C, lit. mp.66-67°C.[101]

IR (nujol) V_{max}: 3500-3050, 1708, 1180, 1050, 910 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.25 (s,1H), 5.56 (s,1H), 3.63 (t,2H), 2.33 (q,2H), 1.29 (m,16H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 160.0 (-COOH), 63.2 ($-CH_2OH$), 32.9 (CH_2-CH_2OH), 29.5, 29.3, 25.9, 24.9.

Examination of the nature of the organoborane species present in the reaction of $CH_3COOH/NaBH_4$ (1:1 equivalent) 1-decene (10 mmol) at room temperature utilising the carbenoidation reaction with $NaOCH_3/CHCl_3$

To the acetoxyborohydride species (10 mmol) prepared from $NaBH_4$ (10 mmol) and CH_3COOH (10 mmol) in dry THF (60 mL) 1-decene (1.4 g, 10 mmol) was added and the mixture was stirred at r.t. for 12 h. The excess hydride was destroyed carefully with methanol (1 mL). To the reaction mixture chloroform (10 mL) was added NaOMe (2.16 g, 40 mol)

was added from a solid addition flask during 1 h and the contents were further stirred at 55°C for 2 h. It was brought to r.t. and water (2 mL) was added. The organoborane was oxidised using H_2O_2/NaOH. The contents were neutralized with 2N HC1 (phcnolphthalein indicator) and extracted with ether (3x30 mL). The ether layer was washed with saturated NaCl solution, dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed on a silica gel column (Hexane-chloroform as eluent) to yield di-1-decylketone (0.73 g, 48%, mp.64°C, lit. mp. 64°C[75]) and 1-decanol (0.63 g, **44%)**.

Synthesis of symmetrical dialkylketones through hydroboration-carbenoidation of alkenes

The procedure for the conversion of 1-decene into di-1-decyl ketone is representative. To the acetoxyborohydride species prepared utilising $NaBH_4$ (10 mmol) and CH_3COOH (10 mmol) in THF (60 mL) 1-decene (2.8 g, 20 mmol) was added and the reaction mixture was stirred at r.t. for 1 h and at 55°C for 2.5 h. The contents were brought to r.t. under nitrogen and chloroform (125 mmol) was injected followed by addition of NaOMe (2.16 g, 40 mmol) from a solid addition flask during 1 h. The mixture was further stirred at 55°C for 2.5 h and brought to r.t. and water (2 mL) was added. The reaction mixture was oxidised using H_2O_2/NaOH. The contents were neutralized with 3N HC1 using phenolphthalein as indicator and extracted with ether (3x30 mL). The combined organic layer was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography using hexane-chloroform as eluent (4:1) to yield di-1-decyl ketone,

2.28 g, 80%, mp.64°C, lit. mp.62°C,[75] and 1-decanol, 0.240 g, 8% based on the starting olefin.

Spectral data for di-1-decylketone:

IR (KBr) ν_{max} : 1710 cm^{-1} (>C=O).

^1H NMR (100 MHz, $CDCl_3$): δ ppm 3.4 (t,4H), 1.75 (m,8H), 1.5 (m,10H), 1.25 (m,4H), 0.9 (m,6H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 211. (C=O), 42.9 (CH_2-CO), 32.1, 29.4, 24.1, 22.8, 14.1 (-CH_3).

The above procedure was followed for the conversion of several other olefins into the corresponding dialky ketones and the results are summarised below and also in Table 6.

1-hexene ⟶ di-1-hexylketone.

Yield: 1.4 g, 70%

B.p: 125°C/10 mm, lit. bp. 216°C/780 mm[75]

^{13}C NMR ($CDCl_3$): δ ppm 211.1, 42.9, 31.6, 28.9, 23.9, 22.4, 13.8.

Cyclohexene ⟶ di-cyclohexylketone

Yield: 1.29 g, 67%

B.p: 64°C/0.4 mm, lit. bp. 96°C/1.2 mm[83]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 215.5, 49.1, 28.6, 25.9, 25.7.

Norbornene ⟶ bis-exonorbornyl ketone

Yield: 1.28 g, 59%

M.p: 53°C, lit. mp. 53-54°C.[83]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 213.4, 52.8, 39.9, 36.0, 33.3, 29.7, 28.7.

$CH_2=CH-(CH_2)_8COOMe \longrightarrow MeOOC(CH_2)_2\overset{O}{\overset{\|}{C}}-(CH_2)_2COOMe$

Yield: 3.3 g, 78%

M.p: 72°C

^{13}C NMR:6 211.5, 174.5, 51.3, 42.8, 34.1, 29.4, 29.2, 25.0, 24.9, 24.0 (spectrum no.1).

Mass, m/e, %: M^+H 427 (100%), $(M-OCH_3)^+$ or $(M+H-CH_3OH)$ 395 (40%).

Analysis calculated for $C_{25}H_{46}O_5$: C,70.45, H,10.89;

Found: C,70.3; H,10.9.

Examination of Trialkylborane formation: **Hydroboration-Oxidation** of **1-decene** (30 **mmol**) with **$CH_3COOH/NaBH_4$** (10 **mmol** each)

To acetoxyborohydride species prepared using $NaBH_4$ (10 mmol) and CH_3COOH (10 mmol) in THF (60 mL) 1-decene (4.2 g, 30 mmol) was added at r.t. under nitrogen atmosphere. The mixture was stirred at 55°C for 3 h, brought to r.t. and oxidised with H_2O_2/NaOH. The organic layer was separated and the aqueous layer was extracted with ether (2x25 mL). The combined organic layer was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed. Distillation of the residue afforded 1-decene (1.3 g, 9.3 mmol, bp. 54.3°C/10 mm) and 1-decanol (2.7 g, 17 mmol, bp.108°C/7 mmHg).

Examination of the question whether a portion of the hydride is utilised for reduction of carboxylic acid at higher temperature (55°C): Hydroboration oxidation of cyclohexene (20 mmol) with decanoic acid-$NaBH_4$ system at 55°C

To a stirred suspension of $NaBH_4$ (0.4 g, 10 mol) in dry THF (60 mL) at 0°C, 1-decanoic acid (1.72 g, 10 mmol) in dry THF (10 mL) was added during 20 minutes under nitrogen atmosphere. The reaction mixture was further stirred until the evolution of the gases had ceased. Cyclohexene (1.6 g, 20 m mol) was added and the contents were stirred for 1 h at r.t. and 2.5 h at 55°C. It was brought to room temperature under nitrogen and oxidised with H_2O_2/NaOH. The organic layer was separated and the aqueous layer was extracted with ether (2x30 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and the solvent was evaporated. GC (SE-30 column) analysis of the residue indicated the presence of 1-decanol. The residue was distilled under reduced pressure to afford cyclohexanol (1.7 g, 85%, bp. 60°C/20 mmHg and 1-decanol (0.16 g, 10%, bp.107°C/7 mmHg). Yield based on the starting 1-decanoic acid).

The aqueous layer was acidified with 3N HC1 and extracted with ether (3x50 mL). The combined organic extract was washed with brine, dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was distilled to recover back 1-decanoic acid (1.52 g, 87%, bp . 170°C/10 mmHg).

Examination of sequential hydroborating ability of the CH_3COOH-$NaBH_4$ system: Attempted unsymmetrical-ketone synthesis

To acetoxyborohydride (10 mmol) reagent in dry THF (50 mL) cyclohexene (0.8 g, 10 mmol) was added and the mixture was stirred at r.t. for 12 h. 1-Decene (1.4 g, 10 mmol) was added and the contents were stirred at r.t. for 1 h and at 50°C 2.5 h. The mixture was cooled to 30°C and carbenoidation reaction was carried with $CHCl_3$ (125 mmol) and CH_3ONa (40 mmol). The contents were cooled to 0°C and oxidised with H_2O_2/NaOH. The crude residue was chromatographed on a silica gel column using hexane/chloroform (4:1) as eluent. The ketones (1.3 g) had very close r.f. values and were collected together besides cyclohexanol (0.4 g) and 1-decene (0.3 g). The ^{13}C NMR spectral signals of the ketone mixture correspond to a mixture of dicyclohexylketone (-C=O 216.0 ppm, -CH-CO 49.2 pm) and di-1-decylketone (-C=O 211 ppm, -CH_2-CO 42.9 ppm).

Chromic acid oxidation of organoborane obtained from the hydroboration of 1-decene with $CH_3COOH/NaBH_4$ system

To the freshly prepared $CH_3COOH/NaBH_4$ reagent system from $NaBH_4$ (20 mmol) and CH_3COOH (20 mmol) in dry THF, 1-decene (20 mmol, 2.8 g) was added and the mixture was stirred at r.t. for 2 h and at 55°C for another 2 h. It was cooled and water (2 mL) was carefully added. THF was distilled out under nitrogen atmosphere. The organoborane residue was cooled to 0°C and ether (75 mL) was added. The oxidation was carried out by adding pre-cooled chromic acid solution (prepared using CrO_3 (5.2 g), water (36 mL), conc.H_2SO_4 (10 mL) during 15 minutes. The reaction

mixture was stirred at r.t. for 10 h. The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic layer was treated with 2N NaOH (3x20 mL). The solvent was removed from the dried ($MgSO_4$) organic layer and the residue was chromatographed on a silica gel column to yield 2-decanone (0.1, 4%), n-decyldecanoate (0.99, 30%).

The combined aqueous extract was acidified with conc. HCl (phenolphthalein indicator), extracted with ether (3x30 mL), dried ($MgSO_4$) and distilled under reduced pressure to yield 1-decanoic acid, 1.7 g, 40%, bp.170°C/10 mmHg, lit. bp.268°C/760 mmHg.[75]

The IR and NMR spectra of samples obtained in this experiment were identical with the spectra of the authentic samples.

Chromic acid oxidation of organoboranes obtained from Hydroboration of terminal alkenes by the $CH_3COOH/NaBH_4$ system in the presence of tertiary butanol: Conversion of terminal alkenes into carboxylic acids

The procedure for the conversion of 1-decene into 1-decanoic acid is representative. To a suspension of acyloxyborohydride species, prepared from CH_3COOH (20 mmol) and $NaBH_4$ (20 mmol), 1-decene (2.8 g, 20 mmol) was added and the mixture was stirred at r.t. for 1 h and at 55°C for 2.5 h. It was brought to r.t. and the excess hydride was destroyed carefully with H_2O (2 mL). To this acetone (60 mL) and t-butanol (10 mL) were added. Precooled (0 to 5°C) chromic acid solution [prepared using CrO_3 (6 g), water (10 mL) and Conc. H_2SO_4 (10 mL)] was added at

0°C during 15 minutes. The reaction mixture was stirred at r.t. for 10 h. The organic layer was separated and the aqueous layer was extracted with ether (2x50 mL) and the solvent was removed from the combined organic extracts. The residue was dissolved in ether (50 mL) and extracted with 2N NaOH (3x20 mL). The solvent was removed from the dried ($MgSO_4$) organic layer and the residue was chromatographed to isolate the neutral components, decane (0.2 g, 7%), 2-decanone (0.12 g, 4%) and n-decyl decanoate (5%).

The combined alkaline extract was acidified with conc. HC1 (phenolphthalein indicator) and extracted with ether (3x25 mL). The combined ether extract was dried ($MgSO_4$) and the solvent was evaporated. The residue was distilled under reduced pressure to afford 1-decanoic acid, 2.06 g, 60%, bp.170°C/10 mm, lit. bp.268°/760 mm.[75]

Spectral data for 1-decanoic acid:

IR (neat) V_{max}: 3500, 2900 (-OH), 1700 (-C=0), 1410, 1280, 920 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$) : 6 ppm 180.0 (COOH), 33.5 ($-CH_2$-CO), 31.3, 28.7, 28.5, 24.0, 23.1, 13.6.

IR spectra for decane and 2-decanone show 1:1 correspondence with the reported spectra.[100]

^{13}C Spectrum of 2-decanone: 6 ppm 209.1, 43.8, 31.9, 29.6, 29.4, 29.2, 23.9, 22.7, 14.1.

Decyldecanoate:

IR (neat) ν_{max} 1735 (C=O), 1450, 1160 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ_{ppm} 0.8 (t,2H), 1.26 (m,16H), 2.26 (t,2H), 2.9 (t,2H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 173.8 (C=O), 64.4 ($C-O-CH_2$), 34.5 (CH_2-C), 32.0, 29.7, 29.4, 28.8, 26.1, 25.1, 22.8, 14.2.

The above procedure was followed for the conversion of several other terminal alkenes into the corresponding carboxylic acids and the results are summarised below and also in Table 7.

1-hexene ⟶ 1-hexanoic acid

Yield: 1.35 g, 58%

B.p: 180°C/20 mm. lit. bp. 205/760 mm.[75]

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 180.4, 34.2, 31.4, 24.5, 24.4, 13.8.

Styrene ⟶ phenylacetic acid

Yield: 1.5 g, 55%

B.p: 104°C/1.5 mm. lit. bp. 266°C/760 mm.[75]

^1H NMR (100 MHz, $CDCl_3$): 6 ppm 9.79 (S,1H), 7.28 (m,5H), 3.63 (s,2H).

Allylbenzene ⟶ 3-phenylpropionic acid

Yield: 1.89 g, 59%

B.p: 136°C/2.5 mm, lit. bp. 285°C/760 mm.[77]

^1H NMR (100 MHz, $CDCl_3$): δ ppm 11.87 (S,1H), 7.4 (m,5H), 2.81 (t,2H), 2.65 (t,2H).

10-undecenoic acid ⟶ 1,11-undecane dioic acid.

Yield: 3.3 g, 75%

M.p: 101°C, lit. mp. 111-112°C.[76]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 186.0, 34.2, 29.2, 29.1, 24.8.

Camphene ⟶ Camphanic acid/isocamphanic acid mixture.

Yield: 1.65 g, 50%

M.p: 65-68°C.

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 180.8, 52.2, 49.1, 40.9, 38.6, 37.6, 31.9, 24.6, 22.8, 21.5, in addition signals corresponding to 12% of isocamphanic acid were also present.

Isocamphanic acid:

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 180.8, 59.0, 48.1, 42.6, 40.9, 37.6, 28.6, 27.7, 25.6, 24.1.

β-pinene ⟶ cis-Myrtanic acid.

Yield: 1.01 g, 30%

M.p: 109-110°C, lit. mp.111°C.[85]

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 183.6, 43.9, 43.0, 40.5, 38.9, 29.1, 27.0, 24.7, 21.7, 15.2.

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CHAPTER 2

Studies on the synthesis and applications of borane and iodoborane N,N-dialkylaniline complexes

INTRODUCTION

Organoboranes are one of the most versatile organometallic reagents which are useful in carbon-carbon bond formation reaction and also in generation of new functional groups.[1-4] Diborane is the starting raw material for most of the organoborane reagents. Initially researchers used to avoid utilising diborane as it was thought that it is a dangerous reagent to handle, even it meant adding more steps to the synthesis or reducing overall yields.[5] But over the years a growing number of borane reagents which can be easily handled were developed and used in organic synthesis. Still there exists a need for development of new reagents and improvement of the existing organoborane reagents.

Diborane itself is difficult to handle and relatively inert towards olefins.[6,7] So it is normally utilized in the form of its complexes (eg. $BH_3.THF$, $BH_3.SMe_2$ and $BH_3.NR_3$).[1,2] Several BH_3-Lewis base complexes are commercially available. Although diborane is commercially available in cylinders, it is still convenient to generate it for utilization in bench-top preparations. In connection with our work on the studies on the mechanism of the hydroboration reaction (Chapter 3), we were seeking a convenient method for the generation of diborane which can be utilized in the synthesis of amine borane complexes. A brief survey of various methods for the synthesis of diborane will be helpful for the discussion.

In 1912, Stock prepared the diborane gas from magnesium borides.[8]

In 1912, Stock prepared the diborane gas from magnesium borides. Later, Schlessinger and Burg prepared it from $_9H^2$ and $BC1^3$ using electric discharge method in a high vacuum apparatus. Schlessinger and Brown prepared diborane utilising lithium hydride in a vacuum line (eq.1).

$$6LiH + 8BF_3.OEt_2 \xrightarrow{Et_2O} B_2H_6 + 6LiBF_4 \quad (1)$$

Reaction of MBH_4 with BCl_3 or BF_3 also yields diborane (eq.2,3).

$$3NaBH_4 + BCl_3 \xrightarrow{diglyme} 2B_2H_6 + 3NaCl \quad (2)$$

$$3NaBH_4 + 4BF_3OEt_2 \xrightarrow{diglyme} 3NaBF_4 + 2B_2H_6 \quad (3)$$

Reaction of MBH_4 with mineral acids also yields diborane (eq.4-6).[14-17]

$$2NaBH_4 + H_2SO_4 \xrightarrow{diglyme} Na_2SO_4 + 2H_2 + B_2H_6 \quad (4)$$

$$2KBH_4 + 2H_3PO_4 \longrightarrow 2KH_2PO_4 + 2H_2 + B_2H_6 \quad (5)$$

$$2NaBH_4 + Me_2SO_4 \longrightarrow Na_2SO_4 + 2CH_4 + B_2H_6 \quad (6)$$

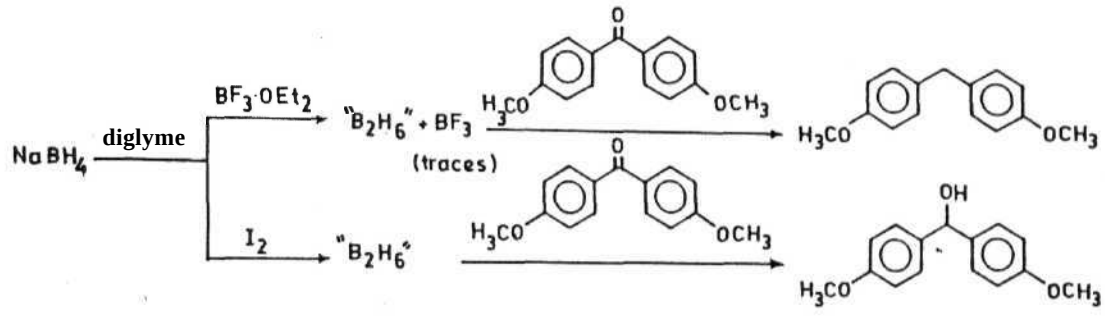
It has been reported in 1965 that the reaction of Hg_2Cl_2 with $NaBH_4$ and I_2 with $NaBH_4$ give diborane in 88 to 90% yield (eq.7,8).

$$2NaBH_4 + Hg_2Cl_2 \xrightarrow[r.t.]{diglyme} 2Hg + 2NaCl + H_2 + B_2H_6 \quad (7)$$

$$2NaBH_4 + I_2 \xrightarrow[r.t.]{diglyme} 2NaI + H_2 + B_2H_6 \quad (8)$$

The authors utilized a vacuum line technique and isolated the diborane using a series of liquid nitrogen traps.[18] It was reported that the diborane generated in this way is free of any detectable impurities. Diborane generated utilizing $BF_3.OEt_2/NaBH_4$ method usually contains small amounts of Et_2O and BF_3.[2] It has been demonstrated that the reactivity of diborane generated utilizing $NaBH_4/BF_3.OEt_2$ and $I_2/NaBH_4$ are different (Scheme 1).[19] The undesirable side reaction utilizing B_2H_6 generated from the $BF_3.OEt_2$ method can be prevented by performing the reaction with the B_2H_6 generated utilizing the $I_2/NaBH_4$ system.

Scheme 1



Clearly, the side reaction due to the presence of 'BF_3' is prevented using the B_2H_6 generated utilizing the $I_2/NaBH_4$ system. In addition, since it is more convenient to handle iodine than BF_3OEt_2, the $I_2/NaBH_4$ system should be more attractive for the generation of diborane for utilization in organic synthesis. The system has not been utilized for organic synthesis but for the application illustrated above (Scheme 1).[19] This may have been, as suggested by Lane in a review article,[20] due to the non-availability of a detailed procedure for diborane generation utilizing the $I_2/NaBH_4$ system. It was of interest to us to examine whether the diborane can be generated in this way for utilization in the preparation of amine-borane complexes in hydrocabron solvents required for our mechanistic studies (Chapter 3).

Diborane reacts with amines to give the corresponding 1:1 complexes[3,21,22] which are relatively more stable than the ether and thioether complexes (eq.9).

$$B_2H_6 + 2NR_3 \longrightarrow 2R_3N{:}BH_3 \qquad (9)$$

Amine borane complexes have been extensively utilized as reducing agents.[23] The reducing ability depends on the nature of the complexed amine. Less basic and more hindered amines formed more reactive complexes.[23]

In the case of aliphatic amine-boranes, the reducing ability decreases with alkyl substitution in the order $H_3N.BH_3 > RH_2N.BH_3 > R_2HN.BH_3 > R_3N.BH_3$. Among aryl and heteroaryl amines, the reducing ability depends on the base strength of the amine i.e. the lower the pK_a value of the amine the stronger the reducing agent.[23] The reduction of functional groups Py various amine-borane complexes has been reviewed.[23] Several efficient synthetic methods involving reduction of carbonyls,[24,25] imines,[26,27] iminium salts,[28,29] enamines,[26,27] indoles,[30-34] oximes,[35] tosylhydrazones[36] and carbon-carbon double bonds[37,38] by amine boranes were developed.[23]

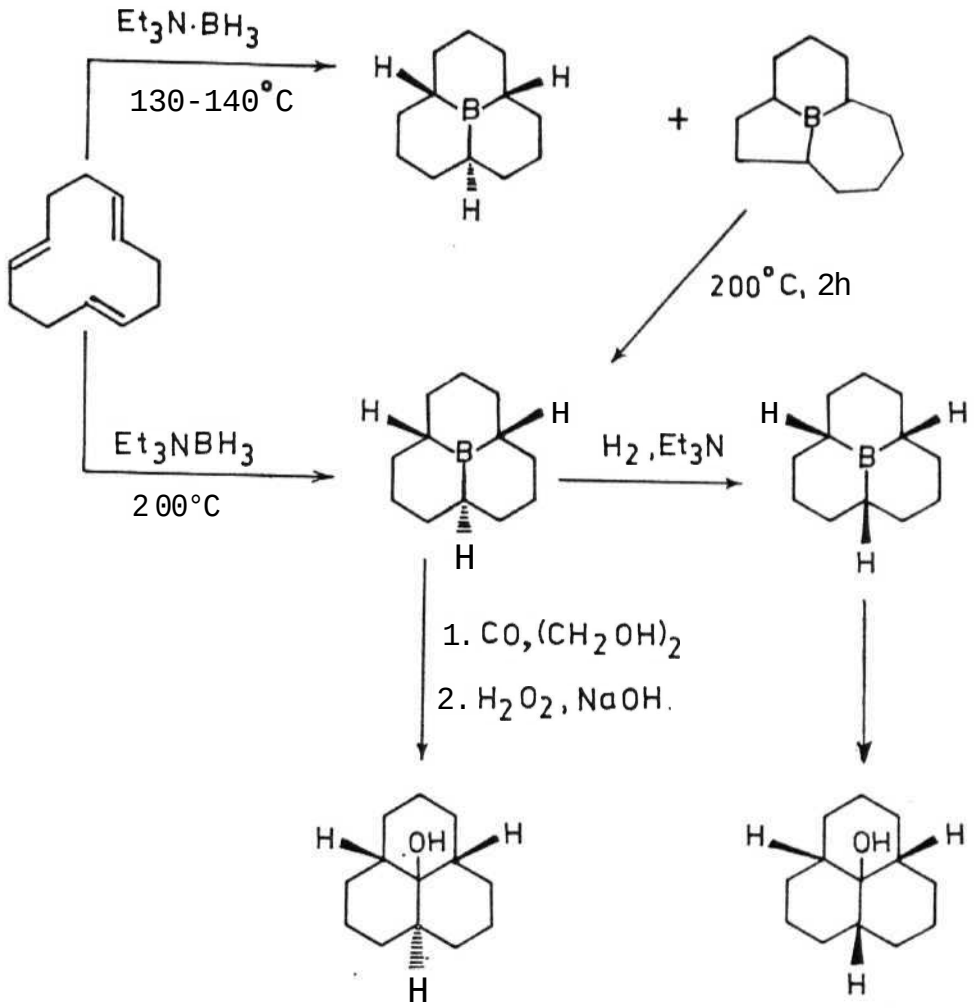
The amine-borane complexes were also utilized for hydroboration of olefins.[39-44,76] However, many amine-borane complexes hydroborate only at above 100°C. Thermal isomerizations of the resulting organoboranes are also observed at higher temperatures.[23]

1-hexene, 2-hexene —$Et_3N.BH_3$, 100°C→ tri-n-hexylborane.

The temperature required for hydroboration of 2-hexene is so

high, dehydroboration to terminal alkene also takes place.[45] The low reactivity of amine boranes has been taken into advantage for cyclic hydroboration of dienes and trienes[46,52] (Scheme 2).

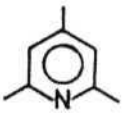
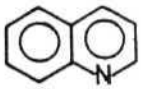
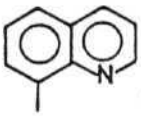
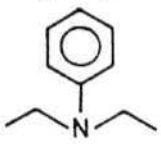
Scheme 2



Utilization of BH_3.THF gives polymeric organoboranes in this case.

Amine-borane complexes readily hydroborate alkenes if the stability of the complex is weakened by steric or electronic effects.[53,54] (Table 2.1)

Table 2.1 : Data for aromatic amine-borane complexes.[55]

Amine-borane	^{11}B (ppm)[a]	T_{min} (100% Hyd)[b]	% HB of 1-octene[c]
	-11.9	12	0
	-18.4	52	11
	-13.2	42	2.5
	-8.2	6	91
	6.0	15	56
	-11.6	2	93

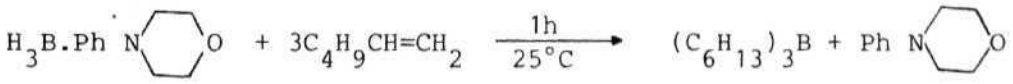
a. Related to BF_3-OEt_2

b. Hydrolysis with 3N HCl/glyccrol/THF, 25°C.

c. THF, 25°C.

The amine-boranes have not been extensively utilized for hydroborations. However, N,N-diethylaniline borane and N-phenylmorpholine borane complexes have been reported to hydroborate at room temperature (eq.10,11).[53]

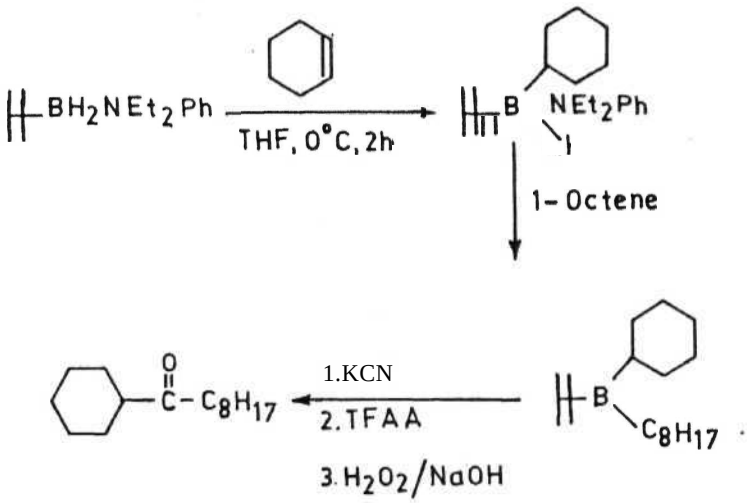
$$H_3B.PhNEt_2 + 3C_6H_{13}CH=CH_2 \xrightarrow{2h,\ 25^\circ C} (C_6H_{13})_3B + PhNEt_2 \qquad (10)$$



(11)

It has been reported that the thexylborane-N,N-diethylaniline complex can be utilized for controlled hydroboration (Scheme 3).[56]

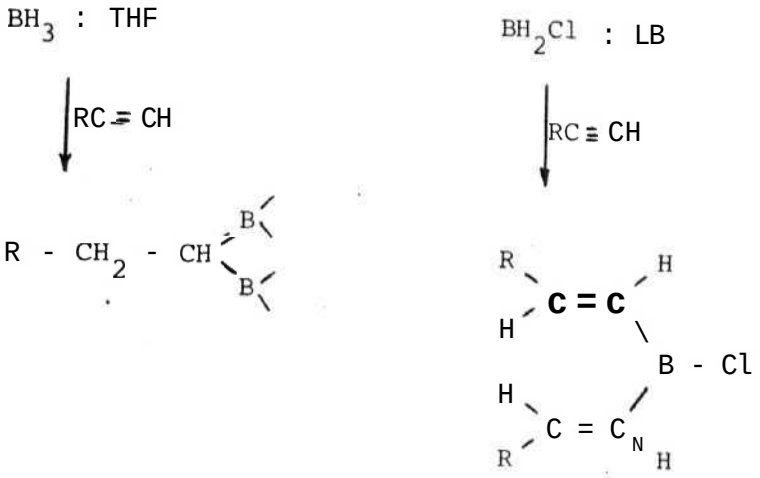
Scheme 3



It was of interest to examine whether the N,N-diethylaniline borane complex itself can be utilized for such controlled hydroborations.

Several reports indicate that $ClBH_2$-Lewis base complex gives more controlled hydroboration (eq.reaction with terminal alkynes) than the BH_3-Lewis base complexes (Fig.1).[2 57]

Fig.1



However, preparation of $ClBH_2OEt_2$ is somewhat difficult.[2,57] Several reports indicate that the monohaloborane-amine complexes can be readily prepared (eq.12-16).[59-62]

$$(CH_3)_3B.NH_3 + HCl \longrightarrow (CH_3)_3B + NH_4Cl \quad (12)$$

$$(CH_3)_3N.BH_3 + HX \longrightarrow (CH_3)_3N.BH_2X + H_2 \quad (13)$$

X = F,Cl,Br

$$2(CH_3)_3N.BH_3 + I_2 \longrightarrow 2(CH_3)_3N.BH_2I + H_2 \quad (14)$$

$$(CH_3)_3N.BH_3 + I_2 + C_4H_9NH_2 \longrightarrow (CH_3)_3N.BH_2I + HI + C_4H_9NH_2 \quad (15)$$

$$R_3N.BH_3 + (CH_3CO)_2NX \xrightarrow[\text{Benzene}]{} R_3N.BH_2X + (CH_3CO)_2NH \quad (16)$$

X = Cl, Br.

It was of interest to examine the preparation of IBH_2-N,N-diethylaniline complex and also to explore its synthetic possibilities.

RESULTS AND DISCUSSION

Synthesis of N,N-diethylaniline-BH_3 complexes utilizing B_2H_6 generated using the $I_2/NaBH_4$ system

In connection with our mechanistic studies (Chapter 3) we were seeking a simple method for the generation of diborane for utilization in the preparation of various amine borane complexes. As outlined earlier, the reaction utilizing the $I_2/NaBH_4$ system following a vacuum line technique has been reported to give diborane in 90% yield (eq.8).[18]

$$I_2 + 2NaBH_4 \xrightarrow[\text{r.t.}]{\text{diglyme}} 2NaI + H_2 + B_2H_6 \qquad (8)$$

The diborane generated in this way was found to be free of any detectable impurities.[18] Although the advantage of the diborane generated in this way over the diborane generated utilizing the $BF_3.OEt_2/NaBH_4$ system has been demonstrated,[19] the $I_2/NaBH_4$ system has not been utilized further in organic synthesis. This may be, as suggested by Lane in a review article,[20] due to the lack of a detailed experimental procedure for the generation of diborane utilizing the $I_2/NaBH_4$ system.

We have observed that the diborane can be readily generated utilizing the $I_2/NaBH_4$ system using the equipments similar to those used with the $NaBH_4/BF_3.OEt_2$ system.[2] The liberated diborane can be readily trapped

as a BH_3-Lewis base complex by bubbling the gases evolved through a flask containing the solution of the Lewis base. We have observed that the diborane generated utilizing I_2 (10 mmol) and $NaBH_4$ (20 mmol) can be trapped as N,N-diethylaniline -BH_3 complex utilizing N,N-diethylaniline (10 mmol) in benzene (40 mL) at 5-10°C. The solution of N,N-diethylaniline-borane complex prepared in this way gives 10 mmol of Ph_3PBH_3 complex on treatment with Ph_3P (15 mmol) which confirms the formation of 10 mmol of the N,N-diethylaniline-borane complex. The $I_2/NaBH_4$ reagent has been utilised in 100% excess in order to ensure complete formation of amine-borane complex. We have also found that a 25% excess of the $I_2/NaBH_4$ reagent is sufficient for the quantitative formation of amine-borane complex. However, we have utilized 100% excess of the $I_2/NaBH_4$ reagent in all cases in order to ensure that the complexation of BH_3 with the amine is complete since presence of a desired quantity of borane is important for utilization in controlled hydroborations.

The IR spectrum of the N,N~diethylaniline borane in benzene solution exhibits strong bands due to >B-H stretchings at (ν_{max}) 2235, 2280 and 2340 cm^{-1}, similar to the absorptions reported for amine-borane complexes.[63]

The N,N-diethylaniline-borane complex in benzene prepared as above readily hydroborates 3 equivalents of terminal alkenes and 2 equivalents of internal alkenes. The results are summarised in Table 2.2.

The ester function was uneffected under the present reaction conditions. The amine can be easily removed as its hydrochloride salt

during workup and can be recovered back if required. When 1-decanol obtained following this method was oxidised with aqueous chromic acid 4% of 2-decanone was formed along with 1-decanoic acid and 1-decyldecanoate. The hydroboration-oxidation product with styrenc was found to contain 20% of 1-phenylethanol (Spectrum No.2). These regioselectivities are comparable to the selectivities observed with BH_3.THF.

We have prepared the BH_3.THF solution following the $I_2/NaBH_4$ method and utilised it for the reduction of tertiary amides, imines and carboxylic acids without any difficulty (Scheme 4). However, we have observed some racemization in the case of reduction of the amide (see Chapter 3 for discussion of this racemization). Also, in the case of camphor-anil the product is a 3:2 mixture of exo and endo products.

Scheme 4

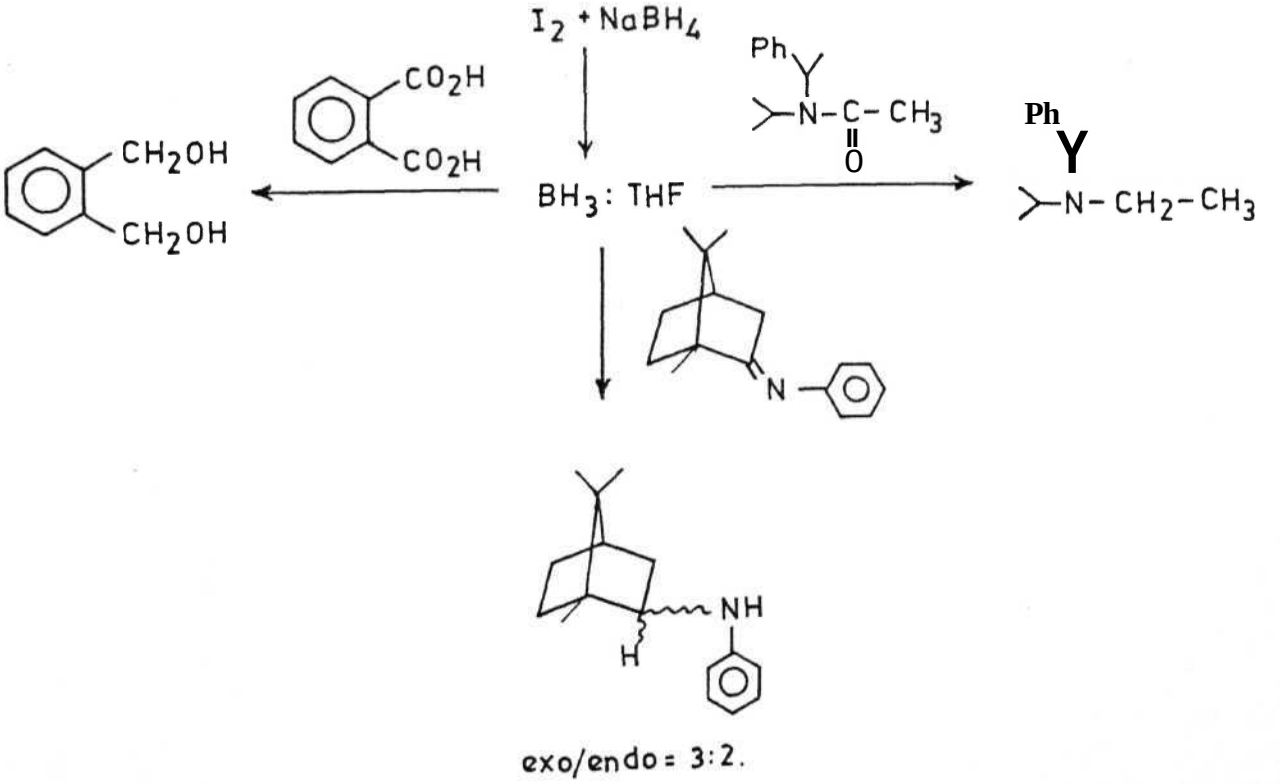
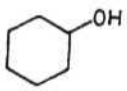
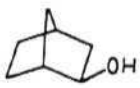
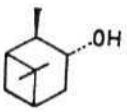
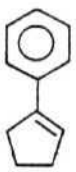
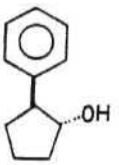
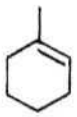
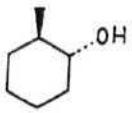
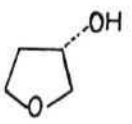


Table 2.2 : Hydroboration-Oxidation of alkenes with N-N-diethylaniline borane complex.[a]

Substrate	Product	Yield[b] (%)
$n\text{-}C_8H_{17}CH{=}CH_2$	$n\text{-}C_8H_{17}CH_2\text{-}CH_2OH$	82[c]
$n\text{-}C_4H_9CH{=}CH_2$	$n\text{-}C_4H_9CH_2\text{-}CH_2OH$	78
$C_6H_5CH{=}CH_2$	$C_6H_5CH_2\text{-}CH_2OH$	72[d]
$CH_2{=}CH\text{-}(CH_2)_8\text{-}CO_2CH_3$	$HOCH_2\text{-}(CH_2)_9\text{-}CO_2CH_3$	80[e,f]
		72
		67[e]
		68
		75
		76
		69[g]

a. For all the substrates 10 mmol of N,N-diethylaniline borane complex in benzene (30 mL) was used. Hydroborations were carried out with 30 mmol of terminal alkenes and 20 mmol of internal alkenes, at room temperature for 3 h and then at 50°C for 1 h to ensure complete hydroboration. After addition of methanol (2 mL) and THF (20 mL), oxidations were carried out with $NaOH/H_2O_2$, following the procedure reported in Chapter 1.

b. Yields are of the products isolated after distillation/recrystallization. Purity of the alcohol was tested by comparison of the spectral data (IR and NMR) with the data reported in Chapter 1.

c. The crude product obtained on oxidation with chromic acid gave 2-decanone in 4% yield.

d. Product contains 20% of 1-phenylethanol (^{1}H NMR) see spectrum No.2.

e. Isolated by column chromatography using hexane/chloroform as eluent.

f. Oxidation was carried out with $NaOAc/H_20_2$.

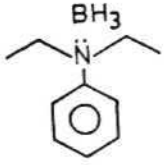
g. After oxidation the aqueous layer was saturated with excess of anhydrous K_2CO_3 and the alcohol was extracted with ether.

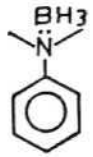
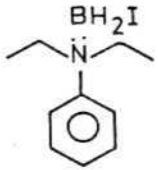
The N,N-diethylaniline-borane complex reacts with 3 equivalents of 1-decene and the resulting organoborane species will be tridecylborane. It is known that such trialkylboranes on DCME reaction (Chapter 1) with $CHCl_2OCH_3$ and $LiOC(C_2H_5)_3$ followed by oxidation give R_3COH.[64] It was of interest to examine the reaction of the $NaOCH_3/CHCl_3$ system with tridecylborane prepared utilizing the N,N-diethylaniline-BH_3 complex. We have observed that in this case no tridecylcarbinol was formed and the products after carbenoidation and oxidation were found to be di-1-decylketone (1.6 g, 34%), 1-decanol (2.1 g, 47%) and n-decane (0.1 g, 3%) (the % yields are based on the olefin utilized). The formation of n-decane can be explained by protonolysis of R^3B by CH^3OH produced during carbenoidation.[2] The methanolysis would give an equivalent amount of R^3BOCH^3 which on carbenoidation-oxidation would give R^2CO (Chapter 1). However, the yield of the di-1-decylketone is much more than the yield of 1-decane. This indicates that at least part of the didecylketone would have formed from R^3B itself. It has been reported that R^3B gives up to 20%[65] of dialkylketone on treatment with $LiOC(C^2H^5)^3$ and dichlorofluoromethane. Presumably, the reaction stops after two migrations in the present case (eq.17). The reason for this is not understood since the mechanism of this carbenoidation reaction has not been completely established.[2] (for a tentative mechanism of carbenoidation reaction see Chapter 1).

$$R_3B \xrightarrow[\text{or } \bar{C}Cl_3]{\bar{C}Cl_2OCH_3} \longrightarrow \underset{\text{I}}{R-B(-CH(OCH_3)-R)-R} \longrightarrow \underset{\text{II}}{)B-C(R)-R} \qquad (17)$$

Hydroboration of two equivalents of 1-decene with one equivalent of N,N-diethylaniline borane followed by carbenoidation using the $NaOCH_3/CHCl_3$ system and oxidation with $H_2O_2/NaOH$ gave di-1-decylketone in 82% yield.

Table 2.3 : Hydroboration-carbenoidation of alkenes using amine-borane complexes.

Entry No.	Amine-borane (10 mmol)	Substrates	Products[a] Ketone	alcohol	Olefin	Remarks
1.		1-decene (30 mmol)	1.6 g	1.8 g	-	
2.	"	1-decene (20 mmol)	1.2 g	1.0 g	-	
3.	"	1-decene (20 mmol) N,N-diethylaniline (20 mmol)	1.9 g	0.7 g	0.1 g	
4.	"	1-decene (20 mmol) N,N-diethylaniline (15 mmol)	1.3 g	1.0 g	0.15 g	
5.	"	1-decene (10 mmol) and cyclohexene (10 mmol)	0.7 g	1.0 g	-	Mixture of ketones (di-1-decyl ketone was major product).
6.	"	N,N-diethylaniline (10 mmol) 1-decene (10 mmol) cyclohexene (10 mmol)	0.7 g (didecyl) +0.5 g (mixture of ketones)	0.6 g	-	

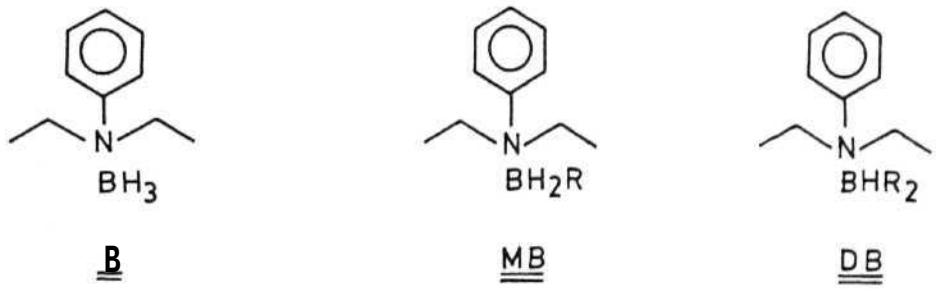
7.		1-decene (10 mmol) cyclohexene (10 mmol)	1.7 g	0.8 g	-	Mixture of ketones-di-1-decyl ketone was major product.
8.	"	cyclohexene (10 mmol) 1-decene (10 mmol)	1.5 g (didecyl + mixed alkyl ketone)	0.6 g	-	mixed alkyl ketone was 50% of the ketones
9.		1-decene (20 mmol)	1.4 g	0.3 g	-	
10.	"	cyclohexene (10 mmol) 1-decene (10 mmols)		IR spectrum of the product shows strong OH stetching absorption and carbonyl absorption was absent.		
11.	"	Cyclohexene (20 mmol)		0.64 g		Cyclohexanol

[A]Products isolated after carbenoidation-oxidation (see the Experimental Section.)

The result indicates that this is a good alternate method to the procedure utilizing the $CH_3COOH/NaBH_4$ system for hydroboration, described in Chapter 1.

As outlined previously, complexing abilities of Lewis bases have been successfully utilized for controlled hydroboration in some cases (Scheme 3).[56] For example, presence of one to two equivalents of THF along with $ClBH_2:OEt_2$ in diethylether gives monoalkylboranes even with terminal alkenes[63] and thexylborane-N,N-diethylaniline complex can be utilized for unsymmetrical ketone synthesis via sequential hydroboration of an internal and terminal alkene.[56] It was of interest to examine whether the N,N-diethylaniline-borane can be utilized for mixed alkylketone synthesis. We have carried out the hydroboration utilizing N,N-dialkylaniline-BH_3 complex by addition of 1-decene and cyclohexene sequentially under various conditions (Table 2.3).

In all cases, the di-1-decylketone was isolated as the major product after carbenoidation-oxidation and the cyclohexyl-decylketone was formed only in small amounts (Table 2.3). The sequential hydroborations with different olefins will work only if the reactivity order of the amine borane complexes present will be as given below (Fig.2).



B MB DB

Fig. 2

The formation of di-1-decylketone in good yields in the hydroboration-carbenoidation-oxidation of 2 eq. of 1-decene indicates that the reactivity of the DB complex (Fig.2) is low but the failure to get mixed alkylketones

here indicates that **MB** reacts as fast as or faster than the B under **the** present reaction conditions.

Synthesis and Reactions of Mono iodoborane-N,N-diethylaniline complex (MIBDA)

The haloborane etherates or dimethylsulphide complexes possess reactivities very much different from BH_3.THF or BH_3.SMe$_2$. [2] **Syntheses** of chloroboranes and bromoboranes from the corresponding BH_3-Lewis base complexes require standardised solutions of HCl, BCl_3 or BBr_3 which **make** the synthesis and handling of such complexes somewhat difficult. However, many interesting aspects of the chemistry of such complexes have been uncovered. [2,3,4]

The mono-iodoborane Lewis base complexes have been readily prepared from the reaction of I_2 with the corresponding BH_3. Lewis base complexes. [58,69,70]

$$2BH_3.SMe_2 + X_2 \xrightarrow[X = Br,\ I]{CS_2} 2H_2BX.SMe_2 + H_2 \qquad (18)$$

$$(CH_3)_3N.BH_3 + I_2 \longrightarrow (CH_3)N.BH_2I + H_2 \qquad (14)$$

$$(CH_3)_3N.BH_3 + I_2 + C_4H_9NH_2 \longrightarrow (CH_3)_3N.BH_2I + HI + C_4H_9NH_2 \qquad (15)$$

It was of interest to examine the possibility of the synthesis of IBH_2-N,N-diethylaniline complex by the reaction of I_2 with N,N-diethylaniline-borane complex in benzene. We have observed that addition of iodine (10 mmol) in benzene into a benzene solution of N,N-diethylaniline-borane (10 mmol) at 5-10°C gives a dark colour solution initially which discharges in **30-45** minutes to give a colourless solution with the evolution of **a gas** (H_2). **The IR spectrum** of the **solution exhibits** >B-H **absorption as a symmetri-**

cal doublet at 2400 and 2450 cm^{-1}. It has been reported[59,63] that Me_2NBH_2Cl exhibits >B-H absorption as a symmetrical doublet at 2500 and 2450 cm^{-1}. Comparison of the >B-H stretching absorptions indicate that the species present in the present case is most probably the mono iodoborane N,N-diethylaniline complex (abbreviated as MIBDA) but presence of other species to a small extent cannot be completely ruled out. We have briefly investigated the reactions of this MIBDA complex with some alkenes and alkynes.

Hydroboration of 3 equivalents of 1-decene with the MIBDA in benzene prepared as above at 25°C for 14 h followed by oxidation gave 1-decanol (88%) and one equivalent of 1-decene was recovered. This indicates that one of the >B-H bonds in the N,N-diethylaniline-BH_3 complex is lost on reaction with iodine.

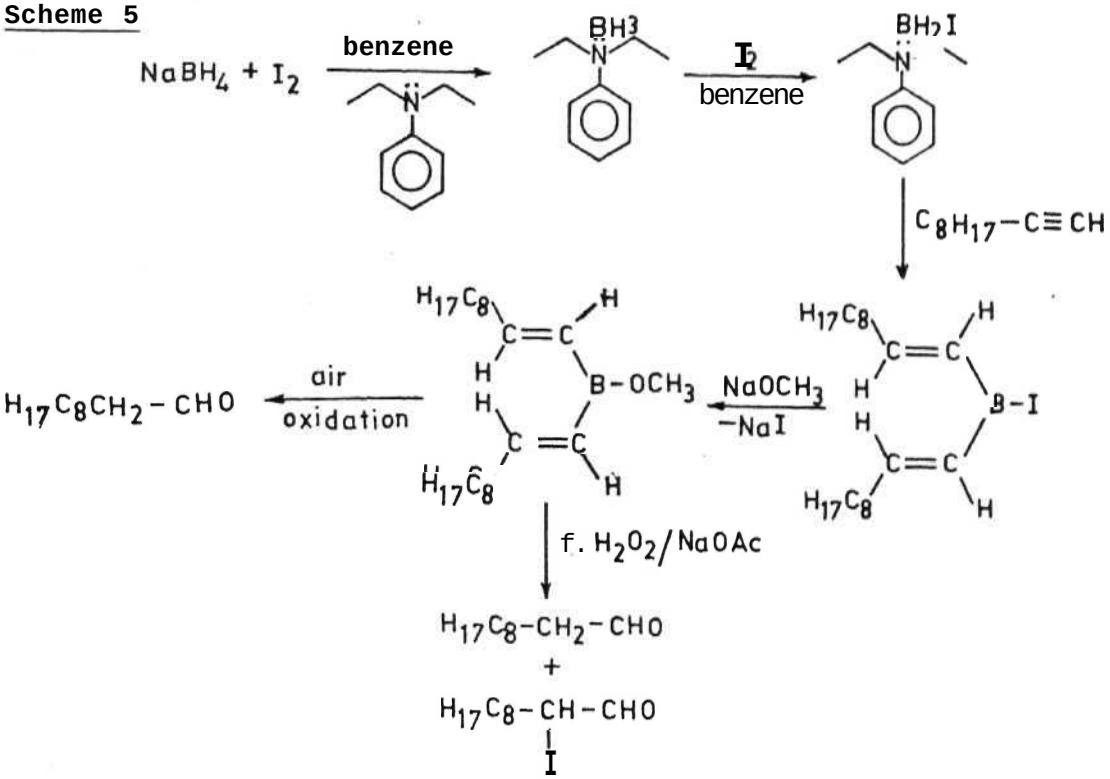
Hydroboration of 2-equivalents of 1-decene with the MIBDA followed by carbenoidation-oxidation gave di-1-decylketone in 84% yield.

The mixed alkyl ketone synthesis was also attempted using the MIBDA reagent by sequential hydroboration of 1-decene and cyclohexene. Carbenoidation with $CHCl_3$/NaOMe system and oxidation with H_2O_2/NaOH gave di-1-decylketone (65% based on the starting 1-decene) and a small amount (270 mg) of cyclohexanol. In order to examine the reactivity of the MIBDA with cyclohexene, we have carried out the hydroboration/carbenoidation/oxidation reactions utilizing 2 equivalents of cyclohexene and isolated 32% of cyclohexanol and no dicyclohexylketone was formed. This indicates that the MIBDA has difficulty in reacting with cyclohexene.

When two equivalents of 1-decyne was hydroborated with MIBDA at 25°C for 14 h and protonolysed[72] with acetic acid at room temperature for

4 h, no 1-decene was formed. Chromatography of the reaction product gave 1-decanal in 58% yield. Presumably, the aldehyde is formed by air oxidation of the intermediate vinylic boron species. However, when the protonolysis with CH_3COOH was carried out under refluxing condition for 6 h, 1-decene was isolated in 57% yield. The results indicate that the vinyl borane formed is somewhat less reactive towards CH_3COOH under the present reaction conditions. Oxidation of the intermediate vinyl boron species with H_2O_2/NaOAc after adding $NaOCH_3$ and THF gave 1-decanal (32%) and 2-iodo-1-decanal (35%). Since the iodoaldehyde has not been formed in the above experiment involving air oxidation, this result indicates that iodination takes place after the 1-decanal is formed.[72]

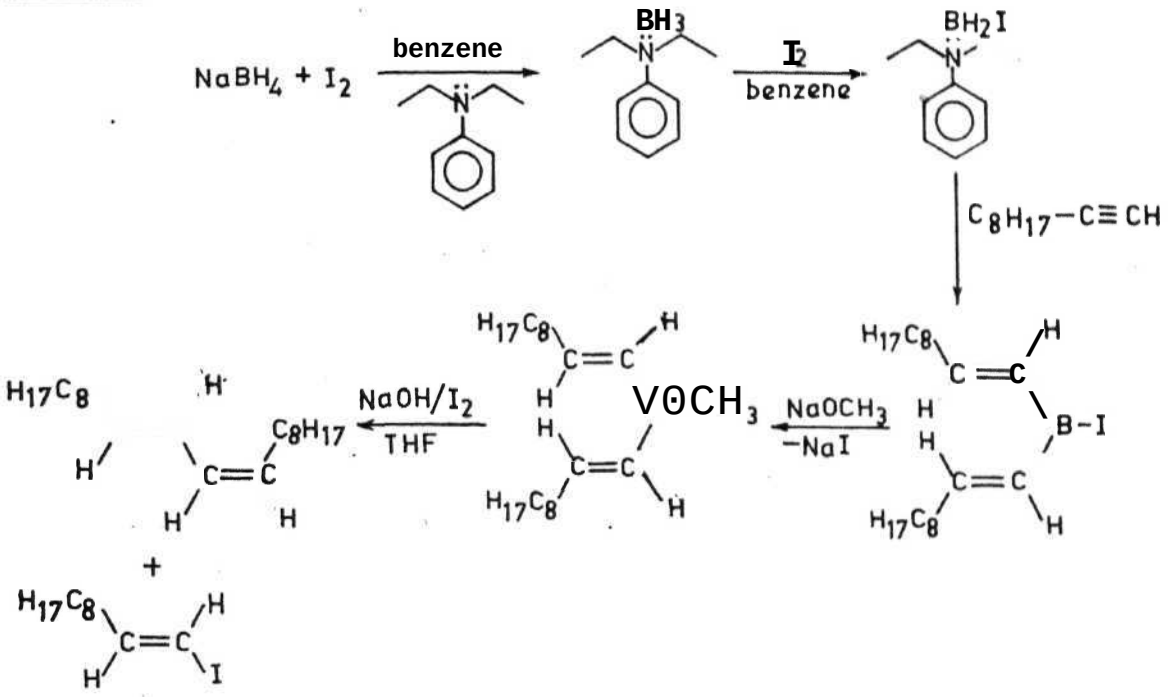
Scheme 5



If hydroboration of two equivalents of 1-alkyne gives divinyliodoborane, it should be possible to achieve the cis, trans-diene synthesis by treatment with I_2/NaOH as envisaged in Scheme 6. Similar transformation

has been reported utilizing $ClBH_2OEt_2$ for the hydroboration of 1-alkynes followed by reaction with $I_2/NaOH$.[73] Such a method will be **interesting** in the present case as the iodine will be utilized in three steps (Scheme 6).

Scheme 6



We have observed that when the experiment was carried out utilizing 1-decyne as outlined in Scheme 6, a product with M^+ peak at m/e 278 has **been** isolated. Unfortunately, the product is not the pure cis, trans-diene. Although the major signals in the ^{13}C NMR spectrum correspond to the cis, trans-diene some additional signals are also present in the spectrum (see spectrum No.3). The signal at 74.2 ppm due to the minor product corresponds

to the olefinic carbon atom substituted with iodine indicating the possibility that the minor product is a vinyl iodide. Further standardisation of conditions is necessary to direct the reaction to obtain monovinylborane **and** divinylborane cleanly.

SUMMARY

Conditions were standardised for the generation of diborane utilizing the simple $I_2/NaBH_4$ system. The generated diborane can be readily utilized for the preparation of N,N-diethylaniline-borane complex in hydrocarbon solvents (benzene, toluene). The utility of this complex in the hydroboration of olefins was studied. The diborane generated utilizing the $I_2/NaBH_4$ system was used for reduction of some representative amide, imine and carboxylic acid. Hydroboration of olefins (2 eq.) utilizing the N,N-diethylaniline-borane complex followed by carbenoidation with the $CHCl_3/NaOMe$ system gave symmetrical dialkylketones in good yields. Monoiodoborane-N,N-diethylaniline complex (MIBDA) was prepared by the reaction of I_2 with borane-N,N-diethyl-aniline complex. Utility of this MIBDA in the hydroboration of alkenes and alkynes was studied.

EXPERIMENTAL

General details

Several items given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. The N,N-diethylaniline was distilled over anhydrous KOH in small quantities (10 ml,) and kept under nitrogen for utilization. 1-Heptyne utilized was a commercial sample. 1-Octyne and 1-decyne were prepared following a reported procedure.[75] The N-acetyl-N-isopropyl-α-methylbenzylamine and camphoranil were prepared following closely related literature procedures and will be described in detail in Chapter 3.

Generation of Diborane utilizing the I_2/$NaBH_4$ system and preparation of N,N-diethylaniline-borane complex

A solution of iodine (2.54 g, 10 mmol) in diglyme (100 mL) was introduced dropwise during 20 minutes from an addition funnel into a generation flask (100mL RB flask with a side arm and side septum) containing $NaBH_4$ (0.8 g, 20 mmol) in diglyme (10 mL) at r.t. (tap water cooling) under a static nitrogen atmosphere. The generated diborane and hydrogen were carried off through a side tube and bubbled through a solution of N,N-diethylaniline (1.49 g, 10 mmol) in benzene (40 mL) in another flask at 5 to 10°C (250 mL RB flask with a side septum, side arm and

a condensor). The outlet from the latter flask was vented through a mercury bubbler and a trap containing adequate amount of acetone to destroy excess diborane. When the bubbling of the gases in the reaction flask had ceased, the bubbler was removed under nitrogen and replaced by a glass stopper. ' The bubbler was connected to an acetone trap and the traces of diborane remained in the generation flask was driven away by a stream of dry nitrogen. The diborane in the gas phase above the benzene solution in the reaction flask was also flushed out with a stream of nitrogen. The N,N-diethylaniline-borane complex thus prepared was utilized for further reactions.

IR (benzene) ν_{max} : 2235, 2280, 2340 cm^{-1}. The Me_2NBH_3 complex has B-H stretching absorption in the same region which appear as a symmetrical triplet.[63]

Reaction of BH_3-N,N-diethylaniline complex with triphenylphosphine

The N,N-diethylaniline-borane complex (10 mmol) in benzene (35-40 mL) was prepared as above and PPh_3 (3.93 g, 15 mmol) in dry benzene (10 mL) was added. The reaction mixture was stirred for 4 h at r.t. Benzene was distilled out from the reaction mixture and the residue was chromatographed on a silica gel column. Hexane eluted triphenylphosphine and hexane/chloroform (4:1) eluted triphenylphosphine borane. Yield, 2.7 g (95%), mp.186°C. lit. mp.189°C.[76] The spectral data for the the PPh_3BH_3 obtained in this way are identical with the data of PPh_3BH_3 obtained utilizing the $CH_3COOH/NaBH_4$ system (Chapter 1).

Hydroboration-Oxidation of olefins with N,N-diethylaniline-borane complex

For all the reactions, N,N-diethylaniline-borane (10 mmol) and benzene (40 mL) were utilised. Hydroborations were carried out with 30 mmol of terminal alkenes and 20 mmol of internal alkenes. The following procedure for the conversion of 1-decene into 1-decanol is representative. To the N,N-diethylaniline borane complex (10 mmol) prepared in benzene (40 mL), 1-decene (4.2 g, 30 mmol) was added and stirred at r.t. for 3 h and at 50°C for 1 h. The organoborane was cooled and CH_3OH (2 mL) was added and stirred for 30 minutes. THF (30 mL) was added and oxidation of the organoborane was carried out using H_2O_2 (16%, 25 mL) and 3N NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x30 mL). The combined organic layer was washed with 2N HC1 (3x15 mL) to remove the amine. The organic layer was washed with saturated NaCl solution (15 mL), dried over anhydrous $MgSO_4$ and the solvent was evaporated. Distillation of the residue under reduced pressure afforded 1-decanol (3.88 g, 83%, bp. 107°C/7 mm Hg). The IR and NMR spectral data were identical with the data reported in Chapter 1.

Several other olefins were converted in to the corresponding alcohols in this way and the results are summarised in Table 2.2.

Reduction of a tertiary amide with B_2H_6 generated using $I_2/NaBH_4$ system

Preparation of N-ethyl-N-isopropyl-α-methyl benzylamine: Diborane generated utilizing I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) was bubbled through the reaction flask containing N-acyl-N-isopropyl-α-methylbenzylamine

(10 mmol) in dry THF (50 mL) for 45 min. The stirring of the contents of the reaction flask was continued under nitrogen atmosphere for 2 h at r.t. and 1 h at refluxing temperature (70°C bath temperature). The reaction mixture was cooled to 0°C and 6N HC1 (10 mL) was carefully added. THF was distilled out and the residue was neutralized with 6N KOH. The amine was extracted with ether (3x25 mL), washed with saturated NaCl solution (15 mL), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was distilled under reduced pressure to yield N-ethyl-N-isopropyl-α-methylbenzylamine (1.53 g, 80%, bp.72°/2 mm).

IR (neat) V_{max}: 1590, 1360, 1356 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.28 (t,5H), 3.84 (q,1H), 2.48 (q,2H), 1.3 (d,3H), 0.92 (m,9H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 146.7, 128.0, 127.5, 126.2, 58.4, 48.2, 39.0, 20.0, 19.7, 19.2, 16.9.

$[\alpha]_D^{20}$ = 5.26 (C4.1824, EtOH).

Reduction of camphor-anil with B_2H_6 generated using $I_2/NaBH_4$ system

Diborane generated utilizing I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) was bubbled through the flask containing camphor-anil (1.2 g, 10 mmol) in dry THF (50 mL) for 45 minutes. The bubbler was removed and the mixture was stirred for 2 h at r.t. and 1 h at refluxing temperature (70°C, oil bath temperature) under nitrogen atmosphere. The reaction mixture was cooled to 0°C and acidified with 6N HC1 (10 mL). THF was distilled

out and the amine was regenerated using 6N KOH (phenolphthalein indicator) and extracted with ether (3x25 mL). The combined ether extract was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was distilled under reduced pressure to yield a (2:3) mixture of bornyl and isobornyl aniline, 1.87 g, 82%, bp.114°C/ 1 mm Hg, lit. bp.173-174/14 mm Hg.[77]

IR (neat) ν_{max}: 3375, 1595, 1360, 1356 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$) : 6 ppm 148.4, 129.4, 116.8, 112.9, 61.7, 48.9, 47.3, 45.3, 40.9, 36.9, 27.6, 20.6, 12.57.

In addition, the following signals corresponding to the presence of bornyl aniline (~ 40%) are also present.

6 ppm 148.0, 129.0, 116.4, 112.4, 58.0, 48.5, 46.9, 44.8, 38.5, 28.1, 27.2, 19.6, 18.4, 14.1.

Reduction of a carboxylic acid with B_2H_6 generated using $I_2/NaBH_4$ system

Diborane generated utilizing I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) was bubbled into the flask containing phthalic acid (1.67 g, 10 mmol) in dry THF (50 mL) at 0°C for 45 min. The contents were stirred for 5 h at r.t. and 1 h at refluxing temperature. It was cooled to 0°C and the excess hydride was destroyed with 1:1 THF-water mixture (10 mL). The reaction mixture was saturated with anhydrous K_2CO_3 (10 g) and extracted with ether (3x30 mL). The combined ether extract was washed with

saturated NaCl solution (15 mL), dried over anhydrous $MgSO_4$ and the solvent was removed. The crude residue was recrystallized from ethanol to yield phthalylalcohol (1.18 g, 85%, mp.64°C, lit.[78] mp. 65°C).

IR (Nujol) V_{max}: 3500-3350, 3050, 1520, 1090, 975 cm^{-1}.

The IR spectrum was superimposable with the spectrum reported in the literature.[79]

Carbenoidation of R_3B prepared by the hydroboration of 1-decene (30 mmol) with $BH_3N(Et)_2Ph$ complex

To a freshly prepared N,N-diethylaniline borane (10 mmol) solution in benzene (40 ML), 1-decene (4.2 g, 30 mmol) was added and the mixture was stirred at r.t. for 2 h and at 50°C for further 2 h to ensure complete hydroboration. The contents were brought to 30°C and THF (30 mL) was added. Carbenoidation was carried out using NaOMe (2.16 g, 40 mmol) and $CHCl_3$ (10 mL, 125 mmol) at 50-55°C following the procedure outlined in Chapter 1. The resultring organoborane was oxidised with H_2O_2 (16%, 25 mL) and 3N NaOH (15 mL). The contents were extracted with ether (3x25 mL). The combined ether extract was washed with 2N HC1 (3x10 mL), saturated NaCl solution (2x15 mL) and dried over anhydrous $MgSO_4$. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate decane (0.1 g, 3%), di-1-decylketone (1.6 g, 34.3%, mp.64°C, lit.[80] mp. 62°C) and 1-decanol (2.1 g, 47%) (yields are based on the starting 1-decene). The spectra of these products were superimposable with the spectra of samples obtained previously (Chapter 1).

Hydroboration-Carbenoidation of 1-decene using N,N-diethylaniline-borane complex: Synthesis of di-1-decylketone

To the N,N-diethylaniline-borane (10 mmol) in benzene (40 mL) 1-decene (2.8 g, 20 mmol) was added and the contents were stirred at r.t. for 4 h under nitrogen atmosphere. Excess hydride was destroyed PV careful addition of CH_3OH (2 mL). After the evolution of gases had ceased, THF (30 mL) was added and carbenoidation was carried out by the addition of $CHCl_3$ (125 mmol) and NaOMe (40 mmol) at 50-60°C following the procedure outlined in Chapter 1. The organoborane was oxidised with H_2O_2 (16%, 25 mL) and 3N NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). From the combined organic extract, the amine was removed by washing with 2N HC1 (3x10 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was evaporated. The crude ketone residue was chromatographed on a silica gel column (hexane/chloroform as eluent) to isolate di-1-decylketone (2.54 g, 82%, mp.64°C) and 1-decanol (0.38 g, 12% based on the starting 1-decene). The IR and NMR spectra of the ketone and 1-decanol were superimposable with the spectra of the corresponding samples obtained previously (Chapter 1).

Attempted unsymmetrical ketone synthesis via hydroboration of cyclohexene and 1-decene with N,N-diethylaniline-borane complex

The N,N-diethylaniline-borane (10 mmol) was prepared in benzene (40 mL) as outlined previously and cyclohexene (0.82 g, 10 mmol) was added. The contents were stirred at r.t. for 2 h under nitrogen atmos-

phere. 1-Decene (1.4 g, 10 mmol) was added and the mixture was further stirred at r.t. for 2 h. Methanol (2 mL) was injected to destroy the excess hydride and THF (30 mL) was added. Carbenoidation was carried out using $CHCl_3$ (125 mmol) and NaOMe (40 mmol) following the procedure given in Chapter 1. The organoborane was oxidised with H_2O_2 (16%, 25 mL) and 3N NaOH (15 mL). After workup, the crude product mixture was chromatographed on a silica gel column using hexane/chloroform as eluent. The product which eluted first was identified as di-1-decylketone (1.1 g, 70%, mp.63°C, lit.mp.62°C) and the fraction (0.5 g) which eluted next was identified as a mixture of di-1-decylketone and cyclohexyldecylketone from the ^{13}C NMR spectral data.

Fraction 1

IR (KBr)V_{max}: 1705 cm^{-1} (>C=O) .

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 13.8, 22.4, 29.1, 29.4, 31.7, 36.7, 39.1, 42.6, 50.8, 214.2 (>C=O).

Fraction 2

IR (neat)V_{max}: 1710 cm^{-1} (>C=O) .

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 13.8, 22.4, 23.5, 25.5, 28.2, 29.1, 29.3, 31.7, 40.3, 50.5, 213.4 (C=O).

Reaction of I_2 with N,N-diethylaniline-borane complex: Preparation of mono iodoborane N,N-diethylaniline complex (MIBDA)

To the N,N-diethylaniline-borane complex (10 mmol) in benzene (40 mL) iodine (1.27 'g, 10 mmol) in dry benzene (20 mL) was added with the aid of a double ended needle at 15°C (the evolution of H_2 gas can be observed). The contents of the flask were stirred at r.t. till the reaction mixture becomes colourless (30 minutes to 1 h) . The mono iodo-borane-N,N-diethylaniline complex thus prepared was utilised for further reactions.

IR (benzene) ν_{max}: 2450, 2400 cm^{-1}. Reported IR absorption (B-H, stretching) for Me_3NBH_2Cl: ν_{max}: 2500, 2450 cm^{-1}.[59,63]

Reaction of 1 eq. of MIBDA with 3 eq. of 1-decene

To the MIBDA complex (10 mmol) in benzene (40 mL) was added 1-decene (4.2 g, 30 mmol) and stirred for 14 h at r.t. NaOMe (0.54 g, 10 mmol) was added and the reaction mixture was stirred for 1 h. THF (30 mL) was added and the organoborane was oxidised with H_2O_2 (16%, 25 mL) and 3N NaOH (10 mL) and extracted with ether (3x30 mL) . The combined ether extract was washed with 2N HC1 (2x15 mL) , saturated NaCl solution (15 mL) and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was distilled to isolate 1-decene (1.5 g, 10.7 mmol) and 1-decanol (2.8 g, 17.7 mmol). The IR spectra of these products are identical to the spectra of samples obtained previously (Chapter 1).

Symmetrical dialkylketone synthesis utilising mono-iodoborane-N,N-diethyl-aniline complex (MIBDA)

To MIBDA (10 mmol) in dry benzene, 1-decene (2.8 g, 20 mmol) was added and the mixture was stirred at r.t. for 14 h. NaOMe (0.54 g, 10 mmol) was added and carbenoidation was carried out utilizing $CHCl_3$ (125 mmol) and NaOMe (40 mmol) at 50-55°C as outlined in Chapter 1. The contents were brought to r.t. and ethylene glycol (10 mmol) was added (in order to facilitate oxidation) and oxidised with H_2O_2/NaOH. The mixture was extracted with ether (3x30 mL) and the combined organic extract was dried over anhydrous $MgSO_4$. The solvent was distilled out and the residue was chromatographed on a silica gel column (hexane/chloroform as eluent) to isolate 1-decene (100 mg, 3%), di-1-decylketone (2.6 g, 84%, mp.64°C) and 1-decanol (100 mg, 5%). The yields are based on the starting olefin. The IR spectra of the products were superimposable with the spectra of the samples obtained previously (Chapter 1).

Attempted unsymmetrical ketone synthesis utilizing MIBDA complex, cyclohexene and 1-decene

To a freshly prepared MIBDA complex (10 mmol) in benzene (40 mL) cyclohexene (0.82 g, 10 mmol) was added and stirred for 12 h at r.t. 1-Decene (1.4 g, 10 mmol) was added and the reaction mixture was stirred for 12 h at r.t. and 2 h at 40°C (warm water bath). After the carbenoidation using $CHCl_3$ (125 mmol) and NaOMe (40 mmol) as outlined in previous experiments, ethylene glycol (10 mmol) was added and the oxidation was carried out using H_2O_2 (16%, 25 mL) and 3N NaOH (15 mL). The reaction

mixture was extracted with' ether (3x3 mL). The combined ether extract was washed with 2N HCl (2x10 mL), saturated NaCl solution and dried over $MgSO_4$. The solvent was distilled out and the residue was chromatographed on a silicagel column (hexane/chloroform as eluent) to isolate di-1-decylketone (1 g, 65%, mp.64°C. lit.[80] 62°C) and 500 mg of (a 40:60) mixture of cyclohexanol and 1-decanol. Dicyclohexylketone and cyclohexyl decylketone were not formed.

The above reaction was carried out utilizing only cyclohexene (1.64 g, 20 mmol) in the hydroboration step. The mixture was stirred for 14 h at r.t. and the carbenoidation was carried out as in the above experiment. Workup and distillation of the residue yielded only cyclohexanol (0.64 g, 32%) and no ketone was formed.

Protonolysis of the Hydroboration product of 1-decyne with MIBDA

To MIBDA complex (2.5 mmol) in benzene (35 mL) 1-decyne (0.69 g, 5 mmol) was added and the contents were stirred for 14 h at r.t. and 30 minutes at 30-35°C. The reaction mixture was brought to 20°C and anhydrous AcOH (7 mL) was added and stirred for 4 h at r.t. The contents were poured into ice water (30 g) and extracted with ether (3x30 mL). The residue did not contain any 1-decene (IR spectrum). Column chromatography (hexane eluent) of the residue gave 1-decanal (0.450 g, 58%). Presumably, the acetic acid does not protonolyse the vinylborane under the present reaction conditions and the aldehyde may be resulting from air oxidation of the vinylboron species during workup and chromatographic separation.

IR (neat) ν_{max}: 2750, 1715 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 9.67 (t,1H), 2.8 (dt,2H), 2.25 (m,4H), 1.95 (m,4H), 1.65 (m,4H) 0.8 (t,3H).

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 202.7 (-CHO), 43.8 ($-CH_2$-CHO), 31.7, 29.7, 29.5, 29.2, 22.5, 22.0, 13.9.

In another run the protonolysis was carried out by stirring the organoborane with acetic acid (10 mL) at r.t. for 1 h and at refluxing temperature for 4 h. The products were isolated by column chromatography on a silica gel column using hexane as eluent. The fraction eluted first was identified as 1-decyne (200 mg, 1.45 mmol) and the fraction eluted next was 1-decene (400 mg, 57% based on the reacted 1-decyne).

Hydroboration-oxidation of 1-alkynes with MIBDA

The procedure for the reaction of 1-decyne is representative: To MIBDA (2.5 mmol) in dry benzene (35 mL), 1-decyne (0.67 g, 5 mmol) was added and the reaction mixture was stirred at r.t. for 24 h. NaOMe (0.135 g, 2.5 mmol) was added and the contents were stirred at r.t. for 1 h. THF (35 mL) was added and the organoborane was oxidised with H_2O_2 (16%, 15 mL) and 3N NaOAc (10 mL). The organic layer was separated and the aqueous layer was extracted with ether (2x30 mL). The combined organic extract was washed with saturated $Na_2S_2O_3$ solution (2x10 mL) and dried over anhydrous $MgSO_4$. The solvent was distilled out and the residue was chromatographed (hexane as eluent) to isolate 2-Iodo-1-decanal (0.5 g, 35%) and 1-decanal (0.25 g, 32%).

2-Iodo-1-decanal: IR (neat) ν_{max} : 2750, 1710, 720 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 191.1(-CHO), 36.3(CH-CHO), 31.5, 31.2, 28.7, 28.5, 28.2, 22.0, 13.5.

The IR and NMR spectra of the 1-decanal were identical with the spectra reported in the previous experiment. The above procedure was followed for the reaction of 1-octyne and the results are summarised below.

2-Iodo-1-octanal: Yield 0.5 g, 39.2%.

IR (neat) ν_{max}: 2750, 1710, 740 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 9.95 (d,1H), 5.15 (dt,2H), 2.65 (m,2H), 2.15 (m,8H), 1.55 (t,3H).

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 191.8(-CHO), 36.9(CHI-CHO), 32.1, 31.5, 29.4, 28.5, 22.5, 14.0.

1-Octanal: Yield 0.2 g, 22%.

IR (neat) V_{max}: 2750, 1720 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): 6ppm 202.0(-CHO), 49.9(CH_2-CHO), 39.2, 31.6, 29.1, 22.6, 22.1, **14.0.**

Reaction of the hydroboration product of 1-decyne with MIBDA with I_2/NaOH system: Attempted synthesis of cis-trans diene

To MIBDA (5 mmol) in dry benzene (40 mL) 1-decyne (1.38 g, 10 mmol) was added and stirred for 24 h at r.t. It was cooled to 0°C under nitrogen atmosphere and THF (25 mL) was added followed by 6N NaOH (8 mL). The contents were stirred for 30 minutes at ambient temperature. To the reaction mixture, iodine (2.74 g) in THF (15 mL) was added at 0°C until a slight iodine colour persisted in the reaction flask. The stirring was continued further for 15 minutes. The excess iodine was decolourised by adding saturated $Na_2S_2O_3$ solution. The organic layer was separated and the aqueous layer was extracted with hexane (2x25 mL). The combined organic extract was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and the solvent was distilled out. The residue was chromatographed on a silicagel column (hexane as eluent) to yield 1.1 g of product in which the eicosa-9,10-(E), 11,12(Z)-diene was the major component.

IR (neat) ν_{max}: 3050, 1600, 1465, 1050 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 147.7, 132.3, 130.5, 129.8, 36.1, 31.8, 29.5, 29.4, 28.9, 28.4, 22.6, 14.0.

In addition, signals due to the presence of another product, most probably a vinyliodide, are also present (see Spectrum No.3).

Mass m/e (%): M^+ 278 (20%), 139 (100%, M^+H-decene), 127 (60%), 111 (40%), 97 (80%).

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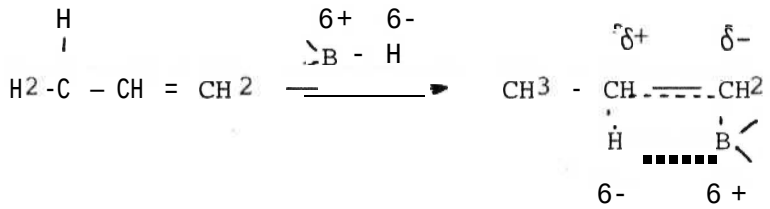
CHAPTER 3

Mechanistic studies of the hydroboration reaction utilizing borane chiral Lewis base complexes for hydroboration of prochiral olefins.

INTRODUCTION

The hydroboration takes place by cis-addition of B-H bond to carbon-carbon multiple bonds.[1,2] The addition takes place from less hindered side of the multiple bond.[1,2] The diborane reacts very sluggishly with olefins in the gas phase[3] and in hydrocarbon[4] solvents but the presence of weak Lewis bases make the reaction fast.[5] For the hydroborations with diborane in ether solvents, a four-centre transition state (eq.1) with direction of the addition controlled by polarisation of the boron hydrogen bond, $>B-H$, has been proposed.



(1)

However, it remains to be established whether the Lewis base moiety in the BH_3-Lewis base complexes is present or absent in the transition state of the >B-H addition to olefins and differences of opinion exist.[6-20] A review of the literature reports on the mechanistic studies of the hydroboration of olefins with BH_3-Lewis base complexes will facilitate the discussion of the present results. The kinetic and mechanistic studies on the hydroboration of olefins with dialkylborane complexes and dibromoborane complexes have been recently reviewed[9] and only relevant details will be reviewed here.

The hydroboration of substituted styrenes by diborane in various solvents (eg. diglyme, THF, diethylether) gives products with essentially no significant difference in regioselectivities.[6] It was suggested that since the solvents do not influence the regioselectivities, they may not be intimately associated in the transition state of the >B-H addition to the olefin. The mechanism given in eq.2-4 involving free 'BH_3' monomer as intermediate was suggested.[6]

$$B_2H_6 + 2\ O(R)R \longrightarrow 2\ BH_3O(R)R \qquad (2)$$

$$BH_3O(R)R \longrightarrow BH_3 + OR_2 \qquad (3)$$

$$BH_3 + >C=C< \longrightarrow -\overset{|}{C}-\overset{|}{C}- \quad (B) \qquad (4)$$

It was suggested that the hydroboration is very fast in ether solvents as they provide an alternate pathway to the reactive species, the 'BH_3' monomer.[6,7] Formation of BH_3 directly from B_2H_6 is highly prohibitive since the B_2H_6 would lose dimerization energy of 36 Kcal/mole in the process.[14]

The kinetic studies of hydroboration of simple olefins with BH_3.THF complex in solution are complicated by three successive >B-H addition reactions (eq.5-7), three redistribution equilibria (eq.8-10) and five monomer dimer equilibria (eq.11-15).

$$\text{Alkene} + BH_3 \longrightarrow RBH_2 \qquad (5)$$

$$\text{Alkene} + RBH_2 \longrightarrow R_2BH \qquad (6)$$

$$\text{Alkene} + R_2BH \longrightarrow R_3B \qquad (7)$$

$$BH_3 + RBH_2 \rightleftharpoons H_2BH_2BHR \qquad (8)$$

$$BH_3 + R_2BH \rightleftharpoons H_2BH_2BR_2 \qquad (9)$$

$$2RBH_2 \overset{*}{\rightleftharpoons} RHBH_2BHR \qquad (10)$$

$$RBH_2 + R_2BH \rightleftharpoons RHBH_2BR_2 \qquad (11)$$

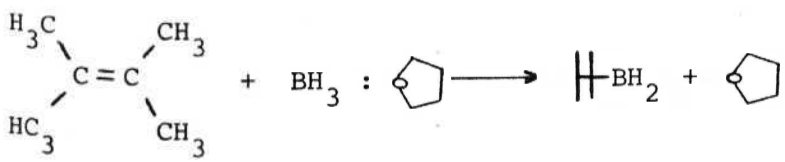
$$2R_2BH \rightleftharpoons R_2BH_2BR_2 \qquad (12)$$

$$BH_3 + R_3B \rightleftharpoons RBH_2 + R_2BH \qquad (13)$$

$$2RBH_2 \rightleftharpoons R_2BH + BH_3 \qquad (14)$$

$$2R_2BH \rightleftharpoons R_3B + RBH_2 \qquad (15)$$

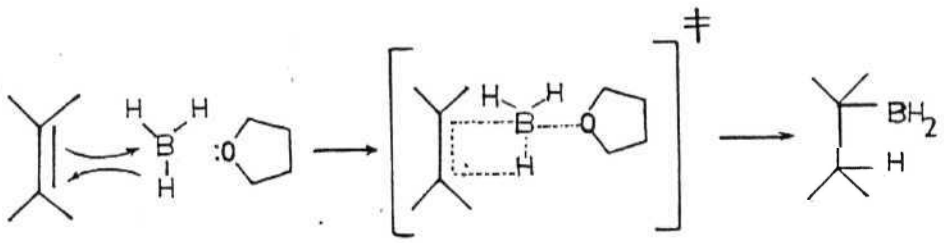
However, kinetic studies had been carried out for the hydroboration of tetramethylethylene in BH_3.THF which is known to give monoalkylborane species.[11]



(16)

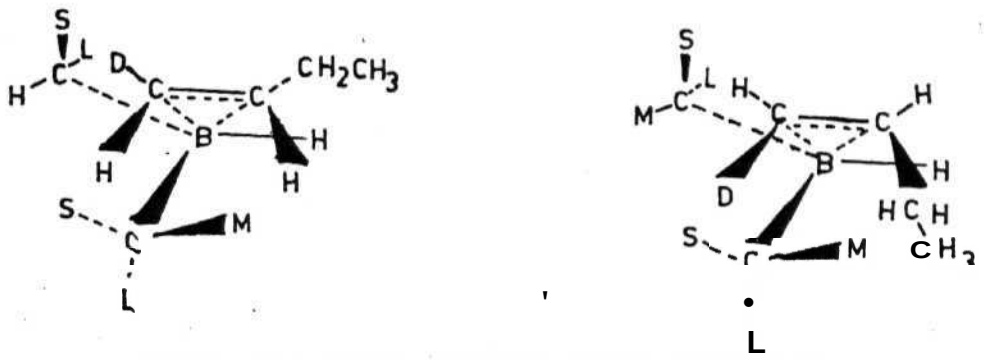
The rate of formation of thexylborane was found to be first order in both BH_3.THF and tetramethylethylene with an activation energy of 9.2 Kcal/mole and entropy of activation of -27 e.u.[11] The hydrogen-deuterium (>B-H(D)) kinetic isotopic effect (k_H/k_D) was found to be 1.18.[11] On the basis of these results, the reaction was considered to involve the direct reaction between a molecule of BH_3.THF and alkene with partial displacement of THF by the olefin in a very early transition state in which the molecule of THF is still rather tightly coordinated with boron atom[11] (Scheme 1).

Scheme 1



It was noted that these studies do not provide any information regarding the possible formation of an intermediate BH_3-olefin π complex for the reaction.[11]

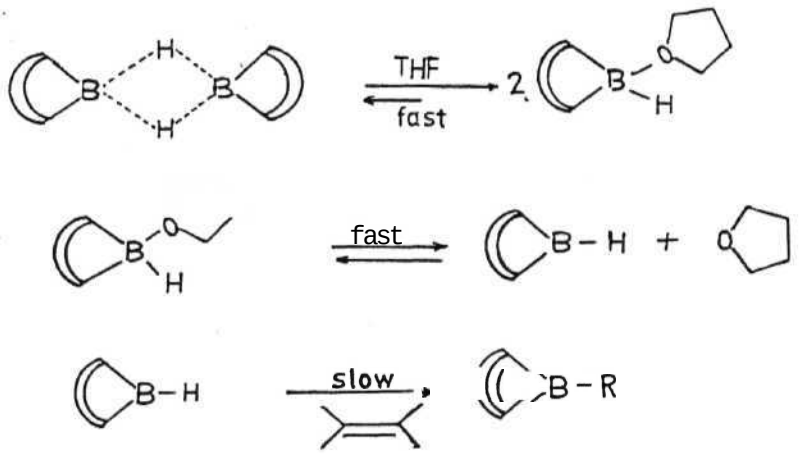
It has been reported that the asymmetric hydroboration of cis-1-butene-d by diisopinocampheylborane can be rationalised considering the formation of a triangular π -complex and that the transition state involves a relatively small perturbation from this triangular structure.[18] It was shown that the four centred rectangular transition state proposed earlier gave incorrect prediction in this case (Fig.1,2).[18]



S,M,L are small medium, large groups in diisopinocampheylborane

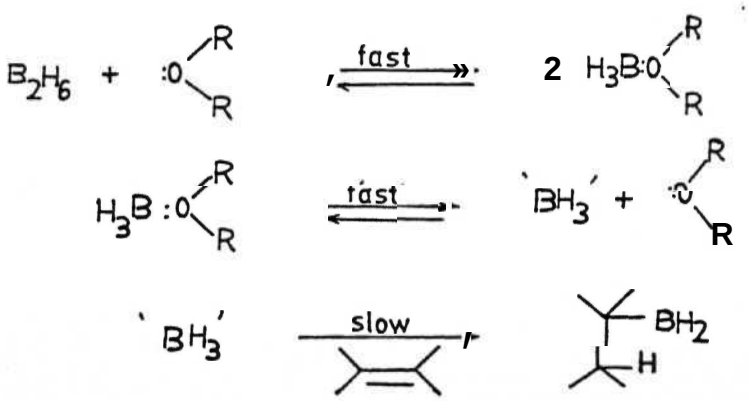
The kinetic data obtained for the hydroboration of olefins with several dialkylborane complexes have been reviewed recently.[8,7] The data were interpreted by considering the mechanism outlined in Scheme 2.

~~Scheme 2~~



On the basis of these studies, a similar mechanism was proposed for the hydroboration of olefins with diborane in ether solvents (Scheme 3).

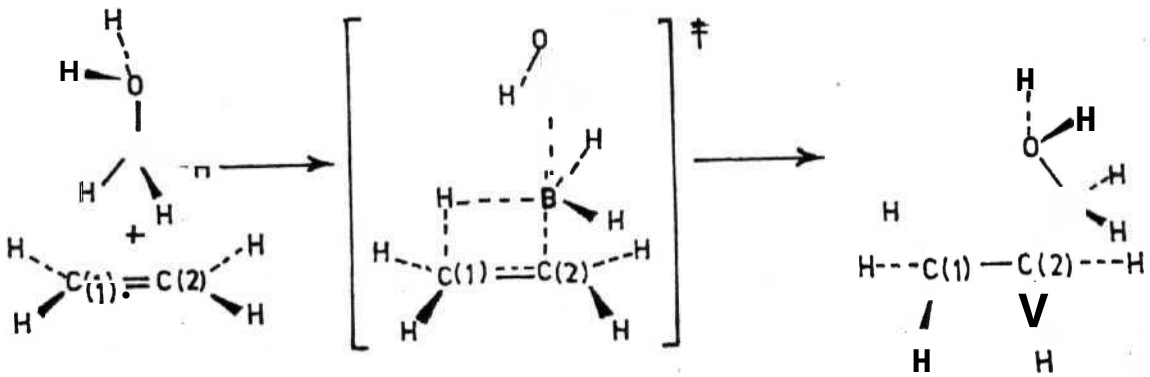
Scheme 3



As pointed out earlier, it was suggested that since the ether solvents provide the alternate pathway (Scheme 3) for the formation of the reactive species (i.e. BH_3 monomer), the catalytic effect of ether solvents can be readily explained on the basis of this mechanism.[7-9]

This mechanistic proposal involving free 'BH_3' monomer formation was questioned.[14] It was pointed out that since the complexation energy of BH_3 monomer with the solvent must be strong enough to overcome the dimerization energy ($2BH_3 \longrightarrow B_2H_6$, -36 Kcal/mol), spontaneous dissociation of BH_3.THF into free BH_3 monomer visualized in Scheme 3, is energetically implausible.[14] On the basis of ab initio calculations for the reaction of ethylenc with $H_3B{:}OH_2$ complex (a model for hydroboration in ether solvents), it was concluded that the reaction resembles an S_N2 displacement of the solvent by the olefin and the solvent plays essentially no role in the transition state but BH_3 never becomes free during the reaction[14] (Scheme 4).

Scheme 4

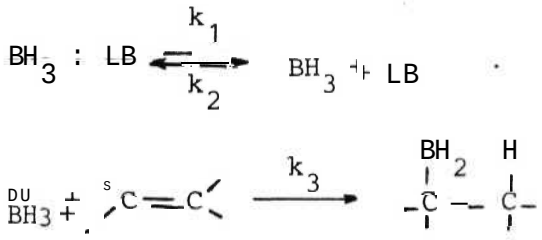


It was contended that the vacant p-orbital of BH_3 must always be engaged; in B_2H_6, in the BH_3-solvent complex and in the hydroboration

transition state.[9] It was also suggested that the solvent in BH_3-solvent complexes provides a better leaving group than the second BH_3 in B_2H_6 and hence the catalytic effect of ether solvents on the hydroboration of alkenes with diborane can be easily explained.[14]

However, strong kinetic evidence for an intermediate formation in the hydroboration reaction has been presented.[9,10] For example, it was observed that the addition of Lewis bases suppresses the rate of hydroboration of olefins with BH_3-Lewis base complexes and the second order rate constants decrease as the reaction progresses.[9,10] These findings indicate that the formation of Lewis-base along with the reactive intermediate in an equilibrium step from the BH_3-Lewis base complex prior to >B-H addition to the olefin (i.e. an S_N1 like mechanism, Scheme 5).[10] It was proposed that the intermediate is the free 'BH 3' monomer.[9]

Scheme 5



Steady state treatment will give the following rate law for this dissociation mechanism (eq.17).

$$-\frac{dp}{dt} = \frac{k_1 k_3 [BH_3LB]\ [Olefin]}{k_2[LB] + k_3[Olefin]} \qquad (17)$$

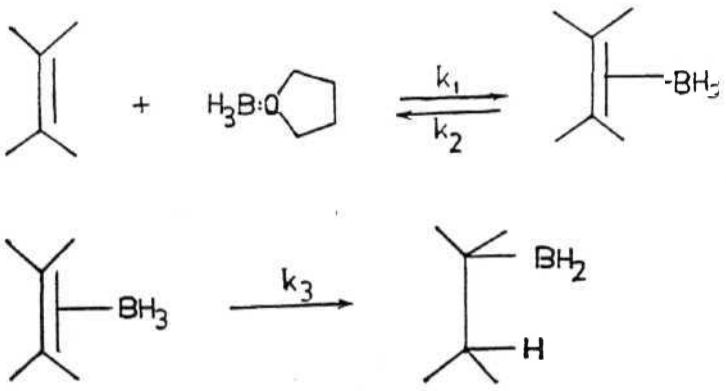
It was pointed out that this rate law will reduce to eq. 18 in the presence of excess LB, k_2 [LB] >> k_3 [olefin]

$$\frac{dp}{dt} = \frac{k_1 k_3 [BH_3LB]\ [Olefin]}{k_2[LB]} \qquad (18)$$

It was argued that the kinetic data obtained previously for the reaction of BH_3.THF with tetramethylethylene in THF[11] can be also rationalised by this rate law (eq. 18) as the LB (i.e. THF) will be in large excess.

Although the rate retardation effect observed clearly points out a reactive intermediate formation in an equilibrium step along with the Lewis-base prior to >BH addition, it is still not clear that such an intermediate is the free 'BH_3' monomer. It should be pointed out that the data can be readily explained by considering the mechanism (Scheme 6) involving the formation of a Dewar type olefin $-BH_3$ π complex along with the Lewis base in an equilibrium step prior to rearrangement to alkylborane.

Scheme 6



Steady state treatment for this mechanism will give the rate law given in eq. 19 and 20.

$$-\frac{dp}{dt} = \frac{k_1 k_3 [BH_3LB] [Olefin]}{k_3 + k_2[LB]} \quad (19)$$

$$-\frac{dp}{dt} = \frac{k_1 [BH_3LB] [Olefin]}{1 + k_2/k_3 [LB]} \quad (20)$$

This rate law (eq.20) will also explain the rate retardation effect fc>y the addition of excess Lewis bases and also it will reduce to the rate law given in equation 18 in the presence of excess Lewis base, if $\frac{k_2}{k_3}$ [LB] >>1.

Surprisingly, the mechanism involving π-complex formation outlined in Scheme 6 was not considered for explaining the rate retardation effect observed by the addition of Lewis bases.[9,10] However, almost all other contributors to the mechanistic studies of the hydroboration reaction considered the possibility of olefin-BH_3 π-complex intermediate for the reaction.[11-20]

As outlined previously, the TT-complex intermediate was proposed to account for the stereochemical outcome in the asymmetric hydroboration of cis-1-butene-d by diisopinocampheylborane.[18] The π-complex intermediate was later considered as an alternate pathway to the apparent symmetry forbidden process of the concerted >B-H σ bond addition to the C-C π bond.[17] However, it was soon pointed out that if the involvement

of vacant p-orbital on boron in BH_3 monomer or the back lobe of the BH_3-Lewis base bond are taken into account, the process will be allowed by orbital symmetry considerations.[11]

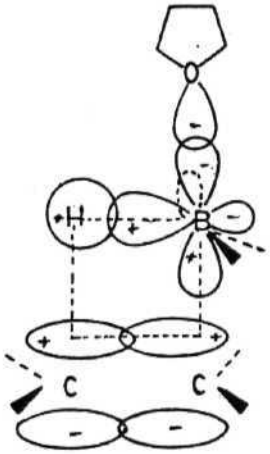


Fig. 3

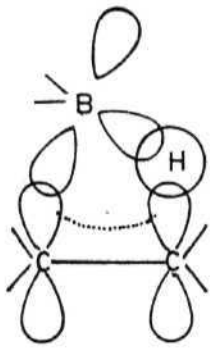


Fig. 4

Gas phase reaction of BH_3 monomer generated from H_3BPF_3 with ethylene was found to have an activation energy of 2±3 Kcal/mole.[21] A loose BH_3-olefin π complex formation prior to hydroboration was suggested.[21]

Theoretical studies of the hydroboration reaction involving BH_3 monomer have lead to the suggestion of a BH_3-olefin π complex as an energy minimum with varying energy relationships to the ground state and transition state.[15] It was predicted that it might be possible to isolate BH_3-acetylene π-complex in matrices at low temperature.[16]

On the basis of ab initio calculations, it was pointed out that the dominant interaction in the early stages of the hydroboration reaction is between the ethylene π-HOMO and the vacant p-orbital (LUMO) of the

BH_3 monomer leading to the formation of the π-complex.[15] It was also reported that the interaction of the ethylene π^* LUMO with one of the degenerated BH_3 HOMO's is initially weak but becomes progressively more important as the reaction proceeds and eventually leads to the delivery of hydrogen from boron to carbon.[15]

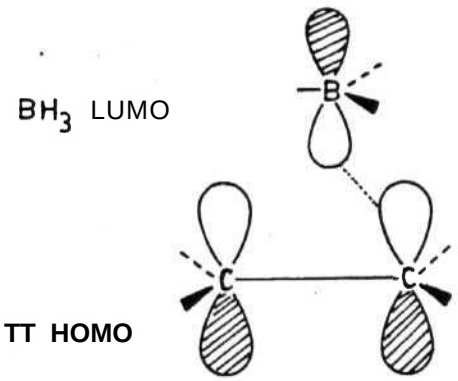


Fig. 5

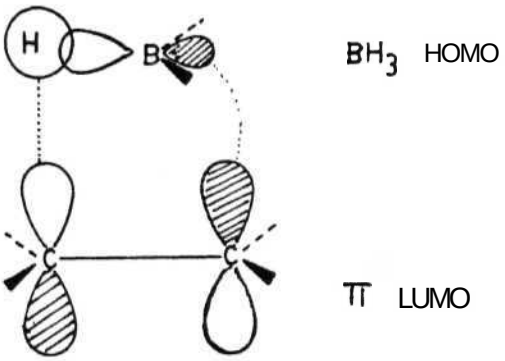


Fig. 6

As outlined previously,[14] on the basis of ab initio calculations for the reaction of ethylene with BH_3OH_2 (model for BH_3.THF), it was concluded that the reaction resembles an S_N2 like mechanism (Scheme 6).[14] It was also suggested that the molecular orbital changes in such a reaction are analogous to those outlined above for the BH_3 monomer reaction with ethylene (Fig.5 and Fig.6) except that the initial donor-acceptor interactions between olefin HOMO and BH_3 LUMO has been replaced by the interaction with the σ^* MO of the $BH_3:OH_2$ complex.[14] It was also reported that the displacement of water is essentially complete before the delivery of hydrogen from BH_3 HOMO to the ethylene LUMO becomes important. However, no comment was made regarding the possibility of a BH3-olefin π-complex formation in this case.[14]

Theoretical calculations have been reported to indicate that

the π-complexes formed in the reaction of substituted ehtylene are unsymmetrical.[13] For example, cyanoethylene prefers to form Markovnikov π-complex leading to placement of boron on the internal position in the alkylborane product and propylene gives anti-Markovnikov π-complex leading to placement of boron on the terminal position.[13] It was suggested that the presence of solvent molecule during >B-H addition to the olefin is not necessary to account for the observed regioselectivity of hydroboration involving simple monosubstituted alkenes such as propylene with borane.[13]

Two compilations appeared summarising the data available in 1979[22] and in 1982.[23]

In the compilation published in 1979,[22] it was concluded that the reaction of BH_3.THF in solution can be considered as involving partial nucleophilic displacement of the THF by interaction of one of the p-orbitals of the π-electron system with the back lobe of the sp^3 orbital on boron involved in the bonding with the oxygen atom of THF. At the same time there is development of bonding between the hydrogen 1s orbital with the other p-orbital of the TT system. This view is essentially same as that proposed for the S_N2-like mechanism.[11] It was also suggested that such a transition state may be preceded by π-complex formation and the molecule of THF must ultimately either become dissociated as the transition state proceeds beyond the point of maximum energy or it must migrate to the boron orbital vacated by the hydrogen atom.[11]

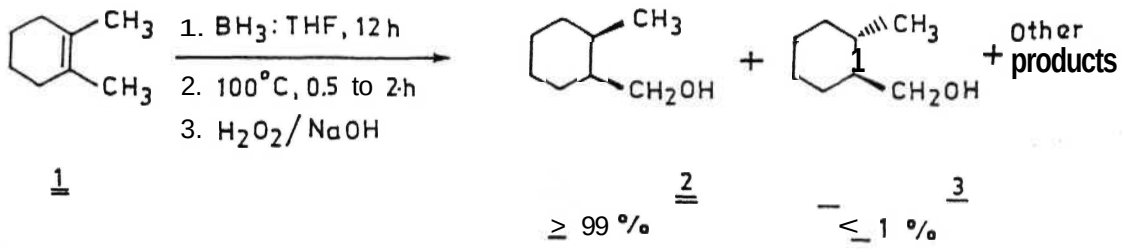
In the 1982 compilation,[23] it was concluded that the data available

in 1982 for hydroborations with borane in solution are more consistant with a concerted [2+2] cycloaddition involving a BH_3.THF complex rather than with a rate determining π-complex formation and in the gas phase, a loose TT complex is probably formed early along the reaction coordinate.[23]

It is interesting to note that both these compilations did not consider the possibility of dissociation of BH_3.THF into free BH_3 monomer before addition of B-H moiety to the olefin.[20,23]

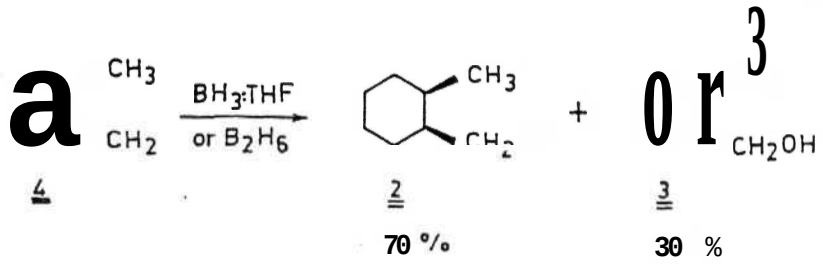
A convincing evidence for π-complex formation in the dehydroboration reaction has been presented.[20] It has been observed that the hydroboration/rearrangement/oxidation of 1,2-dimethylcyclohexene gave the products 2/3 in the ratio > 99:1 which indicates substantial suprafacial selectivity (Scheme 7).

Scheme 7



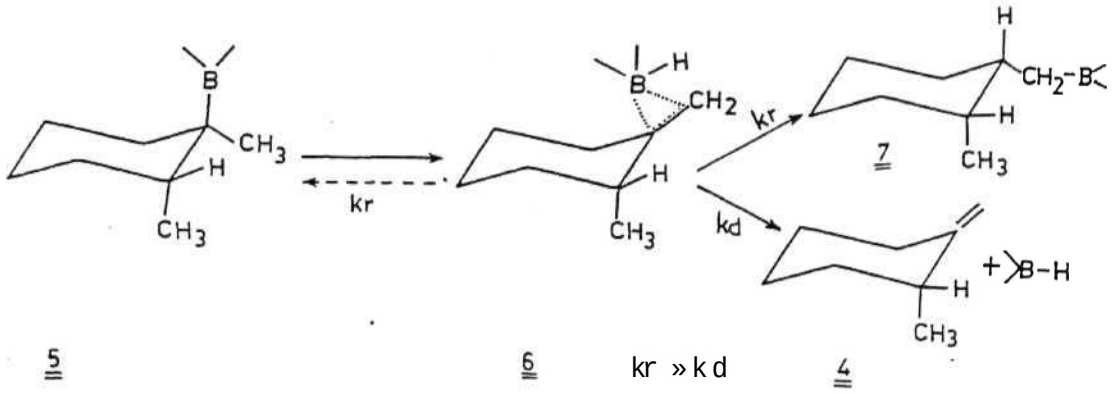
It was demonstrated that the hydroboration-rearrangement does not take place through dissociation of the intermediate alkylborane to the 2-methyl-1-methylene cyclohexene and H-B< (Scheme 8) followed by re-hydroboration since this olefin on reaction with either BH_3.THF or B_2H_6 followed by oxidation gives only a 70:30 mixture of 2 and 3 (Scheme 8).[20]

Scheme 8



It was concluded that the observed stereoselectivity provides strong support for an intramolecular process, most likely involving an intermediate π-complex, which must give rearranged alkylborane faster than dissociated entities (Scheme 9).

Scheme 9



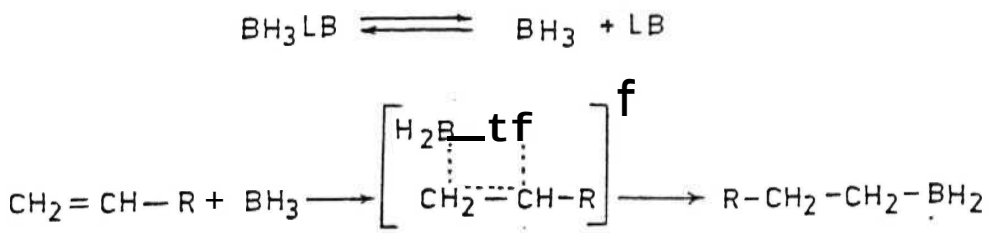
It was observed that the stereochemical results are the same both in the presence or absence of THF, indicating that the solvent plays no critical role in the above intramolecular migration.[20] The rearrangement results were considered in the context of the mechanism of hydroboration and it was suggested that principle of microscopic reversibility would predict a π-complex intermediate for the reverse reaction (i.e. hydroboration) but it was concluded that such an inter-

mediate must be different from that involved in the rearrangement process as the two reactions differ in conditions (temperature, possibly structure of reactants). The authors noted that this conclusion is surprising considering close similarities of the two processes. In any case, this excellent piece of work necessitates that the mechanism involving intermediacy of π-complex should be also considered in the interpretation of data.

From the foregoing survey, three general mechanistic pictures can be deduced for the hydroboration of alkenes with BH_3:LB complexes.

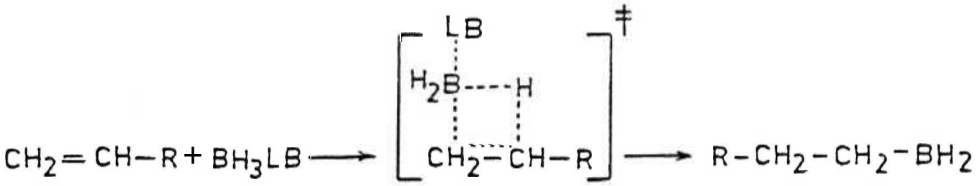
(1) S 1-like mechanism: Involving free 'BH_3' monomer formation in an equilibrium step (Scheme 10).

Scheme 10



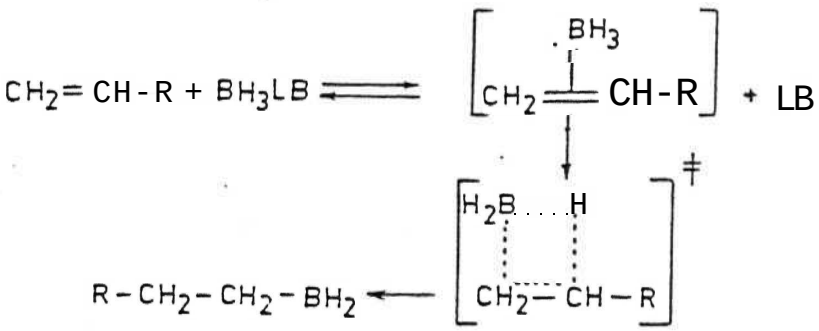
(2) S_N2-like mechanism without any intermediate (Scheme 11).

Scheme 11



(3) Mechanism with π-complex Intermediate: The LB may or may not be present in the transition state of the B-H-addition (Scheme 12).

Scheme 12



From these mechanistic pictures, it is clear that in the S_N1-like mechanism, the Lewis base is absent in the transition state while the >B-H addition to C-C double bond takes place (Scheme 10). It is also clear that in the case of S_N2-like mechanism (without any intermediate), the Lewis base is present in the transition state while the >B-H moiety is added to the olefin (Scheme 11). It is not understood whether the Lewis base will be present or absent in the transition state of the >B-H addition to the olefin in the mechanism with π -complex intermediate (Scheme 12). The possibility of the Lewis base interacting with the boron while the hydrogen is delivered from boron to carbon in the π-complex cannot be completely ruled out. However, any such interaction may not influence the stereochemical outcome very much since the >BH addition here is an intramolecular rearrangement.

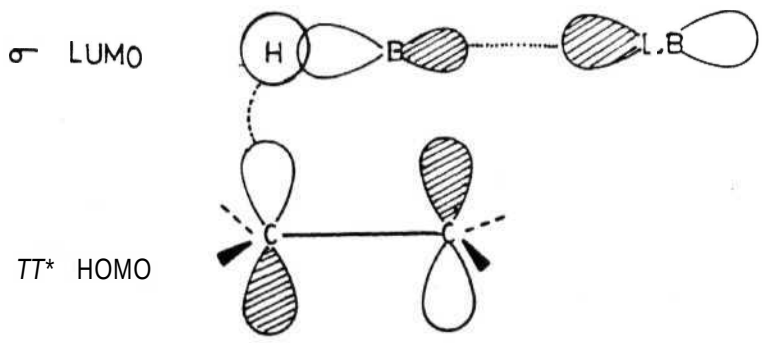
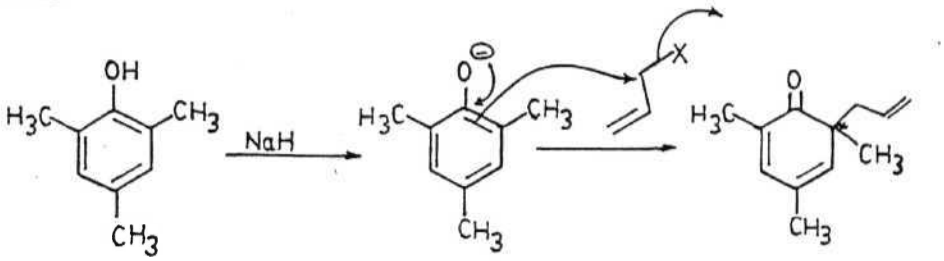


Fig. 7

Answer to the question whether the Lewis base is present or **absent** in the transition state will facilitate the understanding of the mechanism of this important and interesting **reaction.**

In a typical S_N2 displacement reaction, a chiral leaving group is known to give asymmetric induction upto 8.4%ee. This indicates that the presence of a chiral leaving group in the transition state leads to asymmetric induction[24] (Scheme **13).**

Scheme 13



X = Camphor - 10 - Sulphonate

Chiral amine-borane complexes are known to give asymmetric reductions of prochiral ketones into the corresponding alcohols to the **extent** of 42% in the presence of $F_3B{:}OEt_2$.[26] Even in the absence of $F_3B.OEt_2$, chiral N-methyl-α-methylbenzylamine-BH_3 and N,N-dimethyl-α-methylbenzylamine-BH_3 complexes reduce acetophenone into 1-phenylethanol with 3.5 to 5%ee.[27,25] It was suggested that the observations of optical inductions in these cases are not in accord with dissociation of the amine-borane complexes followed by reduction of the ketone by BH_3.[25]

It occurred to us that the question whether the **Lewis** base is **present or absent in the hydroboration transition state can be examined**

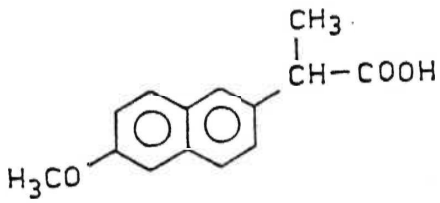
by utilizing chiral Lewis base-borane complexes for hydroboration of prochiral olefins.

RESULTS AND DISCUSSION

Synthesis of Chiral Lewis base precursors

The $RCOOH/NaBH_4$ system hydroborates alkenes (Chapter 1). It was thought that the hydroboration of prochiral olefins with a chiral carboxylic acid/$NaBH_4$ system will throw some light on the nature of the hydroborating species and also on the mechanism of the reaction.

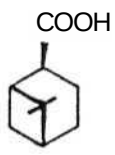
For the present studies, we have selected the commercially available (+)-2-(6-methoxy-2'naphthalene) propionic acid (11), supplied by Sigma, USA and (-) cis-myrtanic acid (12) which can be prepared from the commercially available (-)β-pinene via hydroboration (Scheme 14).



11

$[\alpha]_D^{20} = 61.2$ (C1, $CHCl_3$)

lit. $[\alpha]_D = 65.5$ (C1, $CHCl_3$)[28]

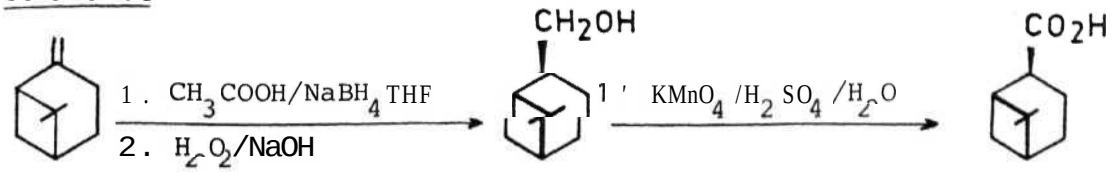


12

$[\alpha]_D = -41.26$ (C3.98, EtOH)

lit. $[\alpha]_D = +48.3$ (C4, EtOH)[29]

Scheme 14



13 14 12

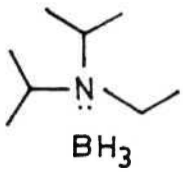
$[\alpha]_D^{20}$ = -21(Neat) $[\alpha]_D^{20}$ = -19.0(C11,CHCl3) $[\alpha]_D^{20}$ = -41.26C39,EtOH)

lit.$[\alpha]_D^{25}$=-22.8°(Neat)[30] lit.$[\alpha]_D$=-19.44(C11,$CHCl_3$)[31] lit.$[\alpha]_D$=+48.3(C4,EtOH)

Hydroboration of $-pinene with $CH_3COOH/NaBH_4$ followed by oxidation with H_2O_2/NaOH gave (-) cis-myrtanol (14). We have carried out the conversion of cis-myrtanol to cis-myrtanic acid (12) utilizing several oxidising reagents following related literature procedures (eg. PDC/DMF[32]; SeO_2[33] followed by oxidation of the aldehyde by Ag_2O[34]; chromic acid/acetone (Jones)[35]; $KMnO_4$/NaOH[36]; sodium bromate/HBr[37]; $KMnO_4/H_2SO_4$ in water system[29]). The yields were not satisfactory in all these cases. The method utilizing $KMnO_4/H_2SO_4$ in water without any solvent has been reported to give cis-myrtanic acid.[29] Following this method, we have obtained pure cis-myrtanic acid (12) in 23% yield with $[a]_D$ = -41.26 (C3.98, EtOH). We have followed this method for accumulating myrtanic acid for utilization in the present studies.

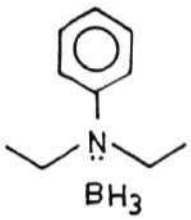
Although hydroborations utilizing chiral carboxylic acid/$NaBH_4$ system will certainly throw some light on the mechanism of the hydroboration reaction, as indicated in Chapter 1, there are some ambiguities about the precise structure of the hydroborating species in this system since the initially formed $RCOOBH_3$ species disproportionates into $NaBH_4$ and $NaB(OOCR)_4$.[38,39]

The amine bases form stable 1:1 complexes with BH_3.[22] Although many amine-borane complexes hydroborate alkenes only at elevated temperatures (> 100°C), some sterically hindered amine-borane complexes such as (15) and N,N-dialkylaniline derivatives (16) give rapid hydroborations.[9,22]



=

Reaction with 1-octene
in toluene at 75°, $t^1/2$ = 5 min.

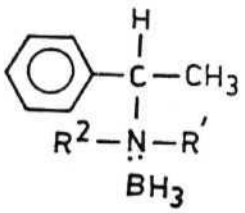


16

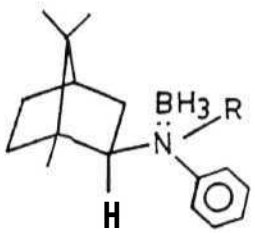
Reaction with 1-octene
in toluene at 25°C $t^1/2$ = 26 min.

In addition, the hydroboration of alkenes with these amine-borane complexes can be carried out in hydrocarbon solvents in the absence of any other Lewis base which is very much desirable for the present studies.

It appeared that the tertiary amine-borane complexes (17) and (18) which have structural features similar to (15) and (16) will hydroborate olefins at ambient temperature.



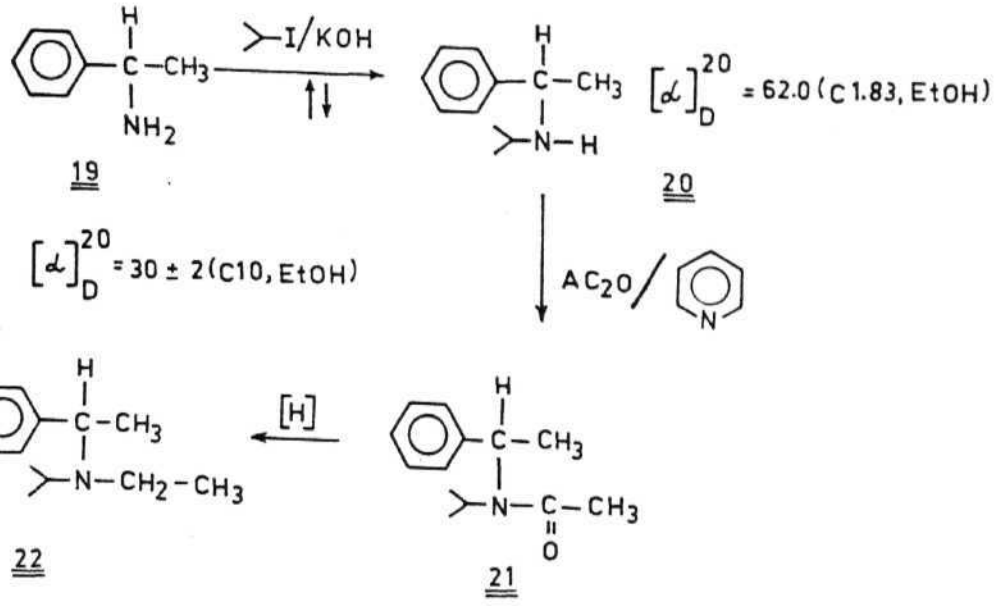
17



18

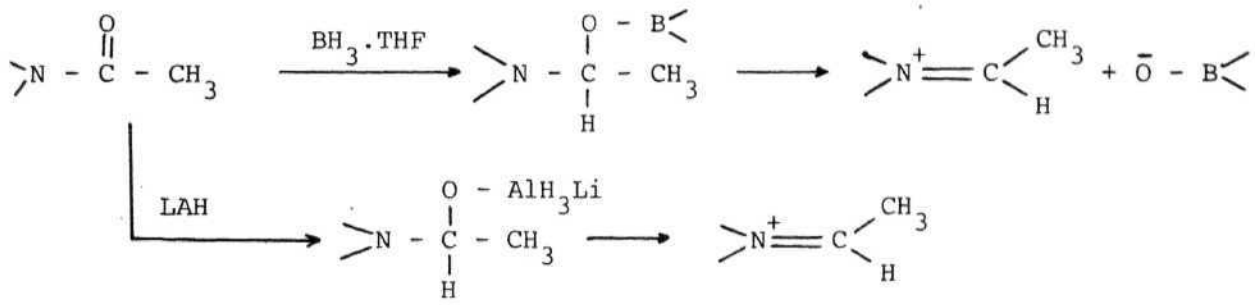
The synthesis of N-ethyl-N-isopropyl-α-methylbenzyl amine was envisaged as given in Scheme 15.

Scheme 15

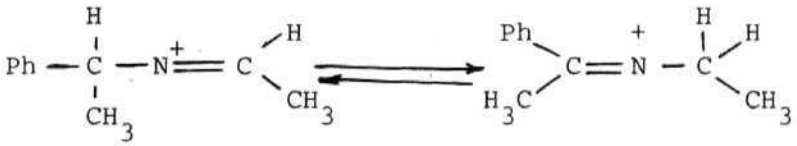


Isopropylation of R(+)-α-methylbenzylamine (19) gave isopropyl-α-methylbenzylamine (20) in 85% yield with $[a]_D$ = 62.0 (C1.83, EtOH) which on acylation with acetic anhydride/pyridine gave the amide (21) in 78% yield.[41] Reduction of the amide with LAH_3[42] gave the t-amine (22A) with $[\alpha]_D$ = 13.78 (C 3.434, EtOH). BH_3.THF reduction of the amide gave the t-amine (223) with $[\alpha]_D$ = 5.26 (C4.1824, EtOH). The results indicate that at least in the case of BH_3.THF reduction racemization takes place during the reaction. It is also possible that LAH reduction also may give some racemization since the mechanism of reduction in both cases are similar, involving the intermediacy of iminium ions[42,43] (Scheme 16).

Scheme 16



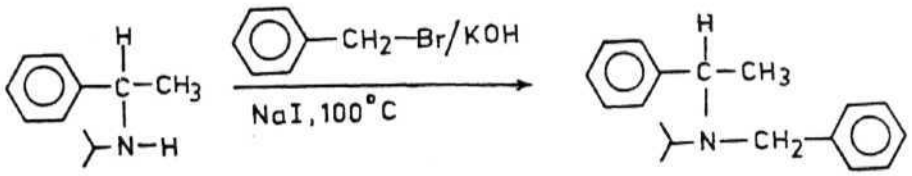
If the iminium ion undergoes the following equilibration, then racemization will result (eq.21). Although mechanism of such an equilibrium is not clearly understood, it is possible that it may proceed by the removal of the benzylic proton by the hydride reagent.[42]



(21)

Direct ethylation of the secondary amine (20) with n-BuLi and C_2H_5I was not successful. The reaction gave elimination of ethylene from C_2H_5I (gas evolution) and the starting secondary amine was recovered. Direct benzylation gave the corresponding tertiary amine (23) and it was utilized for the present studies.[40]

Scheme 17

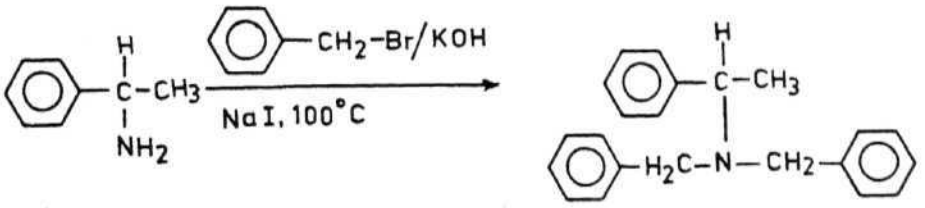


20 $[\alpha]_D^{20}$ = +62.0 (C1.83, EtOH)

23 $[\alpha]_D^{20}$ = 17.29 (C3.932, $CHCl_3$)

Similarly, N,N-dibenzyl-α-methylbenzylamine was also prepared (Scheme 18).

Scheme 18

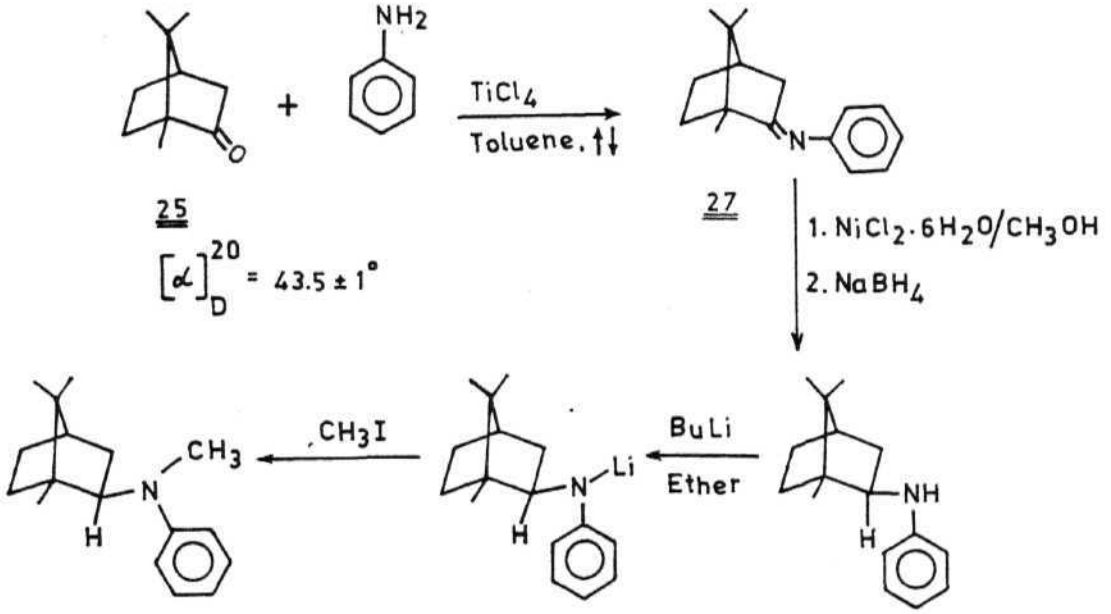


19 $[\alpha]_D^{20}$ = 30±2 (C10, EtOH)

24 $[\alpha]_D$ = 100.5 (C2.54, $CHCl_3$)

The N-methyl-N-isobornylaniline (30) was prepared by following closely related literature procedures as outlined in Scheme 19.

Scheme 19



25 $[\alpha]_D^{20}$ = 43.5 ± 1°

27

28 $[\alpha]_D^{20}$ = −71.5° (C11.6, EtOH)

29

30 $[\alpha]_D^{20}$ = −22.0° (C6, EtOH)

(+) Camphor (25) $(\alpha)_D$ = +43.5±1° supplied by Fluka, Switzerland was condensed with aniline in toluene in the presence of $TiCl_4$ at 125°C

to give camphor-anil (27) in 65% yield.[44] It is known that catalytic hydrogenation of camphor-anil (27) using Pt/C gives N-isobornylaniline (28).[45] We have observed that the Pt/C reduction of camphor-anil (27) gives N-isobornylaniline in 82% yield and the signals corresponding to the endo isomer are not found in the ^{13}C NMR spectrum of the product. We have tried several other methods for this conversion. Utilization of $Pd\text{-}C/H_2$ did not give any reduction.[46] Formic acid which is known to reduce enamines derived from camphor,[47] did not affect the conversion with the camphor-anil. However, $NiCl_2.6H_2O/NaBH_4/CH_3OH$ system[48] and $CoCl_2/NaBH_4/CH_3OH$ systems[49] gave the desired N-isobornylaniline in 75% and 82% yield respectively. We have utilized the $NiCl_2.6H_2O/NaBH_4/CH_3OH$ reagent system for accumulating the amine required for the present studies.

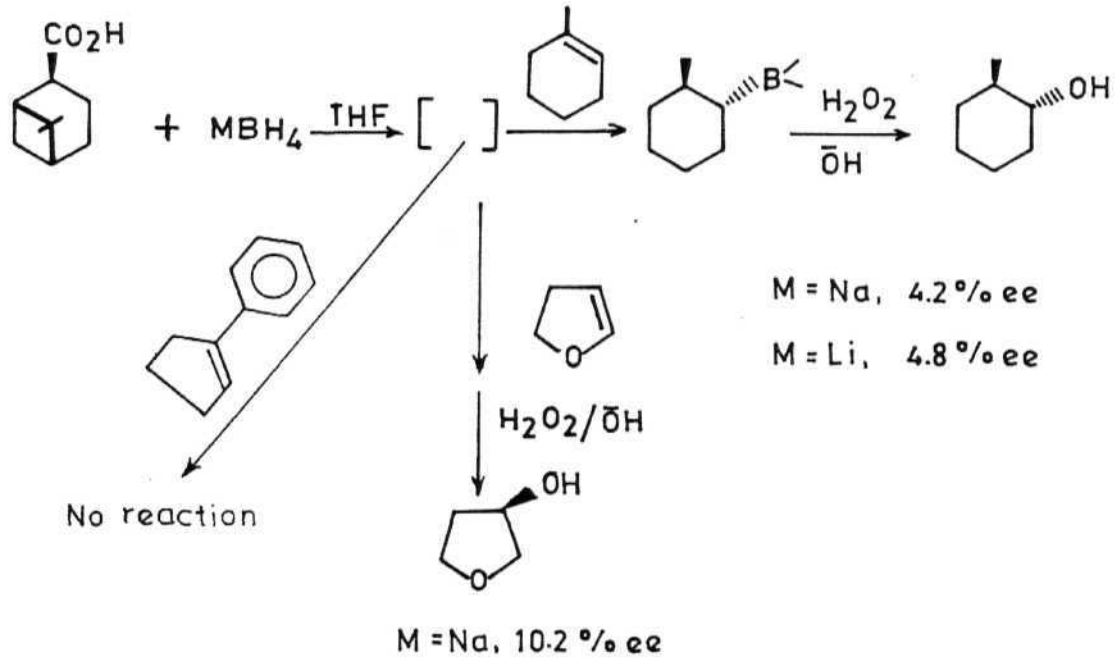
Initially we have carried out the methylation of the N-isobornyl aniline (28) with the $HCHO/HCO_2H$; $HCO_2H/H_2SO_4/NaBH_4$ method[50,51] but the yield was poor. Methylation with CH_3I after preparation of the amide (29) from N-isobornylaniline gave better results.[40] The N-methyl-N-isobornylaniline (30) obtained in this way was chromatographed on a silica gel column using hexane/chloroform as eluent. The chromatographed tertiary amine was distilled under reduced pressure before utilization in the preparation of the corresponding BH_3 complex.

Hydroboration of prochiral olefins with BH_3-chiral Lewis base complexes

The hydroboration of 1-methyl-1-cyclohexene with the cis-myrtanic acid/$NaBH_4$ in THF for 24 h at room temperature followed by oxidation

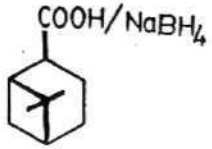
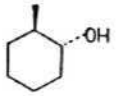
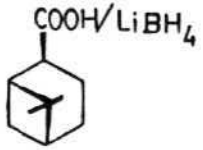
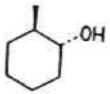
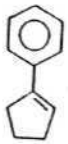
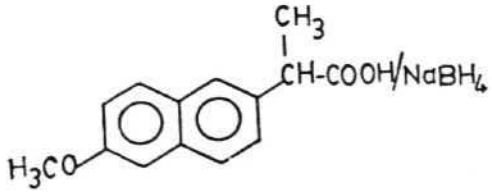
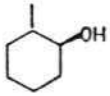
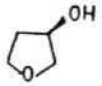
with H_2O_2/NaOH gave the trans-2-methylcyclohexanol in 60% yield with an enantiomeric excess of 4.2% (Table 3.1). Hydroboration of 1-methyl-1-cyclohexene utilizing cis-myrtanic acid/$LiBH_4$ system followed by oxidation gave the trans-2-methylcyclohexanol in 53% yield with 4.8%ee. Both the cis-myrtanic acid/$NaBH_4$ and cis-myrtanic acid/$LiBH_4$ systems failed to hydroborate 1-phenyl-1-cyclopentene even after 72 h at room temperature. We have found that under the same conditions $CH_3COOH/NaBH_4$ system does not have any problem in reacting with 1-phenyl-1-cyclopentene and 68% of trans-2-phenylcyclopentanol can be isolated after oxidation (Scheme 20). Hydroboration-oxidation of 2,3-dihydrofuran with this system gave 3-hydroxytetrahydrofuran in 68% yield with 10.2%ee.

Scheme 20

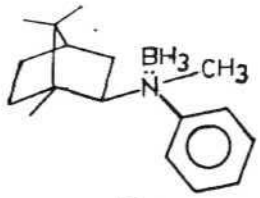
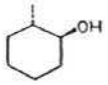
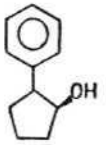
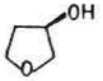
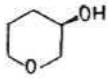
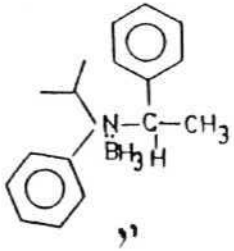
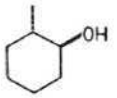
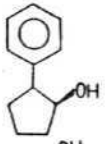
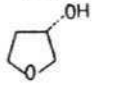
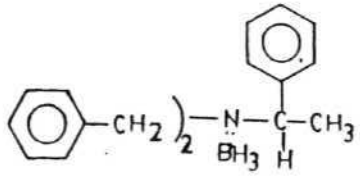
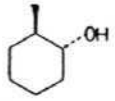
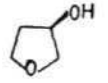


Hydroboration of 1-methyl-1-cyclohexene with the (+)2-(6'-methoxy-2'-naphthalene)propionicacid/$NaBH_4$ system followed by oxidation gave trans-2-methyl-1-cyclohexanol in 68% yield with 2.4%ee (Table 3.1).

Table 3.1 : Hydroboration of prochiral alkenes using chiral Lewis-base complexes.[a]

Entry No.	Olefin	Borane/LB	Reaction time (h)[b]	Product[c]	Yield (%)	$[\alpha]_D^{20}$(C,solvent)[d]	% ee.[i]
1.			24		60	+1.82 (C2.748,CH_3OH)[e]	4.22
2.		"	72	No reaction			
3.		"	12		68	-1.76(C2.832,CH_3OH)[f]	10.2
4.			48		53	+2.08(C2.4,CH_3OH)	4.82
5.		"	72	No reaction			
6.			14		68	-1.06(C2.83,CH_3OH)	2.44
7.		"	12		70	-1.60(C2.5,CH_3OH)	9.2

contd.

8.			24		70	-1.66(C3.86,CH_3OH)	3.9
9.		"	48		63	-0.22(C9,EtOH)[g]	0.31
10.		"	4		76	-3.30(C2.4,CH_3OH)	19.2
11.		"	4		68	-1.25(C4,CH_3OH)[h]	-
12.			24		62	-1.50(C3.33,CH_3OH)	3.4
13.		"	48		60	0.84(C8.33,EtOH)	1.2
14.		"	12		69	+2.00(C2.5,CH_3OH)	11.6
15.			24		55	1.08(C3.7,CH_3OH)	2.5
16.		"	12		67	-1.60(C2.5,CH_3OH)	9.2

contd.

a. The reactions were repeated several times in each case and the measured observed rotations always fell within ±0.01° which is also the accuracy limit of the polarimeter (Autopol II automatic polarimeter). In each case, the condition of the polarimeter was checked by measuring a standard solution of either camphene, $[\alpha]_D^{20} = +17\pm1°$ (C4,Ether) or α-Methylbenzylamine $[\alpha]_D^{20} = +30\pm2°$ (C10,EtOH) supplied by Fluka. The differences in the observed rotations of standard solutions in different runs also fell within ±0.01°. The polarimeter was set to zero reading using the solvent used. Same concentration of racemic compounds were also run and in all cases the reading of racemic compound fell within ±0.01°.

b. Time required for getting optimum chemical yields.

c. Product obtained after oxidation with H_2O_2/NaOH. Products were identified by analysis of spectral data (IR and ^{13}C NMR) and comparison with reported data.

d. In each case the optical rotations were measured in two concentrations and the values for concentrations closer to the concentrations utilized in the literature $[\alpha]_D$ values are given here.

e. Based on the maximum $[\alpha]_D^{25} = +43.1°$(C1,MeOH) (ref.52).

f. Based on the maximum $[\alpha]_D^{25} = -17.3$(C2.4, MeOH) (ref.54)

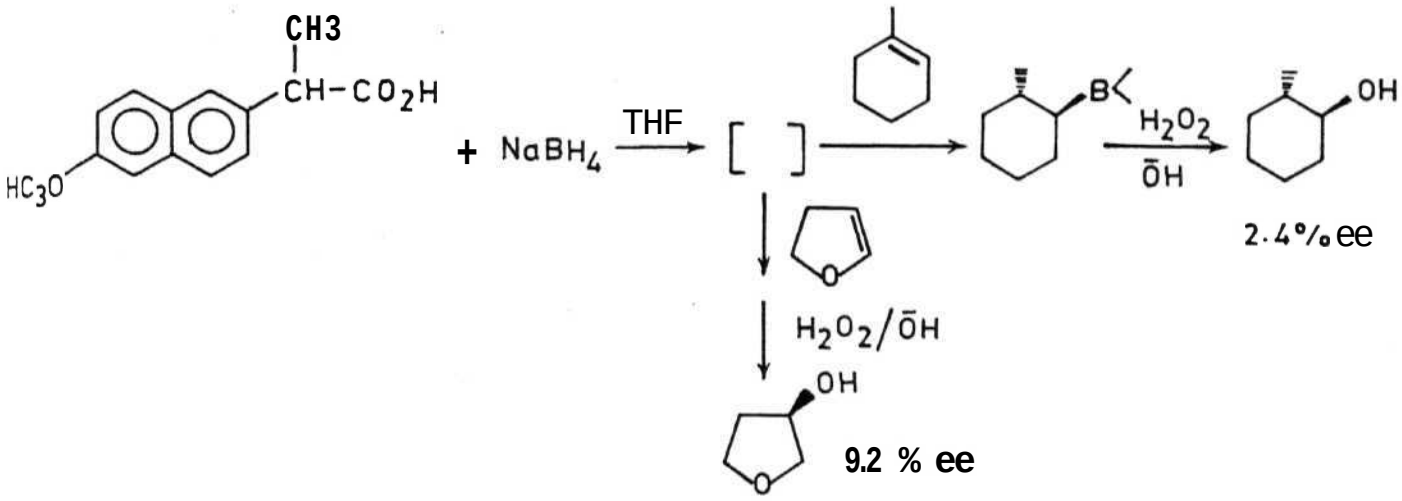
g. Based on the maximum $[\alpha]_D^{25} = +71.1°$(C11.9,EtOH) (ref.53).

h. Based on the maximum $[\alpha]_D^{25} = -11.8$ (neat) (ref.55).

i. Enantiomeric excess.

Hydroboration of 2,3-dihydrofuran followed by oxidation gave the 3-hydroxy-tetrahydrofuran in 70% yield with 9.2%ee (Table 3.1) (Scheme 21).

Scheme 21



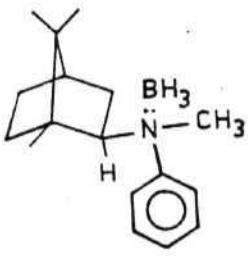
Although the alcohols obtained after distillation were essentially pure (no additional signals in ^{13}C NMR spectra) they were further purified by chromatography on a silica gel column and again distilled under **reduced** pressure before optical rotations were measured.

Asymmetric induction of 2.4%ee to 10.2%ee observed in the above experiments indicate that the acyloxy groups do have some influence on the hydroboration of alkenes. However, there is ambiguity about the structure of the hydroborating species here. As outlined in Chapter 1, it has been found that the mixing of $RCOOH/MBH_4$ system, does not give **cleanly** $CH_3\overline{COOBH}_3$. The resulting species are MBH_4 and $MB(OCOR)_4$[38] or MBH_4 in equilibrium with $MBH_3(OOCR)$, $MBH_2(OCOR)_2$, $MBH(OCOR)_3$ and $MB(OCOR)_4$.[39] However, the fact is that the $RCOOH/MBH_4$ system is able **to hydroborate alkenes. Both** the **chiral carboxylic** acid/MBH_4 **systems**

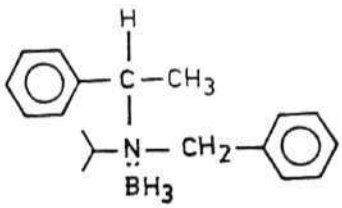
studied here on treatment with Ph_3P gave Ph_3PBH_3 in essentially quantitative yields. Clearly, the $RCOOH/MBH_4$ system is able to supply 'BH_3' moiety. It is known that among the three acyloxyborohydride species, the $NaBH_3OAc$ is the most reactive species in reductions (i.e. $NaBH_3OAc$ > $NaBH_2(OAc)_2$ > $NaBH(OAc)_3$ and under the conditions where the $NaBH(OAc)_3$ will be the species present (neat carboxylic acid/$NaBH_4$) no hydroboration is observed.[56] Accordingly, most probably $NaBH_3OCOR$ will be the hydroborating species in the $RCOOH/NaBH_4$ systems.

Observation of asymmetric inductions in the hydroboration/oxidation of prochiral alkenes with the above $RCOOH/NaBH_4$ systems points out that the acyloxy groups in these cases do have some influence in the transition state of the hydroboration reaction. However, since there is ambiguity about the precise structure of the reactive species in the $RCOOH/NaBH_4$ systems, we have decided to study the mechanism of hydroboration reaction further utilizing chiral amine-borane complexes for hydroboration.

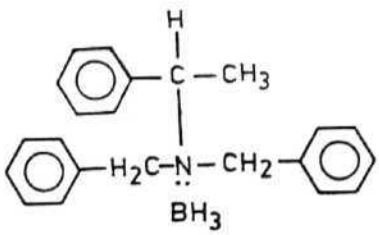
The amine-borane complexes (31), (32) and (33) can be readily prepared in benzene utilizing the $I_2/NaBH_4$ reagent system for diborane generation as outlined in Chapter 2.



31



12



33

The amine-borane complex prepared in benzene utilizing 10 mmol

of the amine gives 10 mmol of Ph_3PBH_3 on treatment with 15 mmols of Ph_3P, confirming the formation of a 1:1 amine borane complex.

The hydroborations were carried out using 10 mmol of chiral amine borane complex in benzene (40 mL) with 10 mmol of prochiral olefins and the reactions were performed for the time indicated in Table 3.1. The reaction mixture was hydrolysed by careful addition of 3N HC1 (2 mL). Oxidation of the organoborane with $H_2O_2/\bar{O}H$ was carried out after adding 40 mL of dry THF in order to facilitate the oxidation. In runs with 1-methyl-1-cyclohexene and 1-phenyl-1-cyclopentene, the alkaline reaction mixture obtained after oxidation with $H_2O_2/\bar{O}H$ was extracted with ether several times and the combined ether layer was washed with 6N HCl (3x10 mL) to recover the chiral amine. In runs with 2,3-dihydrofuran and 3,4-dihydropyran, since the alcohols are water soluble, the alkaline reaction mixtures obtained after oxidation were saturated with solid anhydrous K_2CO_3 and extracted several times with ether. From the combined amine-alcohol residue obtained after evaporation of solvent, the alcohol could be readily distilled out under reduced pressure. Alternatively, the alkaline reaction mixture after oxidation with $H_2O_2/\bar{O}H$ was first extracted with ether (3x30 mL) to isolate the amine and the aqueous layer was then saturated with solid K_2CO_3 and the alcohol was isolated by extraction with ether. We have found that both these procedures gave comparable results but we find the latter method is more convenient. The optical rotation of the recovered amines remained unchanged.

The alcohols obtained in the hydroboration of prochiral olefins with chiral amine borane complexes (31, 32 and 33) were distilled under

reduced pressure, further purified by eluting through a silica gel column and distilled again under reduced pressure before optical rotations were measured. The data are summarised in Table 3.1.

As indicated in Chapters 1 and 2, the resulting organoboron species after hydroborations may not be monoalkylboron species and considerable amounts of dialkylboron species may also be present. In any case, the formation of dialkyl and trialkylboron species will not complicate the interpretation of the results because absence of Lewis base in the hydroboration transition state with either BH_3:LB or RBH_2:LB will not give any asymmetric induction.

The results obtained in the hydroborations utilizing various borane-chiral Lewis base complexes can be summarised as follows. The hydroboration-oxidation of 1-phenyl-1-cyclopentene gives trans-2-phenyl cyclopentanol in 0.3% to 1.2%ee. Hydroboration-oxidation of 1-methyl-1-cyclohexene results in the formation of trans-2-methyl-cyclohexanol in 2.5 to 4.8%ee. The reaction with 2,3-dihydrofuran yields 3-hydroxy-tetrahydrofuran in 9.2 to 19.2%ee.

Let us now consider these results in terms of the three mechanistic Pictures outlined earlier (Scheme 10-12).

The S_N1-like mechanism (Scheme 10) involves the dissociation of BH_3-Lewis base complex into free 'BH_3' and Lewis base followed by addition of the >B-H bond of the free 'BH_3' into the olefin through a four centred transition state.[8-10] The proposed mechanism implies

(Scheme 10) that the Lewis base is not bonded to boron during the actual hydroboration step and hence this mechanism cannot explain the asymmetric inductions obtained in the hydroboration of 1-methyl-1-cyclohexene and 2,3-dihydrofuran. In the case of 1-phenyl-1-cyclopentene, the observed inductions are almost negligible. However, it is doubtful that the mechanism involving free 'BH_3' intermediate would operate even here. For example, as mentioned previously, we have found that the cis-myrtanic acid/MBH_4 (M = Na or Li) system failed to react with 1-phenyl-1-cyclopentene even after 72 h at r.t. However, the $CH_3COOH/NaBH_4$ system does hydroborate 1-phenyl-1-cyclopentene under the same conditions. This difference in reactivity of the two $RCOOH/NaBH_4$ system cannot be explained assuming free 'BH_3' species as the hydroborating species.

The S_N2-like mechanism (Scheme 11) involving displacement of the Lewis base by the olefin during the addition of >B-H moiety to olefin can explain the asymmetric inductions observed in the case of 2,3-dihydrofuran and 1-methyl-1-cyclohexene. The results with 1-phenyl-1-cyclopentene may imply that the Lewis base does not have much influence in the stereochemical outcome in this case. However, it is possible that the mechanism may still be S_N2-like but the transition state may be 'late'[14] (i.e. the Lewis base departs to more extent before >BH addition) in this case and 'early' in the case of 2,3-dihydrofuran[11] with the transition state for 1-methyl-1-cyclohexene being in between the two extremes. It is of interest to note that enol ethers undergo faster hydroboration than alkyl substituted alkenes which in turn reacts faster than styrene derivatives.[23] It may be relevant to point out here that a referee of our preliminary communication on the topic suggested that the present data

can be interpreted in terms of 'early' transition state for the enol ethers and 'late' transition state for other olefins and the question of S_N1-like mechanism does not arise because free 'BH_3' formation is not possible in the hydrocarbon solvents utilized for the present studies.[57]

However, as outlined earlier, there are strong evidences for the formation of an intermediate in the hydroboration of olefins in some cases.[9,10] As pointed out in the introductory section, the intermediate may very well be a BH_3 olefin π complex, formed in an equilibrium step from olefin and BH_3.LB complex as given in the mechanism involving a TT-complex intermediate (Scheme 12).[18-20] As pointed out earlier, it is not clear whether the Lewis base will be present in the transition state while the rearrangement of the π-complex to alkylborane takes place. However, even if the Lewis base gets attached during rearrangement, its influence on the stereochemical outcome may not be very much as the >B-H addition here is an intramolecular rearrangement. It seems likely that the asymmetric inductions will be higher only if the reaction goes through without such a π-complex intermediate (Scheme 11 and 12). The present results can be explained by considering a spectrum of mechanisms between S_N2-like mechanism without intermediate and the mechanism with a TT-complex intermediate. Consideration of the interactions of the frontier orbitals of the reactants will further illustrate this point.[14-17]

As outlined in the introductory section, the frontier orbital interactions in the hydroboration reaction utilizing BH_3LB complex are the interaction of the olefin π-HOMO with the σ LUMO of the borane-

Lewis base bond and interaction of the olefin 71^* LUMO with the 0-HOMO of the one of the degenerate B-H bonds.[15] For enol ethers, the π-HOMO of the olefin will be higher in energy and will have larger coefficient in the β-carbon atom and hence the interaction between the β-carbon atom of the olefin and the σ LUMO of the boron-LB bond will be very much energy lowering and hence the carbon-boron bond formation will be facile (Fig.8). In addition, the delivery of the hydrogen from boron to the α-carbon atom of the enol ether will be also facile as the LUMO of enol ethers will have larger coefficient at the α-carbon atom (Fig. 9). Hence, it is likely that the hydroboration of enol ethers may take place in a concerted manner without the intervention of an intermediate.

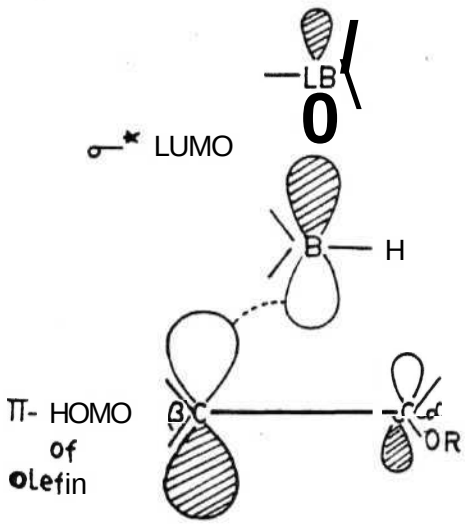


Fig. 8

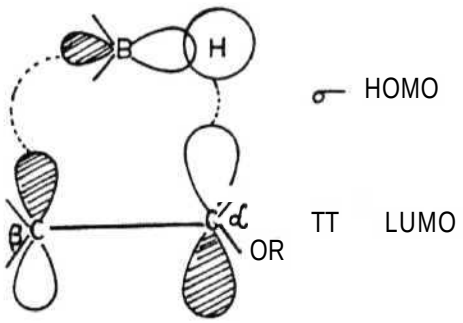


Fig. 9

Alkyl substitution affects the IT-HOMO of the olefin in a similar way and polarizes the HOMO to lesser extent compared to enol ethers. But the coefficients of LUMO of alkyl substituted olefins at α- and β-carbon atoms are the same (Fig. 10 and 11).[58] Phenyl substitution on ethylene affects the TT-HOMO of the olefin in the same way with polarization to lesser extent compared to enol ethers (Fig. 12 and 13) but the

LUMO will be polarised so that the coefficient is smaller at the α-carbon atom. This will make the delivery of the hydrogen from boron to α-carbon atom relatively difficult and hence in the case of 1-phenyl-1-cyclopentene the reaction is likely to go through stages.

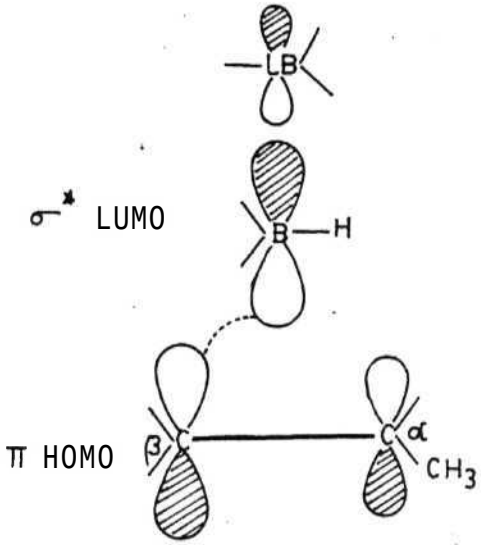


Fig 10

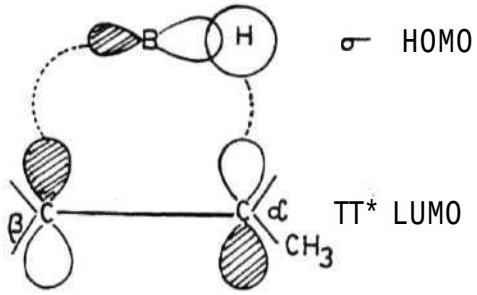


Fig.11

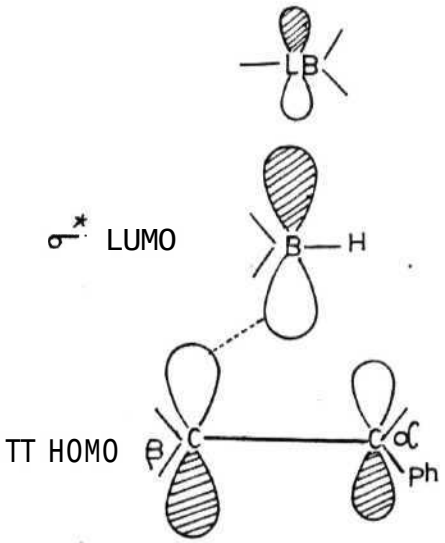


Fig.12

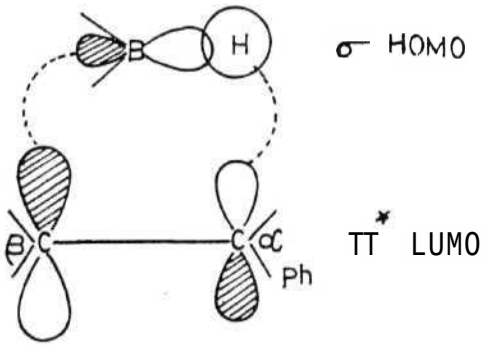


Fig. 13

In the above discussion considering the interactions of the frontier orbitals, the steric effects of the reagents which will certainly play a major role in determining the differences in the diastereomeric

transition states in each case are ignored. However, in the case of 1-phenyl-1-cyclopentene consideration of steric effects will also lead to same conclusion. The reaction in the case of sterically hindered olefins such as 1-phenyl-1-cyclopentene with borane Lewis base complexes will lead to a highly crowded transition state if the reaction goes through a concerted S_N2-like mechanism in which the Lewis base is present in the transition state. Accordingly, steric effects would also shift the mechanism away from the S_N2-like mechanism involving concerted formation of carbon-boron bond and carbon-hydrogen bond.

The present data along with the existing - data in the literature indicate that there is a spectrum of mechanisms possible for the hydroboration reaction, depending on the reactivity of the substrate. However, it should be pointed out that parallel operation of more than one mechanism in each case cannot be also ruled out.

C O N C L U S I O N

Hydroboration of prochiral olefins were carried out utilising five chiral Lewis base-borane systems. Oxidation of the resulting organoboranes gave alcohols with 0.3 to 19.2% enantiomeric excess. The results were considered in the context of mechanisms proposed by various workers for the hydroboration reaction. The results indicate that there is a spectrum of mechanisms possible for the hydroboration reaction.

EXPERIMENTAL

General details:

Several of the general experimental details outlined in Chapter 1 and 2 are also applicable here. +6-methoxy-β-naphthalene-2-propionic acid, $[\alpha]_D$ = +65.5° (C1, $CHCl_3$) supplied by Sigma, USA was utilized. β-pinene, $[\alpha]_D$ = -21° (neat) supplied by Tokyo Kesai, Japan was used for the synthesis of (-) cis-myrtanic acid, $[\alpha]_D^{20}$ = -41.26°(C3.98, EtOH). R(+)α-methylbenzylamine, $[\alpha]_D^{20}$ = +30+2°(C10, EtOH) and camphor $[\alpha]_D^{20}$ = +43.5 ±1° supplied by Fluka, Switzerland was used for the synthesis of the corresponding tertiary amines. Optical rotations were measured on a Autopol II automatic polarimeter. The hydroboration reaction was repeated several times in each case and the measured observed rotations always fell within ±0.01° which is also the accuracy limit of the polarimeter used. In each case, the condition of the polarimeter was checked by measuring a standard solution of camphene, $[\alpha]_D$ = +17±1°(C4, ether) or α-methylbenzylamine, $[\alpha]_D^{20}$ = 30±2°(C10, EtOH) supplied by Fluka. The differences in the observed rotations of standard solutions in different runs also fall within ±0.01°. The polarimeter was set to zero reading using the solvent used. Same concentration of racemic compounds were also run and in all cases the reading of racemic compounds also fall with in ±0.01°. In each case the optical rotations were measured in two concentrations and concentrations closer to the concentration utilized

in the literature $[\alpha]_D$ values are given in the Table 3.1.

The $[\alpha]_D$ values were calculated by substituting the length of the Cell in decimeter (1) and concentration of the solvent per one milli litre (c) in the following equation.

$$[a]_D^{20} = \frac{\text{Observed rotation}}{1 \times c}$$

The conc. of the solute per 100 millilitre of the solvent utilized are given along with the $[\alpha]_D$ values.

Synthesis of cis-Myrtanic acid (12)

cis-Myrtanol (14) was prepared through hydroboration of β-pinene with acetoxyborohydride followed by H_2O_2/NaOH oxidation as described in Chapter 1. The product, bp. 80°C/1.5 mm lit.[31] bp. 68°C/0.2 mm had an $[\alpha]_D^{25}$ value of -19.0 (C11, $CHCl_3$) corresponding to 90.5% optical purity.

The conversion of the alcohol into the acid was carried out following a literature procedure.[29] cis-Myrtanol (6.25 g, 40 mmol) was dispersed in a mixture of 95% H_2SO_4 (25 mL) and water (200 mL) at room temperature. Finely powdered $KMnO_4$ (11.5 g) was added in small portions with stirring as fast as purple colour was discharged. The precipitated MnO_2 was reduced by the addition of sodium metabisulfite and the mixture was extracted with ether (3x30 mL). The combined ether extract was washed with 2N KOH (3x30 mL), dried ($MgSO_4$) and concentrated to yield myrtanic acid (12).

It was recrystallized from acetonitrile (1.5 g, 23%, mp.109°C, lit.[29] mp.111°C; $[\alpha]_D^{25}$ = -41.26 (C3,98, EtOH), corresponding to 85.4% optical purity.[29]

IR (KBr) ν_{max} : 3600-2700 (-OH), 1700 cm^{-1} (>C=O).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 183.6, 43.9, 43.0, 40.5, 38.9, 29.1, 27.0, 24.7, 21.7, 15.2.

Synthesis of N,N dibenzyl-α-methylbenzylamine (24)

A mixture of α-methylbenzylamine (12.1 g, 100 mmol), KOH powder (32.0 g, 500 mmol), benzyl bromide (25 mL, 250 mmol) and NaI (3.0 g, 20 mmol) was refluxed for 20 h. The contents were brought to r.t. and extracted with ether (3x50 mL). The ether layer was treated with 5N HCl (30 mL) to precipitate the amine as hydrochloride salt which was found to be insoluble in water. The amine hydrochloride was once washed with ether (30 mL) and the amine was regenerated with 5N KOH (phenolphthalein indicator). The amine was extracted into ether (3x25 mL), dried ($MgSO_4$) and the solvent was evaporated. The residue was recrystallized from benzene-hexane mixture to yield white crystalline N,N-dibenzyl-α-methyl-benzylamine (24) 24 g, 80%, mp.72°C, $[\alpha]_D^{25}$ = +100.5° (C2.54, $CHCl_3$).

IR (KBr) ν_{max}: 1610, 1400, 1220, 1025 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 143.0, 140.4, 129.3, 128.4, 128.3, 127.0, 56.3, 53.7, 13.9.

Analysis: Calculated for $C_{22}H_{23}N$: C,87.7; H,7.6; N,4.7;

Found: C,88.0; H,7.7; N,5.0.

Synthesis of N-Ethyl-N-isopropyl-α-methylbenzylamine (22)

(a) Preparation of N-isopropyl-α-methylbenzylamine (20): A mixture of α-methylbenzylamine (6.5 g, 50 mmol), KOH powder (22.4 g, 400 mmol) and isopropyl iodide (51 g, 300 mmol) was refluxed for 14 h. The contents were brought to room temperature and extracted with ether (4x25 mL). The ether layer was washed with water (2x20 mL), brine (15 mL), dried ($MgSO_4$) and the solvent was removed. The residue was distilled under reduced pressure to yield N-isopropyl-α-methylbenzylamine (20) 6.9 g, 85%, bp.65°C/3 mm. $[\alpha]_D^{\circ}$ = +62.0° (C1.83, CH_3OH).

IR (neat) V_{max}: 3275, 1600, 1460 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.2 (s,5H), 3.8 (q,1H), 2.56 (p,1H), 1.28 (d,3H), 0.92 (q,6H).

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 146.0, 128.1, 126.5, 126.2, 54.8, 45.1, 24.5, 23.7, 21.8.

(b) Acylation of N-isopropyl-α-methylbenzylamine: An equal volume of freshly distilled acetic anhydride was added to N-isopropyl-α-methyl benzylamine (3.26 g, 20 mmol) and the residue was stirred for 14 h at r.t. 6N HC1 (15 mL) was added and the mixture was extracted with ether (3x20 mL). The combined organic extract was washed with $NaHCO_3$ solution, dried ($MgSO_4$) and evaporated to yield N-acetyl-N-isopropyl-α-methyl

benzylamine (21), 3.2 g, 78%, mp.112°C, $[\alpha]_D^{25}$ = +53.7°(C1.42, EtOH).

IR (KBr) V_{max}: 1625, 1460, 760, 700 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.08 (s,5H), 4.6 (S,1H), 2.42 (p,1H), 1.84 (s,3H), 1.32 (d,3H), 1.08 (d,3H), 0.72 (d,3H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 169.4 (-N-CO-CH_3), 140.1, 127.8, 126.8, 126.4, 54.4, 46.4, 23.4, 20.3, 19.2, 17.2.

Reduction of N-acyl-N-isopropyl-α-methylbenzylamine (21) with BH_3-THF

The amide (21) (2.06 g, 10 mmol) was dissolved in 50 ml of dry THF and diborane generated (Chapter 2) using I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) was bubbled at 0°C and stirred at r.t. for 1 h. The mixture was then refluxed for 6 h. It was brought to r.t. and 6N HCl (15 mL) was added. THF was distilled out and NaOH pellets were added to neutralize amine hydrochloride. The reaction mixture was extracted with ether (3x25 mL), dried ($MgSO_4$) and the solvent was evaporated. The residue was distilled under reduced pressure to isolate N-ethyl-N-isopropyl-α-methyl benzylamine (22B), 1.53 g, 80%, bp.72°/25 mm, $[\alpha]_D$ = +5.26 (C4.1824, EtOH).

IR (neat) V_{max}: 1625, 1440, 740, 700 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.28 (t,5H), 3.84 (q,1H), 2.92 (p,1H), 2.48 (g,2H), 1.3 (d,3H), 0.92 (m,9H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : 6 ppm 146.7, 128.0, 127.5, 126.2, 58.4, 48.2, 39.0, 20.0, 19.7, 19.2, 16.9.

Reduction of N-acyl-N-isopropyl-α-methylbenzylamine with LAH/Ether

To the amide (**21**) (1 g, 5 mmol) in dry ether (30 mL), LAH (6 g) was added in portion from a solid addition flask and the contents were stirred for 14 h at r.t. The mixture was cooled and ethylacetate (5 mL) was added followed by 6N NaOH (10 mL). The reaction mixture was extracted with ether (3x20 mL), washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was distilled to isolate N-ethyl-N-isopropyl-α-methylbenzylamine **(22A),** 0.57 g, 75%, bp.85°C/3.5 mm, $[\alpha]_D^{\sim}$ = +13.78 (C3.99, EtOH).

The IR, ^{1}H-NMR and ^{13}C-NMR spectra were identical with the sample obtained by the BH_3.THF reduction in the previous experiment.

Synthesis of N-Benzyl-N-isopropyl α-methylbenzylamine (23) by benzylation of N-isopropyl-α-methyl benzylamine (20)

A mixture of N-isopropyl α-methylbenzylamine (20) (16.3 g, 100 mmol), NaI (3 g, 20 mmol), powdered KOH (40 g, 625 mmol) and benzyl bromide (21.3 g, 125 mmol) was refluxed for 14 h at 100°C. The mixture was cooled and extracted with ether (3x50 mL) and the combined ether extracts were treated with 5N HC1 (3x10 mL). The combined aqueous extract was once again extracted with ether (15 mL) and the amine was regenerated **from** the amine hydrochloride solution by the addition of 5N KOH (phenolph-

thalein indicator). It was extracted with ether (3x25 mL), dried ($MgSO_4$) and the solvent was removed. The residue was distilled to obtain N-benzyl-N-isopropyl-α-methylbenzylamine (20.3 g, 80%, bp.124°C/1 mm Hg). The amine thus obtained was purified by column chromatography on a silica gel column (hexane/chloroform as eluent) and distilled Under reduced pressure to isolate and N-benzyl-N-isopropyl-α-methylbenzylamine (23), $[\alpha]_D^{20} \doteq 17.29°$ (C3.932, $CHCl_3$).

IR (neat) V_{max}: 3095, 3075, 1600, 1350, 1145, 690 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.4 (m,5H), 7.2 (m,5H), 3.88 (q,1H), 3.64 (d,2H), 2.96 (p,1H), 1.28 (d,3H), 0.96 (p,6H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 145.9, 143.3, 128.2, 128.0, 127.7, 126.6, 126.4, 58.2, 49.4, 48.0, 20.7, 19.1, 18.7.

Analysis: Calculated for $C_{18}H_{23}N$: C,85.41 H,9.1; N,5.5;
Found: C,85.1; H,9.0; N,5.9.

Synthesis of N-methyl-N-isobornyl aniline (30)

(a) Preparation of camphor-anil (27): To a stirred solution of camphor (20.4 g, 150 mmol) and aniline (41.85 g, 450 mmol) in dry toluene (200 mL), $TiCl_4$ (10 mL) was added carefully and the reaction mixture was refluxed for 14 h under nitrogen atmosphere. The mixture was brought to room temperature. TiO_2 was filtered off and washed with petroleum ether (150 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was removed.

The residue was distilled under reduced pressure to isolate camphor-anil (22 g, 65%, bp.110°C/0.6 mm, lit.[59] bp.118°C/1 mm).

IR (neat) V_{max}: 1680, 1600 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.16-6.68 (m,5H), 2.08 (m,1H), 1.72 (m,6H), 1.08 (s,3H), 0.92 (s,3H), 0.84 (s,3H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : 6 ppm 184.1, 152.2, 128.8, 122.7, 119.7, 53.6, 46.7, 43.4, 35.8, 31.7, 27.1, 19.2, 18.7, 10.9.

(b) Conversion of camphor-anil (27) into isobornyl aniline (28) using $NiCl_2.6H_2O/NaBH_4$ system: Camphor-anil (2.27 g, 10 mmol) and $NiCl_2.6H_2O$ (5.7 g, 20 mmol) were taken in methanol (100 mL) and cooled to -30°C. $NaBH_4$ (3.8 g, 100 mmol) was added in portions from a solid addition flask over a period of 1 h and stirred further for 1 h at -30°C and 4 h at r.t. 3N NaOH (15 mL) was added followed by ether (100 mL) and the black precipitate was filtered off and the layers were separated. The organic layer was washed with saturated NaCl solution, dried ($MgSO_4$) and distilled to yield N-isobornyl aniline (28). 1.72 g, 75%, bp.134°C/1 mm, lit.[45] bp.131°C/1 mm. $[\alpha]_D^{20}$ = -71.5° (C11.6, EtOH), lit. $[\alpha]_D^{19.5}$ = -89.1 (unverified).[45]

IR (neat) ν_{max}: 3350, 1685, 1600 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 148.4, 129.4, 116.8, 112.0, 61.7, 48.4, 47.3, 45.3, 40.9, 36.9, 27.6, 20.6, 12.5.

The above secondary amine on acylation with Ac_2O or acetyl chloride gave the corresponding amide mp.124°C, lit.mp.123°C.[45]

IR (KBr) ν_{max}: 1650, 1590 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 172.12, 140.3, 132.1, 130.8, **128.8,** 127.9, 62.9, 50.9, 45.9, 44.7, 37.8, 34.4, 26.3, 24.3, 21.2, 20.7, 11.6.

(c) Conversion of isobornyl aniline (28) into N-isobornyl-N-methyl aniline (30) ; To the isobornyl aniline (2.29 g, 10 mmol) in dry ether (30 mL), butyllithium (12 mmol, 12 mL) was added at 10-15°C and the mixture was stirred further for 1 h at r.t. The reaction mixture was refluxed for 2 h, cooled to 0°C. Methyl iodide (3 mL, 50 mmol) was added and the contents were stirred further for 4 h at r.t. Excess BuLi was destroyed with water-methanol (10 mL V/V) and extracted with ether (2x30 L). The combined organic layer was washed with saturated NaCl solution, dried ($MgSO_4$) and the solvent was evaporated. The residue was distilled to isolate N-methyl-N-isobornyl aniline. The product was purified by column chromatography on a silica gel column (hexane as eluent) and distilled to yield pure amine (30), (1.82 g, 75%, bp. 120°C/1.5 mm), $[\alpha]_D^{20}$ = -22 (C6, EtOH).

IR (neat) V_{max}: 1590, 1480 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 7.88-8.6 (m,5H), 4.4 (t,1H), 3.72 (s,3H), 2.64 (m,1H), 2.28 (m,6H), 2.0 (s,3H), **1.88** (s,6H).

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 153.5, 128.7, 120.1, 114.0, 68.2, 50.4, 46.8, 44.8, 40.4, 37.2, 35.9, 27.3, 21.3, 20.4, 13.5.

Analysis: Calculated for $C_{17}H_{25}N$: C,84.0, H,10.3, N,5.8;
Found: C,83.7; H,10.3; N,5.8.

Hydroboration of 1-Methyl-1-cyclohexene with $NaBH_4$/2-(6'-methoxy-2'-naphthalene) propionic acid (11) system

To a stirred suspension of $NaBH_4$ (0.8 g, 20 mmol) in dry THF (40 mL) the carboxylic acid (11) (4.6 g, 20 mmol) in THF (20 mL) was slowly added at 0°C under nitrogen atmosphere. The mixture was stirred at r.t. for 1 h and 1-methyl-1-cyclohexene (1.92 g, 20 mmol) was added. The contents were stirred for 14 h at r.t. The excess hydride was destroyed fry adding water (2 mL) and the organoborane was oxidised with H_2O_2 (16%, 25 mL) and 3N NaOH (20 mL). The organic layer was separated and the aqueous layer was extracted with ether (2x30 mL). The combined organic extract was washed with brine, dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methylcyclohexanol. The product was further purified by distillation under reduced pressure. Yield: 1.52 g, 68%, bp.65°C/10 mm, lit.[60], bp.166°C/760 mm, $[\alpha]_D^{20}$= -1.06 (C2.83, CH_3OH) $[\alpha]_D^{20}$ = +43.1 (C1, MeOH) (maximum reported value).

IR (neat) V_{max}: 3500-3200, 1440, 1050, 900, 790 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 76.2, 40.2, 35.1, 33.7, 25.7, 25.2, 18.6.

Hydroboration of 2,3-dihydrofuran with $NaBH_4$/2-(6'-methoxy 2'-naphthalene)-propionic acid system

The acyloxyborohydride species was prepared at 0°C by addition of carboxylic acid CH) (4.6 g, 20 mmol) in THF (20 mL) to a stirred suspension of $NaBH_4$ (0.8 g, 20 mmol) in dry THF (40 mL). The reaction mixture was stirred at r.t. for 1 h. 2,3-Dihydrof uran (1.4 g, 20 mmol) was added and the contents were further stirred for 12 h at r.t. The excess hydride was destroyed with water (1 mL) and oxidation was carried out with H_2O_2/NaOH. The reaction mixture was adjusted to pH 5, with 6N HC1 and extracted with ether (3x30 mL). The organic extract was washed with water (2x10 mL) and the combined aqueous layer was neutralized to pH 8 with 5N NaOH. From the organic layer carboxylic acid was recovered. The aqueous layer was saturated with anhydrous K_2CO_3 (~ 40-50 gms) and extracted with ether (3x40 mL). It was dried over anhydrous $MgSO_4$, the solvent was evaporated and the residue was chromatographed on a silica gel column (hexane/ether as eluent) to isolate 3-hydroxytetrahydrofuran. The chromatographed alcohol was distilled under reduced pressure to afford pure 3-hydroxy tetrahydrofuran, yield, 1.23 g, 70%, bp.70°C/10 mm, lit.[-] bp.80°C/15 mm, $[\alpha]_D$= -1.6 (C2.5, CH_3OH), lit.[-] $[\alpha]_D^{\angle}$ = -17.3 (C2.4, CH_3OH) (maximum reported value).

IR (neat) V_{max}: 3450, 2940, 2878, 1441, 1272, 1120, 1065 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): 6 ppm 4.3 (m,1H), 4.0 (m,2H), 3.75 (d,2H), 1.92 (m,2H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 75.3, 71.3, 66.8, 55.3.

Hydroboration of 1-methyl-1-cyclohexene with cis-myrtanic acid/$NaBH_4$ system

To a stirred suspension of $NaBH_4$ (0.4 g, 10 mmol) in THF (35 mL) myrtanic acid (**12**) (1.6 g, 10 mmol) in THF (10 mL) was slowly added at 0°C under nitrogen atmosphere. The mixture was stirred for 1 h at r.t. and 1-methyl-1-cyclohexane (0.96 g, 10 mmol) was added. The contents were stirred for 24 h at r.t. The excess hydride was destroyed by addition of water (2 mL) and it was oxidised with H_2O_2/NaOH. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extract was washed with brine, dried ($MgSO_4$) and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methyl cyclohexanol (0.68, 60%). It was further purified by distillation under reduced pressure, bp.78°C/20 mm, lit.[60], bp. 166°C/760 mm, $[\alpha]_D^{20}$ =+1.819(C2.748, CH_3OH), lit.[52] $[\alpha]_D^{25}$ = +43.1(C1. CH_3OH) (maximum reported value).

The spectral data were identical with the data reported in the earlier experiment.

The above experiment was carried out by replacing 1-methyl-1-cyclohexene with 1-phenyl-1-cyclopentene but there was no hydroboration in this case even after 72 h at room temperature.

flydroboration of 1-methyl cyclohexene with Li BH_4/cis-myrtanic acid system

Lithiumborohydride was prepared in situ in THF following a reported

procedure by refluxing a mixture of lithium bromide (1.1 g, 11 mmol) and $NaBH_4$ (0.440 g, 11 mmol) in THF for 16 h in nitrogen atmosphere.[63] cis-Myrtanic acid (12) (1.6 g, 10 mmol) in THF (10 mL) was carefully added at 0°C and stirred further for 1 h at r.t. 1-Methyl-1-cyclohexene (0.96 g, 10 mmol) was added and the mixture was stirred for 24 h at r.t. The excess hydride was destroyed with water (1.5 mL) and the organoborane was oxidised with H_2O_2/NaOH. The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with brine, dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methylcyclohexanol (0.6 g, 53%). The product was further purified by distillation under reduced pressure, bp.64°C/10 mm, lit.[60] bp.166°C/60 mm, $[\alpha]_D^{20}$ = +2.08(C2.4, CH_3OH), lit.[52] $[\alpha]_D^{20}$ = 43.1(C1, CH_3OH). The spectral data were identical with the data reported previously.

The above experiment was carried out by replacing 1-methyl-1-cyclohexene with 1-phenyl-1-cyclopentene but there was no hydroboration in this case even after 72 h at room temperature.

Hydroboration of 2,3-dihydrofuran with cis-myrtanic acid/$NaBH_4$ system

To a stirred suspension of $NaBH_4$ (0.8 g, 20 mmol) in dry THF (40 mL), myrtanic acid (3.36 g, 20 mmol) was slowly added at 0°C under nitrogen atmosphere and the mixture was stirred for 1 h at r.t. 2,3-Dihydrofuran (1,4 g, 20 mmol) was added and the mixture was stirred further for 12 h. The excess hydride was destroyed by careful addition of water

(1 mL) and the organoborane was oxidised with H_2O_2/NaOH. It was acidified to pH 5 with 6N HC1 and extracted with ether (3x30 mL). The ether extract was washed with water (2x10 mL) and the combined aqueous layer was neutralized to pH 8 with 5N NaOH and saturated with anhydrous K_2CO_3 (50 g). It was extracted with ether (3x40 mL), dried ($MgSO_4$) and the solvent was evaporated. The residue was chromatographed on a silica gel column (hexane/ether as eluent) and the product was distilled under reduced pressure to isolate pure 3-hydroxytetrahydrofuran, yield: 1.18 g, 68%, bp.70°C/10 mm lit.[54] pp.80°/15 mm, $[\alpha]_D^{25}$ = -1.762(C2.832, CH_3OH), lit.[54] $[\alpha]_D^{25}$ = -17.3(C2.4, MeOH).

The spectral data were identical to the data for the sample obtained previously.

Reaction of $NaBH_4$ (10 mmol)/cis-myrtanic acid (10 mmol) with Ph_3P

To a freshly prepared suspension of $NaBH_4$ (2.5 mmol) and myrtanic acid (2.5 mmol) in THF (25 mL) Ph_3P (3.5 mmol) in THF (5 mL) was added and the mixture was stirred for 24 h at r.t. To the reaction mixture water (5 mL) was added. Work up (Chapter 1) and chromatography of the residue over a silica gel column (hexane/chloroform as eluent) gave 0.65 g (95%) of triphenylphosphineborane. The spectral data of this product were identical to the data reported in Chapter 1. Mp.186°C, lit.[61] mp.189°C.

Hydroboration of **1-methyl-1-cyclohexene with borane-N,N-dibenzyl-α-methyl-benzylamine** complex (33)

Diborane (12.5 mmol) generated using I_2 (12.5 mmol) and $NaBH_4$ in diglyme (25 mmol) was bubbled through N,N-dibenzyl α-methylbenzyl amine (3.07 g, 10 mmol) in dry benzene (40 mL) at 5 to 10°C. The amine borane slurry was brought to r.t. and flushed with dry nitrogen to remove traces of diborane gas above the benzene solution. 1-Methyl-1-cyclohexene (0.96 g, 10 mmol) was injected and the mixture was stirred at r.t. for 24 . The contents were brought to 0°C and ethanol (2 mL) and THF (35 mL) were added. The mixture was oxidised with H_2O_2 (16%, 20 mL) and 3N NaOH (10 mL) . The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with 3N HC1 (3x10 mL) to separate the amine. The organic extract was washed with $NaHCO_3$ (10%) solution, brine solution, dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methylcyclohexanol. The product was distilled under reduced pressure 0.62 g, 55%/ bp.70°C/10 mm, lit.[60] bp.166°C/760 mm and optical rotation was measured, $[\alpha]_D^{25}$ = +1.08(C3.7, CH_3OH), lit.$[\alpha]_D^{25}$ = 43.1(C1, CH_3OH).[52] The spectral data were identical to the data for the sample obtained previously.

Hydrboboration of **2,3-dihydrofuran with borane-N,N-dibenzyl-α-methyl** benzylamine complex (33)

Amine borane (20 mmol) in benzene was prepared as described above and 2,3-dihydrofuran (1.4 g, 20 mmol) was injected. It was stirred at

r.t. for 12 h, cooled to 0°C and ethanol (2 mL) and THF (35 mL) were added. The organoborane was oxidised with H_2O_2 (16%, 25 mL) and 3N NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with water (2x10 mL) and the combined aqueous layer was saturated with anhydrous K_2CO_3 and extracted with ether (3x40 mL). It was dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed on a silica gel column (hexane/ether as eluent) to isolate pure 3-hydroxy tetrahydrofuran. The alcohol was distilled under reduced pressure and optical rotation was measured. Yield, **1.18** g, 67%, bp.68°/10 mm, lit.[54] bp.80°C/15 mm), $[\alpha]_D^{20}$ = -1.6(C2.5, CH_3OH), lit.[54] $[a]_D^{20}$ = -17.3{C2.4, CH_3OH). The spectral data were identical to the data of the sample obtained previously with other borane Lewis base systems.

Hydroboration of 1-methyl-1-cyclohexene with borane N-benzyl-N-isopropyl-α-methylbenzylamine complex (32)

Diborane (12.5 mmol), generated using I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) system was bubbled through N-benzyl-N-isopropyl-α-methylbenzylamine (2.53 g, 10 mmol) in dry benzene (40 mL) at 5-10°C. The mixture was stirred for 30 minutes at r.t. and diborane gas (if any) present above the solution was driven off by a stream of dry nitrogen and 1-methyl-1-cyclohexene (0.96 g, 10 mmol) was added. The mixture was stirred at r.t. for 24 h. The contents were brought to 0°C and 2N HCl (1.5 mL) was carefully added and stirred for 30 minutes at r.t. 3N NaOH (10 mL) and THF (35 mL) were added and the organoborane was oxidised with H_2O_2 (16%, 25 mL). The aqueous and organic layers were separated and the

aqueous layer was extracted with ether (3x25 mL). The combined organic layer was treated with 6N HC1 (3x10 mL) and the amine was regenerated from the aqueous layer after neutralization with 5N NaOH (phenolphthalein indicator). The ether layer was washed with saturated aqueous $NaHCO_3$ (10 mL) solution, brine solution (10 mL), dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate trans-2-methylcyclohexanol. The alcohol was purified further by distillation under reduced pressure yield. 0.7 g, 62%, bp.68°C/15 mm, lit.[60], bp.166°C/760 mm, $[\alpha]_D^{20}$ = -1.5 (C3.33, CH_3OH), lit.[52] $[\alpha]_D^{20}$ = +43.1(C1,CH_3 OH). The spectral data were identical to the data for the sample obtained previously.

Hydroboration of 1-phenyl-1-cyclopentene with borane-N-benzyl-N-isopropyl-α-methylbenzylamine complex (32)

Diborane prepared using I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) in diglyme was passed through the amine (2.53 g, 10 mmol) in dry benzene at 5-10°C. The contents were flushed with dry nitrogen. 1-Phenyl-1-cyclopentene (1.44 g, 10 mmol) was injected and the contents were stirred at r.t. for 48 h. The mixture was cooled to 0°C and 2N HCl (2 mL) was carefully added and stirred at r.t. for 30 minutes. 3N NaOH (15 mL) THF (35 mL) were added and the organoborane was oxidised with H_2O_2 (16%, 25 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic layer was treated with 6N HCl (3x10 mL) and the amine was recovered from amine hydrochloride. The ether layer was washed with saturated aqueous sodium-bicarbonate (10 mL), brine (15 mL) and dried over anhydrous $MgSO_4$. The

solvent was removed and the residue was chromatographed on a silica gel column (hexane/chloroform as eluent) to isolate trans-2-phenylcyclopentanol. The alcohol was purified further by distillation under reduced pressure. Yield. 0.97 g, 60%, bp.87°C/1 mm; lit.[52] bp.129-131°/6 mm, $[\alpha]_D^{20}$ = -0.84(C8.33, • EtOH), lit.[53] $[\alpha]_D^{20}$ = + 71.1(C11.9, EtOH) (maximum reported value).

^{13}C NMR (25.0 MHz, $CDCl_3$) : 6 ppm 144.1, 128.7, 127.8, 126.5, 80.3, 54.4, 34.3, 33.2, 32.1.

Hydroboration of 2,3-dihydrofuran with borane-N-benzyl-N-isopropyl-α-methylbenzylamine complex (32)

Borane-N-benzyl-N-isopropyl-α-methylbenzylamine complex (20 mmol) was prepared as given in the above experiment. 2,3-Dihydrofuran (1.4 g, 20 nunol) was added and the mixture was stirred at r.t. for 12 h. **Water** (1 ml) and 2N HCl (1 mL) were added followed by the addition of 3N NaOH (10 mL) and THF (35 mL). Oxidation was carried out using H_2O_2 (16%, 20 mL). As the 3-hydroxytetrahydrofuran is highly soluble in water, the work up was carried out after saturation of the contents with anhydrous K_2CO_3. The contents were extracted with ether (4x30 mL). The combined organic extract was dried ($MgSO_4$) and the solvent was removed. The alcohol was distilled out under reduced pressure leaving the amine residue. The distilled alcohol was chromatographed on a silica gel column using hexane/ether as eluent to isolate pure 3-hydroxytetrahydrofuran. The chromatographed alcohol was distilled once again under reduced pressure to isolate pure 3-hydroxytetrahydrofuran, yield: 1.2 g, 69%, bp.70°C/8 mm,

lit. bp.80°C/15 mm, $[\alpha]_D^{20}$ = +2(C2.5, MeOH), lit. $[a]_D^{20}$ = -17.3(C2.4, CH_3OH). The spectral data were identical with the data of the sample obtained previously with other borane-Lewis base systems.

Hydroboration of 1-methyl-1-cyclohexene using borane-N-isobornyl-N-methylaniline complex (31)

Diborane generated using I_2 (12.5 mmol) and $NaBH_4$ (25 mmol) was bubbled through N-methyl-N-isobornylaniline (2.43 g, 10 mmol) in dry benzene (40 mL) at 5-10°C. The diborane gas (if any) present above the benzene solution was driven off by a stream of dry nitrogen. 1-Methyl-1-cyclohexene (0.96 g, 10 mmol) was added and the mixture was stirred for 24 h at r.t. Excess hydride was decomposed by addition of water (1 mL) and 2N HC1 (2 mL). The mixture was further stirred for 30 minutes at r.t. 3N NaOH (10 mL) and THF (30 mL) were added and the organoborane was oxidised with H_2O_2 (16%, 20 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with 5N HC1 (3x10 mL) to separate the amine as its hydrochloride salt from which the amine was regenerated using 3N NaOH (phenolphthalein indicator). The ether extract was washed with saturated $NaHCO_3$ (15 mL), brine (15 mL) and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on a silica gel column (hexane/chloroform as eluent) to isolate trans-2-methylcyclohexanol. The alcohol was distilled under reduced pressure to isolate pure trans-2-methylcyclohexanol, yield; 0.8 g, 70%, bp.65°C/10 mm, lit.[60] bp.166°C/760 mm, $[\alpha]_D^{25}$ = -1.66(C3, CH_3OH), lit.-$[\alpha]_D^{25}$ = +43.1°(C1,CH_3OH). The spectral data were identical to the data of the sample obtained previously in reactions with other BH_3-Lewis base complexes.

Hydroboration of 1-phenyl-1-cyclopentene using borane-N-isobornyl-N-methyl aniline complex (31)

The amine borane complex (10 mmol) in benzene (40 mL) was prepared as outlined in the previous experiment. 1-Phenyl-1-cyclopentene (1.44 g, 10 mmol) was added and the stirring was continued for 48 h. The reaction mixture was oxidised and worked up following the procedure described in the previous experiment and the alcohol was chromatographed on a slicagel column (hexane/chloroform eluent) to isolate trans-2-phenylcyclopentanol, which was again distilled, under reduced pressure to isolate pure alcohol. Yield. 1.02 g, 63%, bp.84°C/1 mm, lit.[62] bp. 129°C/6 mm, $[a]_D^{20}$ = -0.22(C9, EtOH), lit. $[\alpha]_D^{20}$ = +71.1°(C11.9, EtOH)[53] (maximum reported value). The spectral data were identical to the data of the sample obtained previously.

Hydroboration of 2,3 dihydrofuran with borane-N-isobornyl-N-methylaniline complex (31)

Diborane generated using I_2 (25 mmol) and $NaBH_4$ (50 mmol) was bubbled through N-isobornyl-N-methylaniline (4.86 g, 20 mmol) in dry benzene (40 mL) at 5-10°C. The diborane gas (if any) present above the benzene solution was driven off by a stream of dry nitrogen. 2,3-Dihydrofuran (1.4 g, 20 mmol) was added and the mixture was stirred for 4 h at r.t. 2N HCl (2 mL) was carefully added and the contents were stirred for 30 min at r.t. 3N NaOH (15 mL) and THF (35 mL) were added and oxidation was carried out using H_2O_2 (16%, 20 mL). The contents were extracted with ether (3x25 mL) and the combined ether extract was washed with

water (10 mL) and the combined aqueous layer was saturated with anhydrous K_2CO_3 (50-60 g). The contents were extracted with ether (3x40 mL), dried ($MgSO_4$) and the solvent was removed. The alcohol was distilled under reduced pressure and passed throgh a silica gel column (hexane/ether eluent) to isolate pure 3-hydroxytetrahydrofuran. The chromatographed alcohol was again distilled under reduced pressure to isolate pure alcohol. Yield: 1.3 g, 76%, bp.70°C/10 mm, lit.[54] bp.80°C/15 mm, $[\alpha]_D^{20}$ = -3.3(C3, MeOH), lit.[54] $[a]_D^{20}$ = -17.3(C2.4, CH_3OH). The spectral data were identical to the data obtained previously in reactions with other borane-Lewis base complexes.

Hydroboration of 3,4-dihydro-2H-pyran with borane-N-isoboranyl-N-methyl aniline complex (31)

The amine borane complex (20 mmol) was prepared following the procedure outlined in the previous experiment. 3,4-Dihydro-2H-pyran (1.68 g, 20 mmol) was added and the reaction mixture was stirred for 4 h at r.t. The oxidation and workup were carried as in the above experiment and the alcohol isolated was distilled under reduced pressure, chromatographed on a silica gel column (hexane/ether eluent) and again distilled under reduced pressure to isolate pure 3-hydroxytetrahydropyran. Yield: 1.4 g, 68%, bp.70°C/8 mm Hg, lit.[54] bp.90°C/20 mm, $[\alpha]_D^{20}$ = -1.24 (C4, MeOH), lit.[55] $[\alpha]_D^{30}$ = -11.8 (neat) (maximum reported value).

IR (neat) V_{max}: 3380, 2930, 2840, 1441, 1048 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): 63.25-3.9 (m,5H), 3.1 (s,1H), 1.65-2.15 (m,4H).

^{13}C NMR (25.0 MHz, $CDCl_3$): 6 ppm 72.9, 67.9, 65.7, 31.5, 23.3.

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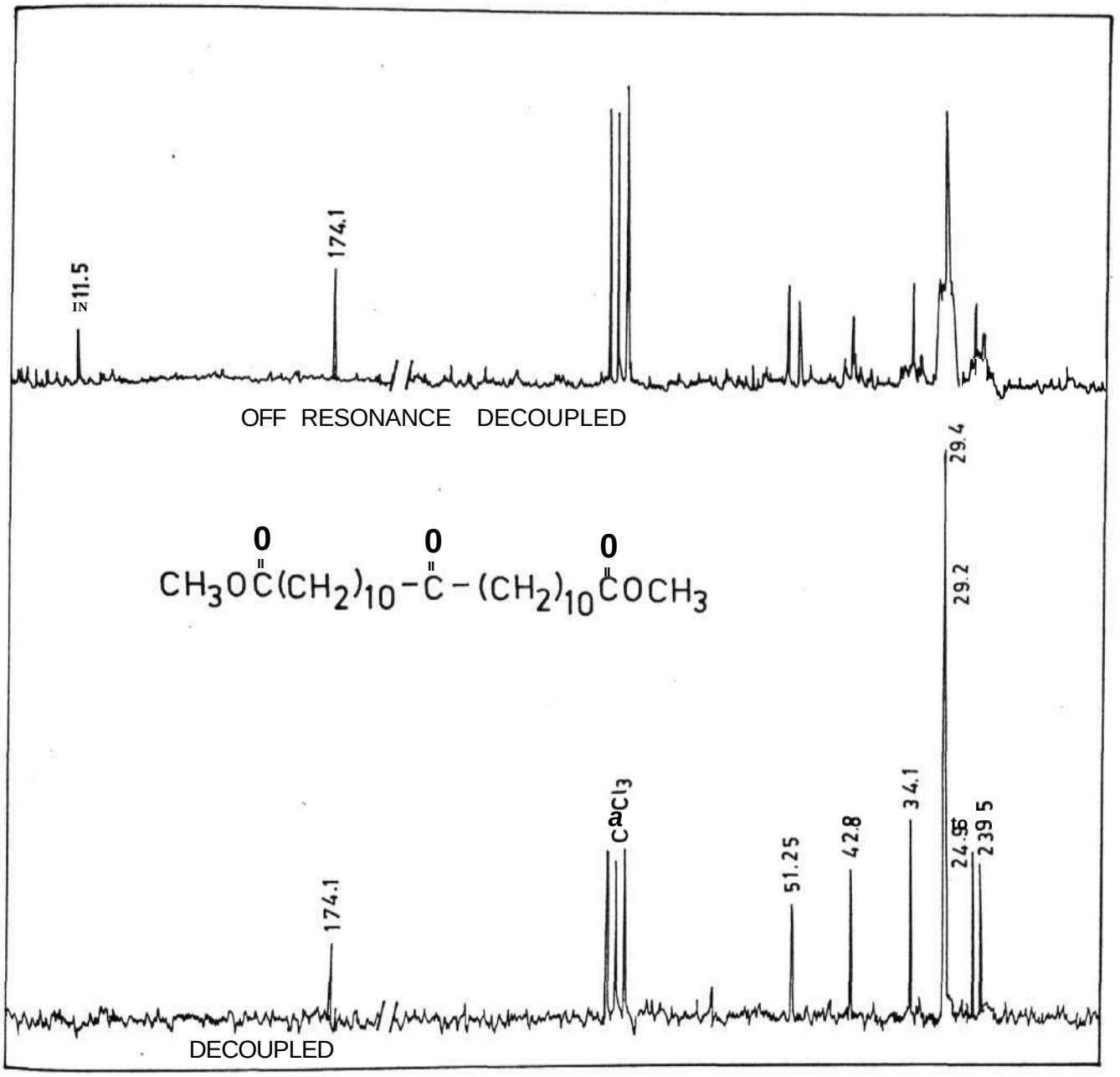
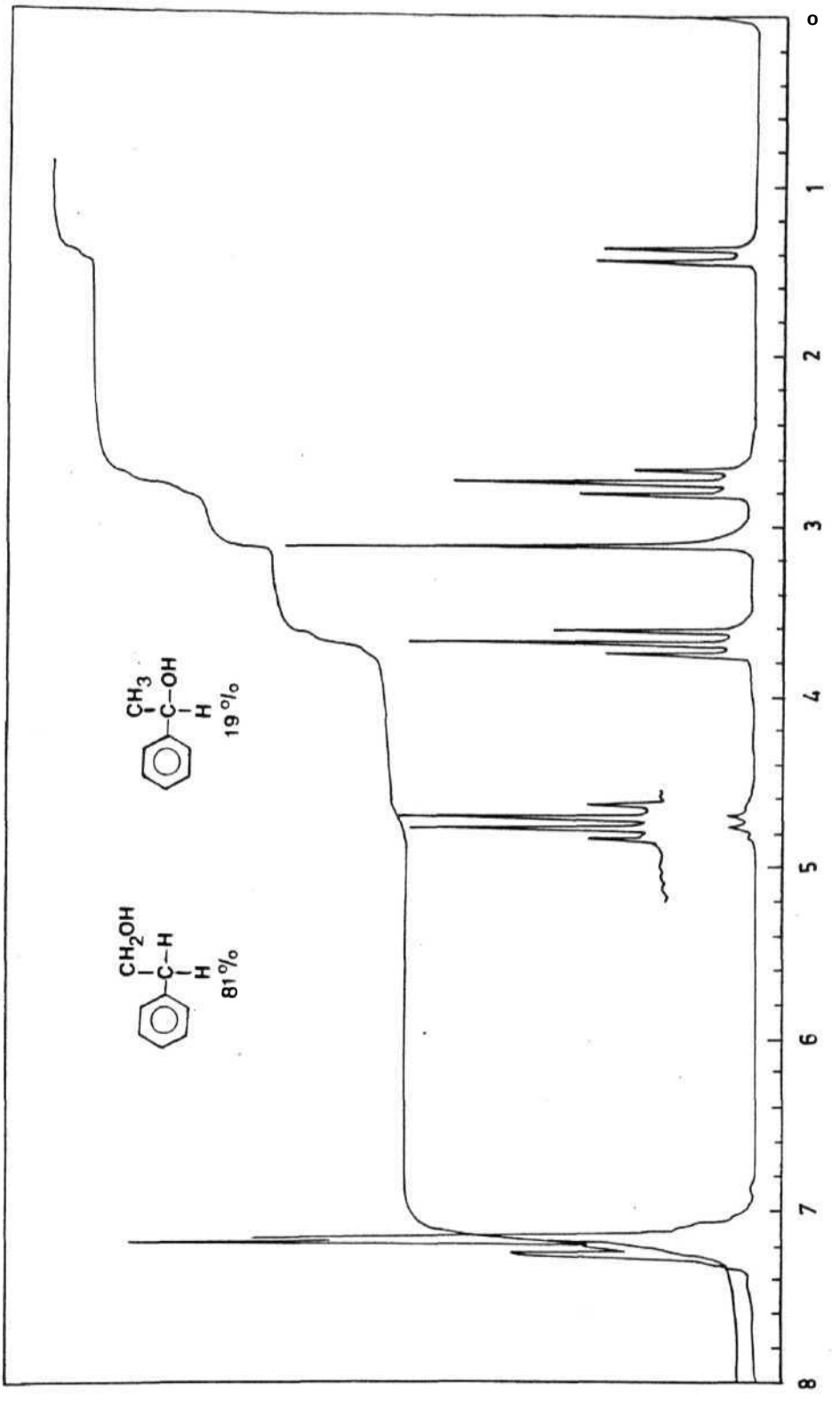
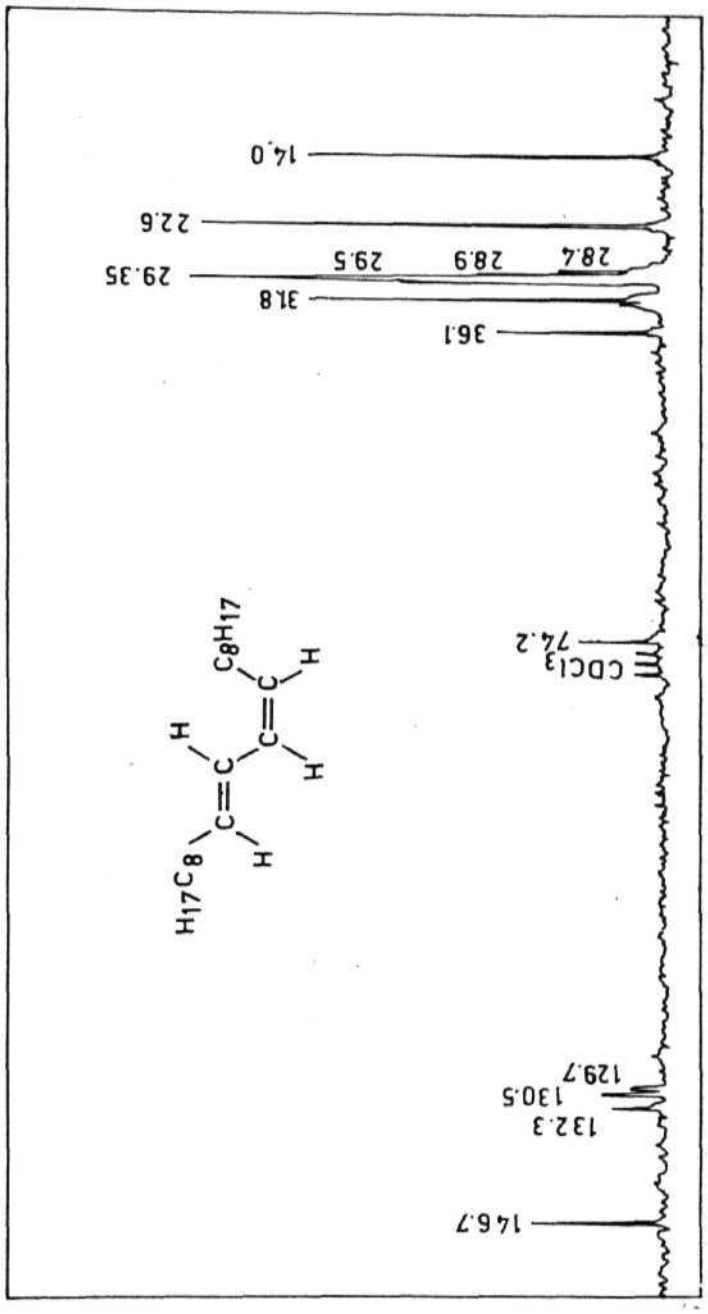


$$CH_3O\overset{O}{\overset{\|}{C}}(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}\overset{O}{\overset{\|}{C}}OCH_3$$

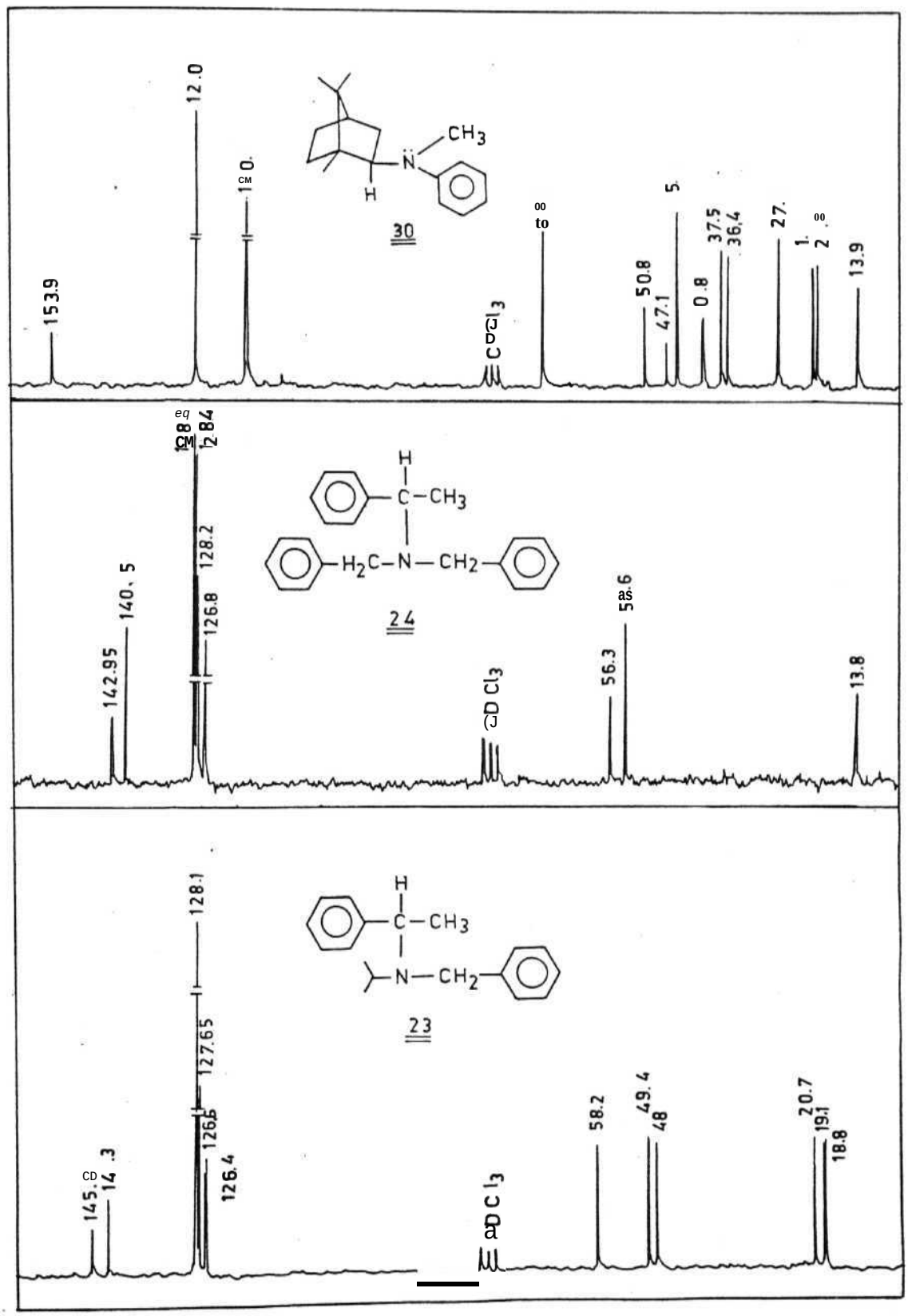
Spectrum No. 1: ^{13}C NMR Spectrum (25.0 MHz, $CDCl_3$)



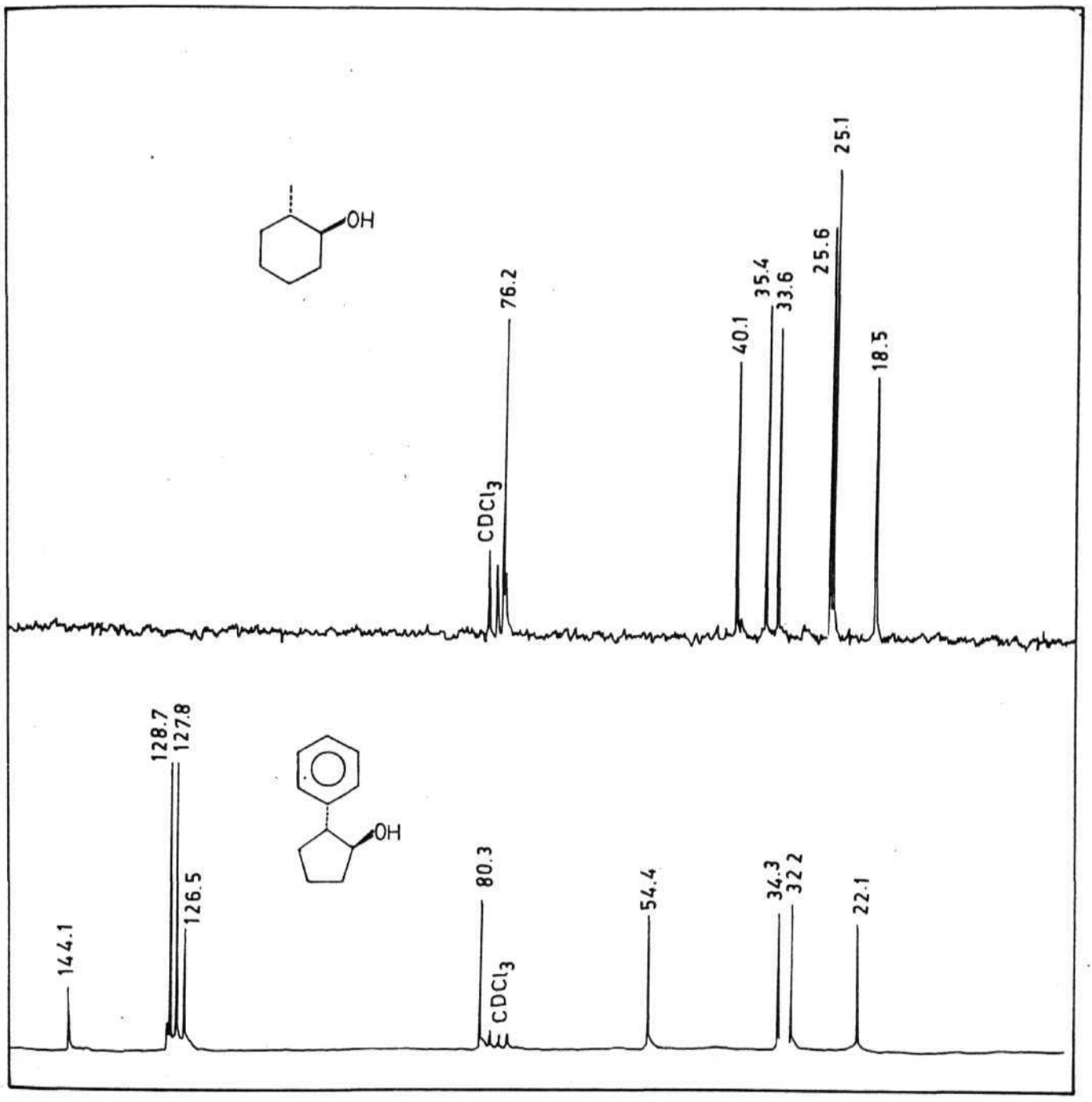
Spectrum No 2: ^1H NMR Spectrum (100 MHz, $CDCl_3$)



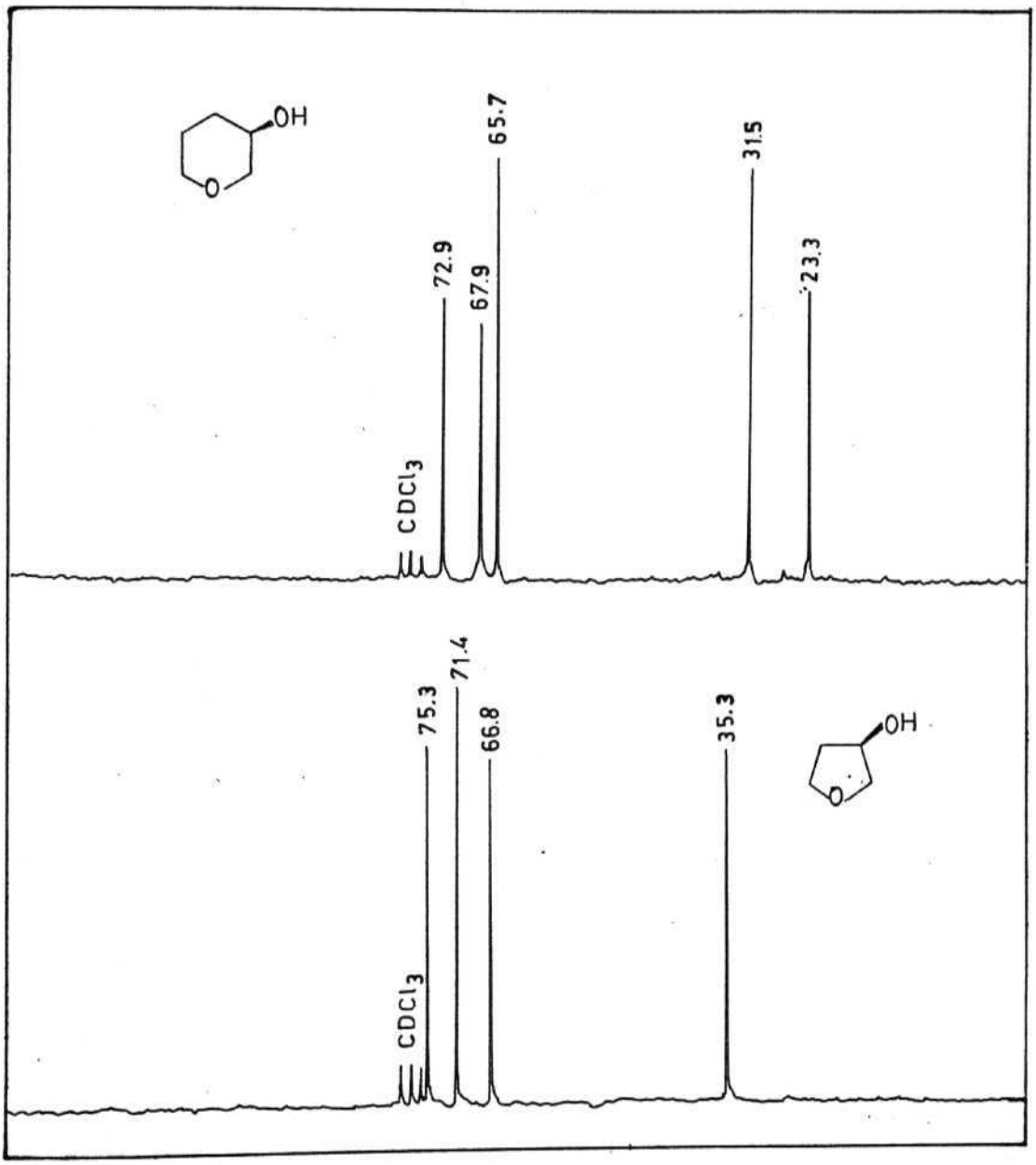
to ectrum No. 3: $^{13}_{o}$ z R S pvctr m (25.o MXz, CDCl)



Spectrum No. 4: ^{13}C NMR Spectrum (25.0 MHz, $CDCl_3$)



Spectrum No. 5: ^{13}C NMR Spectrum (25.0 MHz, $CDCl_3$)



Spectrum No. 6: ^{13}C NMR Spectrum (25.0 MHz , $CDCl_3$)

V I T A E

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List of publications

1. Organic Synthesis via Carbonylation of Organometallic reagents with carbon monoxide.
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2. Acetoxyborohydride: A Simple Selective Hydroborating Agent,
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5. A convenient method for the generation of diborane from $NaBH_4$ and I_2. C. Narayana and M. Periasamy, J. Organomet Chem. **1987,** 323, **145.**

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7. Syntheses of Chiral Amines via Reduction of Imines and Enamines with the $CoCl_2/NaBH_4$ system.
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Chatla Narayana and Mariappan Periasamy. Communicated.