DEVELOPMENT OF ORGANIC SYNTHETIC METHODS VIA BORANE, IODOBORANES AND CHIRAL AMINE BORANE COMPLEXES

A THESIS
SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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To

My Teachers and Parents

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STATEMENT

I here by 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 Professor 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.

CH. KISHAN REDDY

CERTIFICATE

Certified that the work contained in this thesis entitled "Development of Organic Synthetic Methods Via Borane, Iodoboranes and Chiral Amine Borane Complexes" has been carried out by Mr. Ch. Kishan Reddy, under my supervision and the same has not been submitted elsewhere for a Degree.

M. Periasamy
25/9/93

PROFESSOR M. PERIASAMY

(THESIS SUPERVISOR)

DEAN 27/9/93

SCHOOL OF CHEMISTRY

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D.S. Reddy, P. Bheema Rao, M. Praveen, M. Prabhakar, Raghu, Prem and all my other friends, who made my stay here an enjoyable and memorable one.

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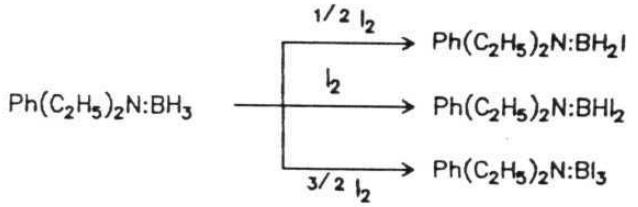
ABBREVIATIONS

DG	diglyme
MCBS	monochloroborane dimethylsulfide
MBBS	monobromoborane dimethylsulfide
MIBS	monoiodoborane dimethylsulfide
DCBS	dichloroborane dimethylsulfide
DBBS	dibromoborane dimethylsulfide
DIBS	diiodoborane dimethylsulfide
Thexyl	2,3-dimethyl-2-butyl
9-BBN	9-borabicyclo[3.3.1]nonane
Chx_2BH	dicyclohexylborane
Ipc_2BCl	diisopinocampheylchloroborane
B-Cl-9-BBN	B-chloro-9-borabicyclo[3.3.1]nonane
B-Br-9-BBN	B-bromo-9-borabicyclo[3.3.1]nonane
B-I-9-BBN	B-iodo-9-borabicyclo[3.3.1]nonane
Tf	triflate
MEM	2-methoxyethoxymethyl
MIBDA	monoiodoborane diethylaniline
DIBDA	diiodoborane diethylaniline
n-BuLi	n-butyllithium
AcOH	acetic acid
DCME	α,α-dichloromethyl methyl ether
p-TsOH	p-toluenesulphonic acid
DMF	N,N-dimethylformamide
NBS	N-bromosuccinimide
ee	enantiomeric excess
EE	diethyl ether
Me	methyl
Et	ethyl
Pr	propyl
Ph	phenyl
α-naph	α-naphthyl
THF	tetrahydrofuran

ABSTRACT

This thesis deals with the development of organic synthetic methods, through boranes, iodoboranes and chiral amine borane complexes. It comprises of three chapters. Each chapter is subdivided into three parts, Introduction, Results and Discussion and Experimental sections.

Synthetic applications of iodoboranes are described in chapter 1. Synthesis and utilization of various haloboranes have been briefly reviewed in the introduction. The $Ph(C_2H_5)N:BH_2I$, $Ph(C_2H_5)_2N:BHI_2$ and $Ph(C_2H_5)_2N:BI_3$ complexes were prepared through the reaction of appropriate amounts of I_2 with $H_3B:N(C_2H_5)Ph$.



Hydroboration of 2-equivalents of 1-decene with $BH_2I:N(C_2H_5)_2Ph$ followed by carbenoidation-oxidation gave di-1-decylketone in 84% yield. It was found that the $BH_2I:N(C_2H_5)_2Ph$ complex on reaction with 2-equivalent of 1-decyne followed by I_2/NaOH treatment gives a mixture of the *trans*, *trans*-diene and the iodoolefin.

The synthetic utilities of $BHI_2:N(C_2H_5)_2Ph$ complex have been investigated in detail. It was found that this reagent is useful for the hydroboration of alkenes, alkynes, reductive iodination of carboxylic acids, aldehydes and ketones, iodination of alcohols, reduction of amides and also in certain selective transfomrations.

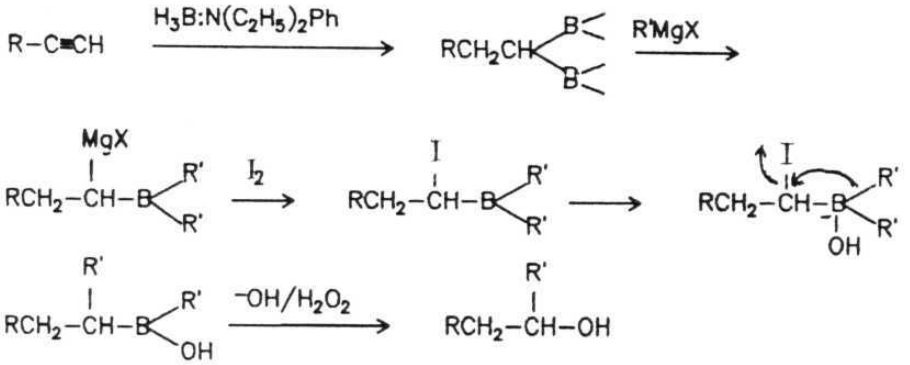
Hydroboration of 1-decene, styrene and 1-decyne was studied. Reduction characteristics of the BHI_2:$N(C_2H_5)_2Ph$ complex were examined in detail. It was found that the carbonyl compounds and carboxylic acids give the corresponding alkyl iodides in moderate good yields, on reaction with BHI_2:$N(C_2H_5)_2Ph$. It was also observed that the BHI_2:$N(C_2H_5)_2Ph$ complex converts, alcohols to the corresponding iodides in moderate to good yields. Cetyl alcohol is converted to cetyl iodide at 80^oC in 12h. The *exo* and *endo*-2-norborneols were converted to *exo*-2-norbornyl iodide at room temperature for 6 h. The BHI_2:$N(C_2H_5)_2Ph$ complex reduces amides to the corresponding amines in moderate yields. In order to examine the chemoselectivities of this reagent system, several experiments were carried out using bifunctional substrate or a mixture of two substrates. These results are discussed.

A new convenient procedure for the generation of HI *in situ* from BI_3:$N(C_2H_5)_2Ph$ complex and acetic acid was developed. The HI prepared in this way readily adds to alkenes and alkynes in Markovnikov fashion to form alkyl and alkenyl iodides in good yields under mild conditions.

The Chapter 2 describes the synthesis and utilization of gem-diboryl derivatives. 1,1-Diboryl decyl derivative was synthesized by the reaction of 1-decyne with H_3B:$N(C_2H_5)_2Ph$ complex. It was observed that the reaction of n-butyllithium with the 1,1-diboryl compound prepared in this way affords boron-stabilized carbanions which upon treatment with certain alkyl bromides and esters followed by oxidation gives secondary alcohols and carbonyl compounds

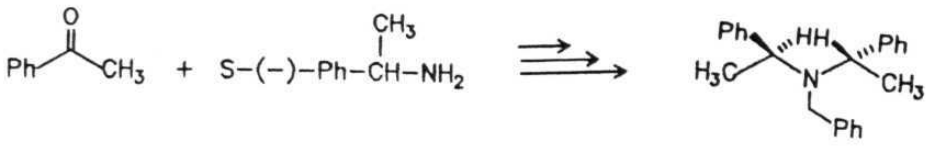
respectively. Similar, transformations were also observed using the readily accessible RMgX in the place of n-BuLi.

It was also observed that the addition of Grignard reagent/ BF_3:OEt_2 to 1,1-diboryl compound followed by $I_2/\bar{O}H$ lead to rearrangement of the alkyl group through α-iodoboron intermediates. Oxidation of the resulting secondary alkyl boron compound gives the mixed alkyl secondary alcohols in moderate yields.



The Chapter 3 deals with the synthesis of chiral amines and studies on the reductions and hydroborations, using chiral amine-borane complexes. Convenient procedures for the synthesis of these chiral amine systems have been developed following closely related reported procedures.

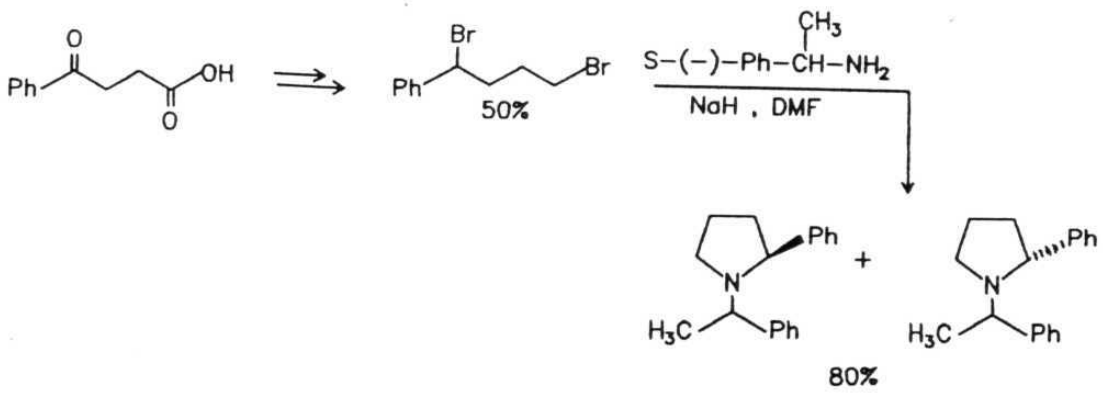
The S-(-)-N,N-dibenzyl-α-methylbenzylamine-BH_3 reduces acetophenone in the presence of 1 equivalent of BF_3OEt_2, 1-phenylethanol was obtained with 30% e.e. Several other prochiral ketones were also reduced following this procedure in 5.5-39% e.e. The N-benzyl-α,α'-dimethyldibenzylamine was prepared starting from acetophenone and chiral α-methylbenzylamine following closely related literature procedures.



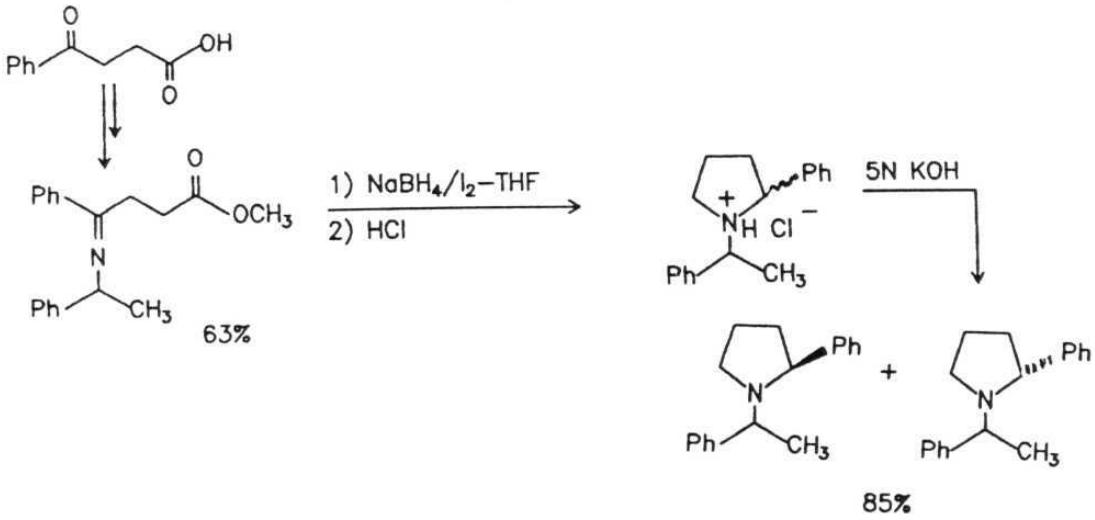
It was found that the S,S(-)-N-benzyl-α,α'-dimethyldibenzylamine-borane reduces acetophenone with 15% e.e in the absence of BF_3:OEt_2. In the presence of BF_3:OEt_2, 1-phenylethanol was obtained in 48% e.e. Several other prochiral ketones were also reduced following this procedure in 10.1-51.9% e.e.

It was anticipated that the chiral amine-boranes with nitrogen atom in a ring would give better results. The 2,5-diphenyl system would be a good choice for examining this. Unfortunately, our efforts to prepare the 2,5-diphenyl system were not successful.

It was then decided to prepare the 2-phenylpyrrolidine system, since it could be expected that in the resulting complex, the BH_3(or BF_3) would be *cis* to the chiral amine discriminating 2-phenyl substituent. The synthesis was envisaged using the chiral S-(-)-α-methylbenzylamine and separation of the diastereomers in the final step.

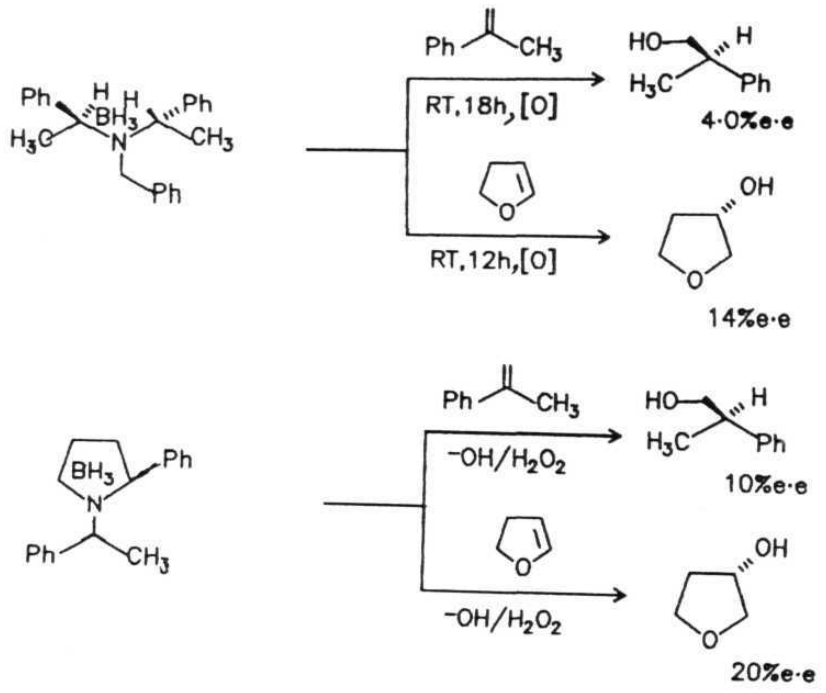


An alternative procedure for the synthesis of (-)-N-α-methylbenzyl-2-phenylpyrrolidine has been developed. In the above procedure, the dibromo compound was obtained only in 50% yield from that corresponding diol. So, the synthesis was envisaged without going through this intermediate.



We find this method is better than the previous method and hence we followed this for accumulation of this chiral amine system for our studies. It was found that the amine-borane prepared from this amine reduces acetophenone with 16.2% e.e in the absence of BF_3:OEt_2. It was also found that this amine-borane reduces acetophenone with 53% e.e in the presence of BF_3:OEt_2. Several other prochiral ketones were also reduced following this procedure in 15-56% e.e.

Hydroboration studies were carried out using the S,S(-)-N-benzyl-α,α'-dimethyldibenzylamine-borane and (-)-N-α-methylbenzyl-2-phenylpyrrolidine-borane complexes. These chiral amine-borane complexes hydroborated 2-methylstyrene and 2,3-dihydrofuran at room temperature. However, the enantioselectivities observed are some what poor.



The results are discussed in the context of various mechanisms proposed for the hydroboration reaction.

CHAPTER 1

Synthetic Applications of Iodoboranes

INTRODUCTION

Synthetic Applications of Haloboranes:

Organoboranes are one of the most versatile organometallic reagents which are useful in carbon-carbon bond formation reactions and also in generation of new functional groups.[1-4] Diborane, generated using $NaBH_4$ and $F_3B{:}OEt_2$ is the starting material for the synthesis of organoboranes from olefins (eq. 1).

$$3NaBH_4 + 4BF_3 \xrightarrow{DG} 3B_2H_6 + 3NaBF_4 \quad \text{—— (1)}$$

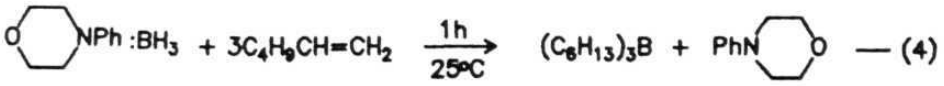
Diborane itself is difficult to handle and relatively inert towards olefins.[5,6] So, it is normally utilized in the form of its complexes (*eg.* BH_3.THF, $BH_3.SMe_2$ and $BH_3.NR_3$) which hydroborate olefins to give organoboranes.[3,7,8] Amine-boranes are relatively more stable than the ether and thio ether complexes (*eq.*2).

$$B_2H_6 + 2NR_3 \longrightarrow 2R_3N{:}BH_3 \quad \text{—— (2)}$$

Amine-borane complexes have been extensively utilized as reducing agents.[9] The reducing ability depends on the nature of the complexed amine. Less basic, more hindered amines form more reactive complexes.[9] Amine-borane complexes readily hydroborate alkenes if the stability of the complex is weakened by steric or electronic effects.[10,11] The amine-boranes have not been extensively utilized for hydroborations. However, N,N-diethylaniline-borane and N-phenyl morpholine-borane complexes have been reported to hydroborate at room

temperature[10] (eq 3 and 4).

$$BH_3{:}PhNEt_2 + 3C_8H_{13}CH{=}CH_2 \xrightarrow[25^oC]{2h} (C_8H_{17})_3B + PhNEt_2 \quad \text{— (3)}$$



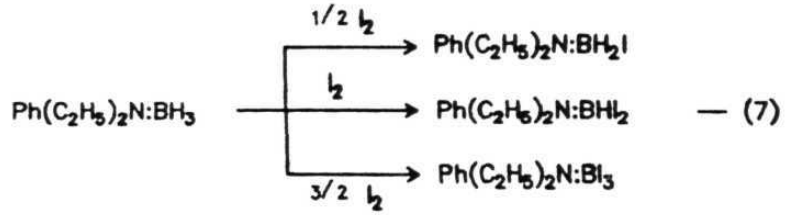
Several reports indicate that $ClBH_2$-Lewis base complexes give more controlled hydroboration than the BH_3-Lewis base complexes.[2,12] Monohaloboranes and dihaloboranes can be used for hydroboration reaction of alkenes and alkynes. These haloalkylboranes and haloalkenylboranes are useful intermediates for the synthesis of variety of organic compounds.

Recently, a convenient method has been developed in this laboratory for the generation of B_2H_6 using the $I_2/NaBH_4$ system by a slight modification of a reported method.[13] The diborane generated in this way has been used for the synthesis of $H_3B{:}N(C_2H_5)_2Ph$ complex which hydroborates olefins under ambient conditions (eq. 5 and 6).

$$NaBH_4 + I_2 \xrightarrow{DG} B_2H_6 + 2NaI + H_2 \quad \text{—— (5)}$$

$$B_2H_6 + N(C_2H_5)_2Ph \xrightarrow{\text{benzene}} 2H_3B{:}N(C_2H_5)_2Ph \quad \text{—— (6)}$$

It was of interest to examine the synthesis of various iodoboranes from the $H_3B{:}N(C_2H_5)_2Ph$ and study their utilities in functional group transformations (eq. 7).



It will be helpful to briefly review the synthesis and utilization of various haloboranes. Dialkylhaloboranes and trihaloboranes have been extensively used as reagents for the cleavage of a wide variety of ethers, acetals, esters, and enolization of ketones. These are also very effective as catalysts in Diels-Alder reactions. Dialkylhaloboranes and trihaloboranes can be also used as haloborating agents. Chiral haloboranes have been prepared for utilization in the asymmetric reduction of prochiral ketones.

Haloboranes as Hydroborating Agents:

1. Monochloroborane:

Earlier attempts to prepare $ClBH_2$ by the reaction of diborane with boron trichloride in gas phase failed due to the instability of the compound.[14] However, in ether solvents, diborane readily reacts with boron trichloride to form the corresponding chloroborane etherates[15] (eq. 8). The reaction in diethyl ether of boron trichloride with lithium borohydride (soluble in ether) provides a simpler preparative procedure (eq. 9).[16]

$$B_2H_6 + Cl_3B{:}OEt_2 \xrightarrow{Et_2O} 3ClBH_2{:}OEt_2 \quad \text{---- (8)}$$

$$LiBH_4 + BCl_3 \xrightarrow{Et_2O} LiCl + 2ClBH_2{:}OEt_2 \quad \text{---- (9)}$$

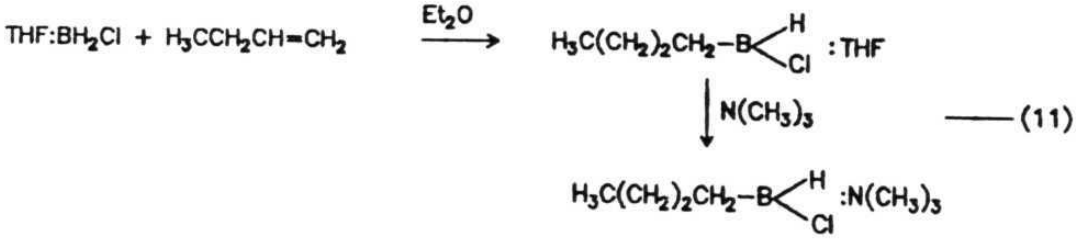
The presence of a strongly electronegative atom attached to boron, should make the haloboranes more effective as hydroborating agent. Indeed, neat chloroborane reacts vigorously with alkenes and

alkynes than does diborane.[17] However, as a strong Lewis acid, the compound forms strong complexes with donor solvents. Since the rate of hydroboration partly depends on the ease with which a particular complex dissociates, the hydroboration is slow. It was shown that monochloroborane–THF at $0^{o}C$ reacts only slowly with alkenes.[18,19] It was believed that the reaction proceeded to give dialkylchloro - borane (R_2BCl). Brown *et al* showed that the products were not dialkylchloroboranes but mixtures of trialkylboranes and alkyl-dichloroboranes ($RBCl_2$), with very little of the desired dialkyl-chloroborane (R_2BCl)[16] (eq. 10).

$$2R_2BCl \rightleftharpoons R_3B + RBCl_2 \qquad \text{—— (10)}$$

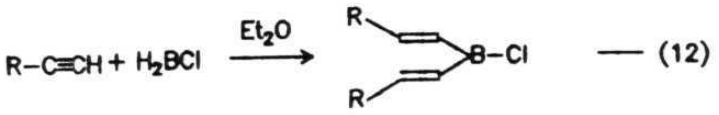
In diethyl ether, a solvent of lower basicity than THF, hydroboration is considerably faster. The regioselectivity of chloro borane diethyl ether is a little less than that of disiamylborane but more than that of borane–THF.[16]

Reaction of monochloroborane with alkenes in the presence of 1–2 molar equivalents of THF proceeds cleanly to give pure monoalkyl-chloroboranes (RBHCl) 94–97% yields. Under these conditions, the competing dihydroboration is prevented as the THF complex of n-BuBH(Cl) is not readily attacked by the olefin. The corresponding monoalkylchloroboranes can be isolated as trimethylamine complexes (eq. 11).[16]



—— (11)

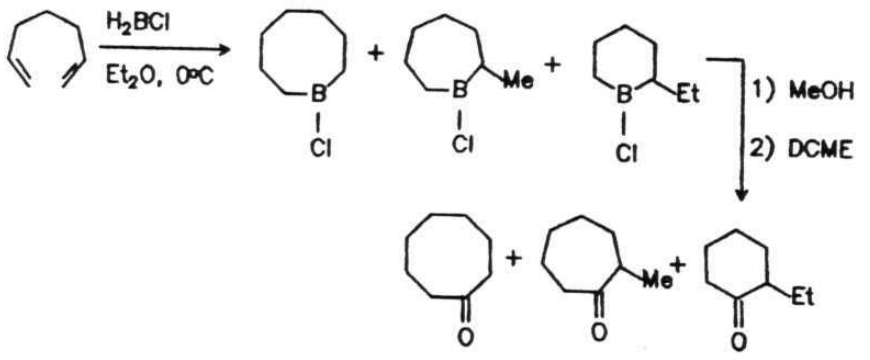
The reaction of terminal alkynes with monochloroborane etherate (2:1) is extremely fast at $0^{o}C$, affording dialkenylchloroboranes cleanly.[16] In this reaction 30–49% excess of 1-alkyne must be used to minimize dihydroboration which results in gem-diboryl derivatives (eq. 12).



— (12)

Dialkyl- and dialkenyl-chloroboranes have proved to be useful synthetic intermediates. Among the most important applications are, transformations into ketones,[20] tertiary alcohols,[21] dienes,[12] secondary amines[21] and ethyl alkyl acetates.[22]

The difunctional nature of monochloroborane favours the cyclic hydroboration of dienes. Several α,ω-dienes have been transformed into B-chloro-boraheterocycles in good yields.[23,24] Polymeric organoboranes, which are formed in addition to cyclic products, are readily depolymerized by heating under vacuum. In this way, five-to-eight-membered rings have been obtained (eq.13). Also, *cis,cis*-1-5-cyclooctadiene undergoes cyclic hydroboration with monochloroborane[25] (eq. 14). It is interesting to note that B-chloro-9-borabicyclo[4.2.1] nonane is the main product in the reaction mixture. It is converted into B-chloro-9-borabicyclo[3.3.1]nonane upon heating.



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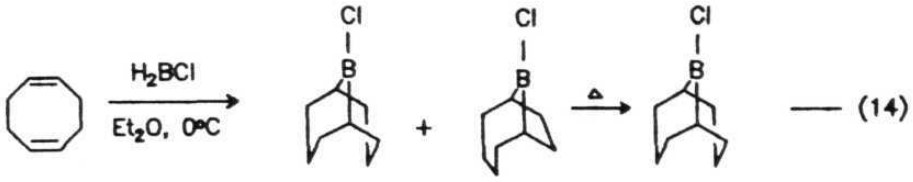


— (14)

Recently, monochloroborane–dimethylsulfide complex[26] (MCBS) has been prepared in a very simple way by redistribution of borane–dimethyl sulfide with boron trichloride–dimethyl sulfide (eq. 15). The product also exists in equilibrium with small amounts of borane and dichloroborane.[27] It has several advantages over the etherate as a hydroborating agent. MCBS is a neat liquid, stable indefinitely at room temperature. It can be obtained in higher concentrations than the etherate and hydroboration with MCBS can be carried out in various solvents *eg.* in DCM, $CHCl_3$, diethyl ether and pentane. Both monochloroborane etherate and MCBS hydroborate alkenes readily at 0^oC and 25^oC respectively. The reagents exhibit high regio–and stereoselectivity.[20]

$$2BH_3{:}SMe_2 + BCl_3{:}SMe_2 \xrightarrow{25^oC} 3BH_2Cl{:}SMe_2 \qquad \text{— (15)}$$

Monobromoborane–dimethyl sulfide complex (MBBS) and monoiodoborane–dimethyl sulfide complex (MIBS):

Both these reagents can be synthesized by treating $BH_3.SMe_2$ with ether $BBr_3.SMe_2$ and $BI_3.SMe_2$ or with required amounts of bromine and iodine respectively (eq. 16 and 17).[26,28]

$$2BH_3{:}SMe_2 + BBr_3{:}SMe_2 \longrightarrow 3H_2BBr{:}SMe_2 \quad \text{—— (16)}$$

$$2BH_3{:}SMe_2 + I_2 \xrightarrow{CS_2} 2H_2BI{:}SMe_2 + H_2 \quad \text{—— (17)}$$

Hydroborations of alkenes with these regents are most conveniently carried out in dichloromethane.[20] Monobromoborane dimethyl sulfide complex is more reactive than monoiodoborane dimethyl sulfide complex and hydroboration with the first compound is usually completed in 12h at 25°C. Reactions of alkene with monoiodoborane dimethyl sulfide complex require refluxing in dichloromethane. The corresponding dialkylhaloboranes are obtained in good yields.[20]

Dihalogenoboranes:

Dichloroborane-etherate is most conveniently synthesized by the reaction of lithium tetrahydridoborate with boron trichloride in ether[29] (eq. 18). It has only a limited stability, slowly cleaving ether even at 0°C. Complexes of dihalogenoboranes with dimethyl sulfide are more stable. They are prepared in a similar way[26-28] (eq. 19-21).

$$LiBH_4 + 3BCl_3 \xrightarrow[0°C]{Et_2O} 4HBCl_2{:}OEt_2 + LiCl \quad \text{—— (18)}$$

$$BH_3{:}SMe_2 + 2BCl_3{:}SMe_2 \longrightarrow 3HBCl_2{:}SMe_2 \quad \text{—— (19)}$$

$$BH_3{:}SMe_2 + 2BBr_3{:}SMe_2 \longrightarrow 3HBBr_2{:}SMe_2 \quad \text{—— (20)}$$

$$BH_3{:}SMe_2 + I_2 \xrightarrow{CS_2} HBI_2{:}SMe_2 + H_2 \quad \text{—— (21)}$$

The products are stable at room temperature. Dichloroborane reacts readily with alkenes in the gas phase.[17] In THF, dichloroborane reacts extremely slowly with alkenes.[18,19] The reaction of dichloro borane-EE with hex-1-ene in diethyl ether is incomplete after 2h at 25°C. Though the reagent without solvent reacts somewhat faster, it still requires 17h at 25°C completion.[29] The difficulty in the hydroboration using dichloroborane-EE has been solved by adding a mixture of the alkene and BCl_3 in pentane to the reagent.[29] It has been suggested that the stronger Lewis acid complexes with the ether and liberates free dichloroborane (eq. 22) which rapidly hydroborates the alkene (eq. 23).

$$BHCl_2{:}OEt_2 + BCl_3 \longrightarrow BCl_3{:}OEt_2 + BHCl_2 \quad \text{—— (22)}$$

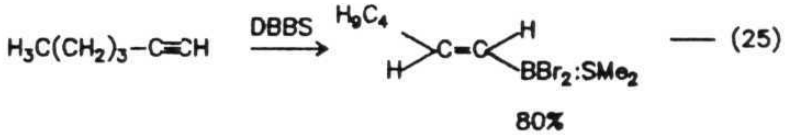
$$BHCl_2 + H_5C_2{-}CH{=}CH_2 \longrightarrow H_3C(CH_2)_2CH_2{-}BCl_2 \quad \text{—— (23)}$$

Several alkyldichloroboranes have been obtained by this method in 76-90% yields.[29,30] In the same way, 1-hexyne and 3-hexyne have been cleanly transformed into trans-1-hexenyldichloroborane and cis-3-hexe nyldichloroborane respectively, demonstrating the utility of the reagent for the synthesis of alkenyldichloroboranes.[29] Use of dichloroborane etherate and 1-alkyne in 2:1 ratio, leads to total dihydroboration resulting in the formation of gem-diboryl derivatives[29] (eq. 24).

$$H_3C(CH_2)_3{-}C{\equiv}CH + 2BHCl_2 \longrightarrow H_3C(CH_2)_4{-}CH\begin{matrix}BCl_2\\BCl_2\end{matrix} \quad \text{—— (24)}$$

In contrast to the complexes of dichloroborane with ether and dimethyl sulfide, the addition compounds of dibromoborane and diiodoborane with dimethyl sulfide (DBBS and DIBS) hydroborates alkenes directly.[30] This unexpected trend in the reactivity of dihalogenoborane complexes is of theoretical interest, pointing to the importance of the Lewis base participation in the transition state of the hydroboration reaction.[30]

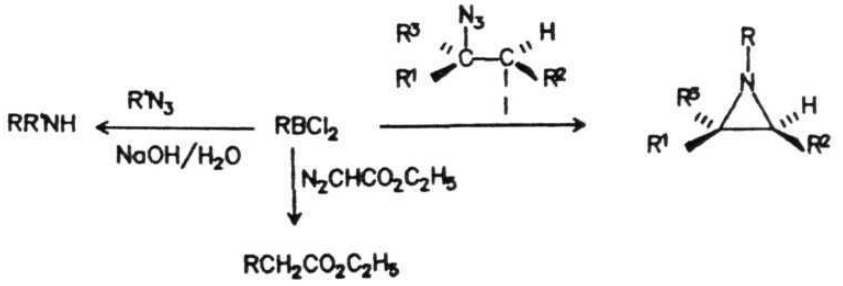
In recent years DBBS has found extensive use in organic synthesis. Terminal and internal alkynes are cleanly transformed into the corresponding alkenylbromoboranes by DBBS with high isomeric purity[31] (eq. 25).

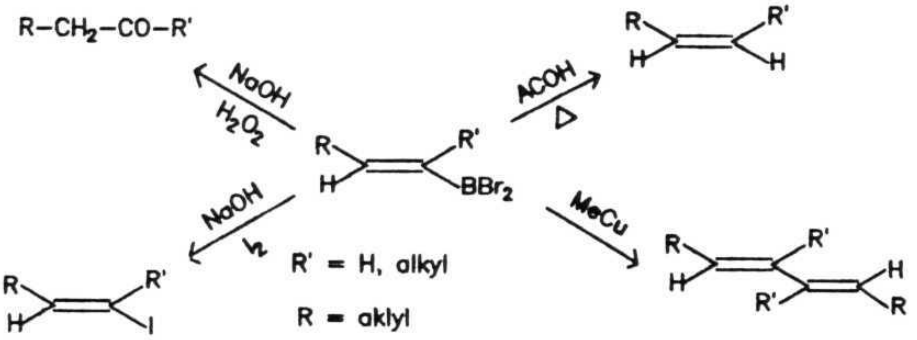


— (25)

Alkenyldibromoboranes undergo a number of synthetically useful transformations *e.g.* protonolysis to 2-alkenes,[31] oxidation to the carbonyl derivatives,[31] iodination to (E)-alkenyl iodides[31] and conversion to (E,E)-1,3-dienes via organo cuprates.[31] Similarly, alkyldichloro boranes have proved to be useful intermediates in the synthesis of alkyl hydroperoxides,[32] alkyl aziridines,[33] secondary amines[34] and in the transformation of alkenes to their corresponding two carbon chain- lengthened ethyl esters[35] (Scheme 1).

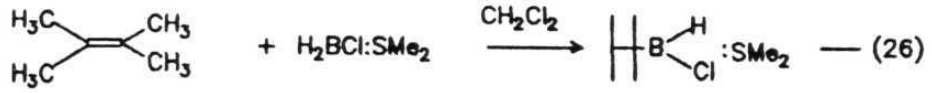
SCHEME 1

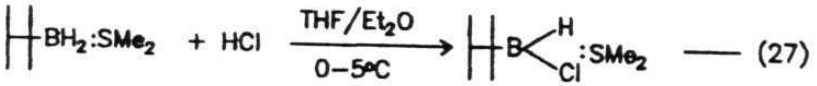




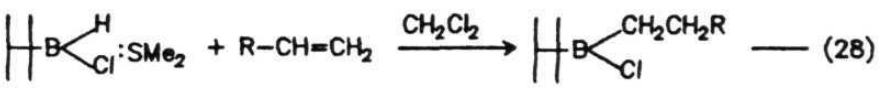
Thexylchloroborane:

Thexylchloroborane can be prepared by hydroboration of 2,3-dimethyl-2-butene with monochloroborane-THF[36] or MCBS[36] and by the reaction of thexylborane with hydrogen chloride[37] (eq. 26 and 27).





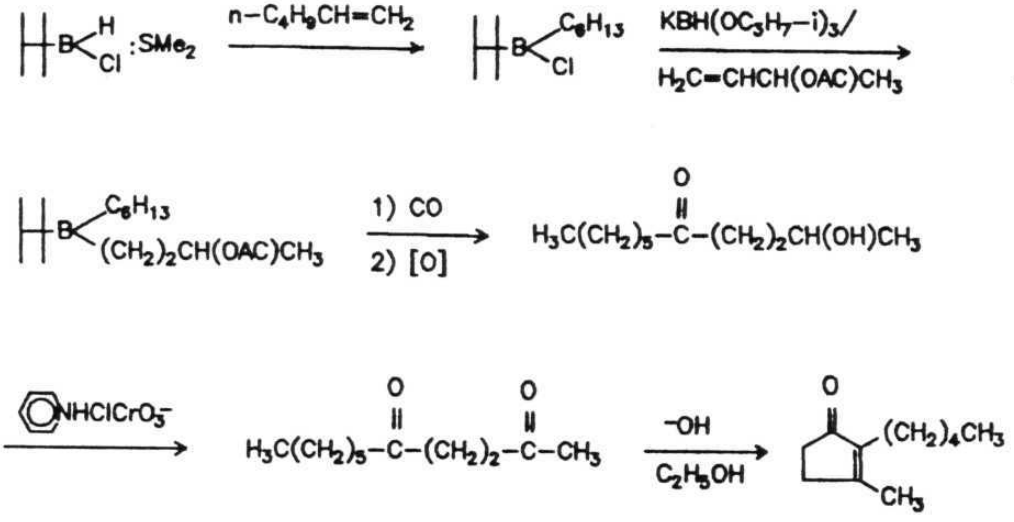
Thexylchloroborane readily hydroborates alkenes, providing a convenient route to thexylalkylchloroborane (eq. 28).[36,37]



Reduction of thexylalkylchloroboranes with potassium triisopropoxyborohydride (KIPBH) in the presence of an alkene leads to dialkylthexylboranes (eq. 29).[38]

— (29)

Thexyl chloroborane has been used in the synthesis of dihydrojasmone[39] which is an important perfume ingredient and is a constituent of barganot oil (Scheme 2).



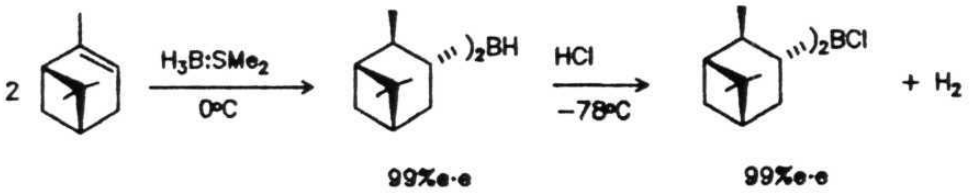
Haloboranes as Reducing Agents:

Diisopinocampheylchloroborane:

Diisopinocampheylchloroborane (Scheme 3), readily prepared in high chemical and optical purities (99% ee) from (+)-α-pinene (92% ee) via hydroboration, followed by treatment with dry hydrogen chloride in

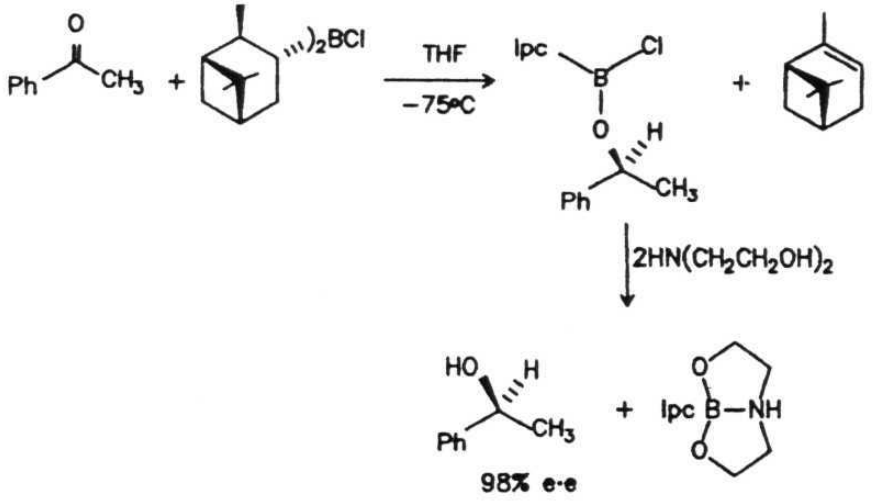
ether, reduces ketones at convenient rates at $-25^{o}C$. The chiral induction is excellent for the reduction of aromatic prochiral ketones.[40,41]

SCHEME 3



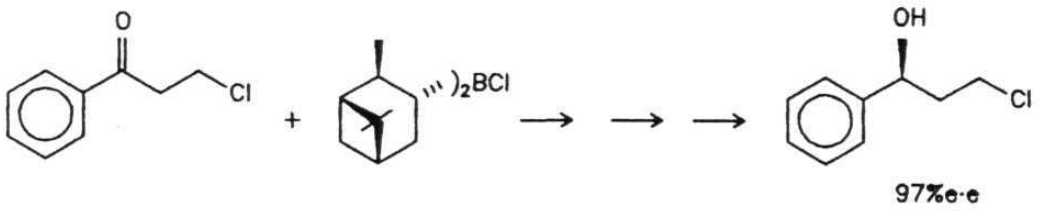
For example, acetophenone could be reduced to (S)-1-phenyl ethanol in 95% ee and in 72% isolated yield (Scheme 4).

SCHEME 4



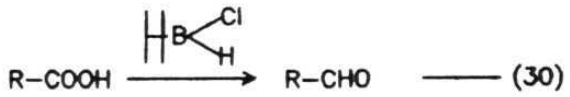
Diisopinocampheylchloroborane, also reduces ring and chain substituted halo alkyl aryl ketones to the corresponding halo alcohols in excellent enantiomeric excess.[42] These chiral halo alcohols are versatile intermediates. They can be readily cyclized to oxiranes and 2-substituted tetrahyrofurans with retention of chirality (Scheme 5).

SCHEME 5



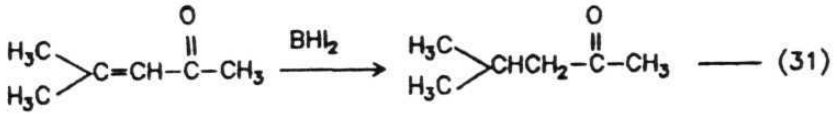
Thexylchloroborane:

An useful application of thexylchloroborane (eq. 30) is in the reduction of RCOOH into RCHO.[40] Other borane reagents generally lead to over reduction to the corresponding alcohols.



Diiodoborane:

Ashby *et al* prepared BHI_2.THF by adding I_2/THF to BH_3.THF at 0^oC. This reagent is useful for regioselective conjugate reduction of enones (eq. 31).[44]



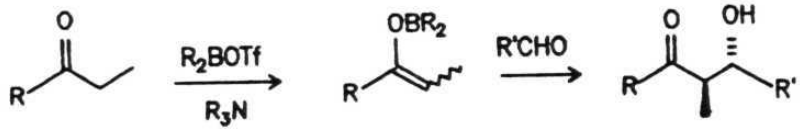
Haloboranes for use in Aldol and Diels–Alder Reactions:

Enol borinates are valuable intermediates in organic synthesis. The ready synthesis and ease of handling of dialkylboron chlorides, R_2BCl, compared to triflates, R_2BOTf, give the chlorides a significant

advantage as reagents to achieve the conversion of ketones into enol borinates, regiospecifically and quantitatively.

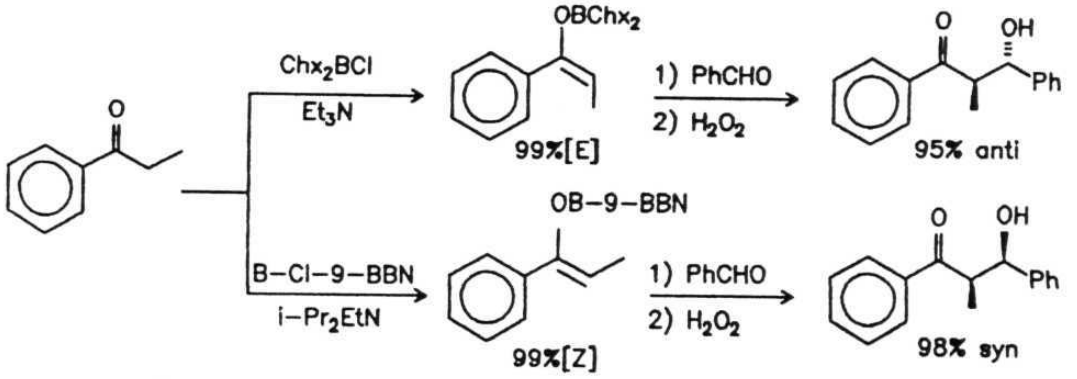
The dialkylboron triflates, R_2BOTf, reagents achieve the conversion of representative ketones into the corresponding enol borinates for subsequent conversion into the corresponding aldols in good yields (Scheme 6).[45]

SCHEME 6



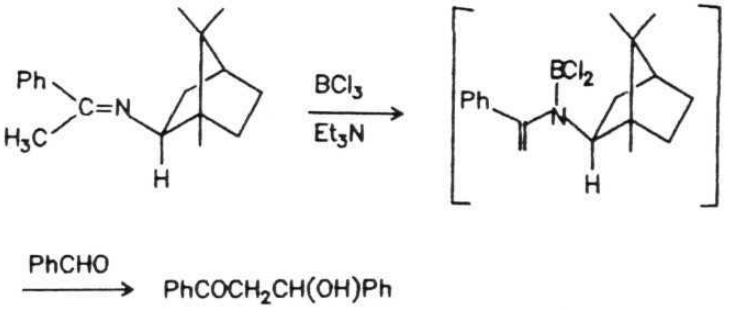
Brown *et al* [46] found that the dialkylboron chlorides in the presence of tertiary amines rapidly and quantitatively convert ketones into the corresponding enol borinates. Moreover, the R_2BCl reagents greatly influence the stereochemistry of the enol borinate formed, making it possible to produce preferentially either (Z) or (E)-enol borinate, leading to the corresponding *syn* or *anti* aldols on reaction with PhCHO. Both B-chloro-9-borabicyclo[3.3.1]nonane, B-Cl-9-BBN, and dicyclohexyl chloroborane, ChX_2BCl, can be readily synthesized.[20] They react readily with ketones in the presence of either Et_3N or i-Pr_2(Et)N (Scheme 7).

SCHEME 7



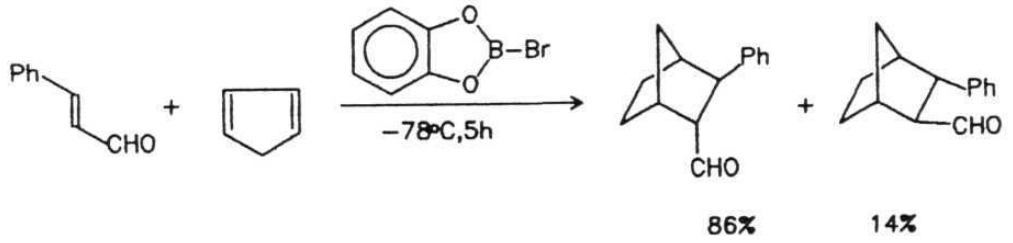
Sugasawa and Toyoda studied the asymmetric aldol condensation of acetophenone and benzaldehyde with chiral vinylaminodichloroborane.[47] It was found that the S-(-)-N-(α-methylbenzyliden)isobornylamine, when treated with boron trichloride in the presence of triethyl amine gives the chiral boron intermediate. This intermediate reacts with benzaldehyde to give R-(+)-β-hydroxy-β-phenylpropiophenone in 30% chemical yield and with an optical purity of 48% (Scheme 8).

SCHEME 8



Kelly *et al* found that the bromocatecholborane catalyzes Diels-Alder reactions.[48] Bromocatecholborane can be readily prepared by the reaction of catechol with boron tribromide (Scheme 9).[49]

SCHEME 9

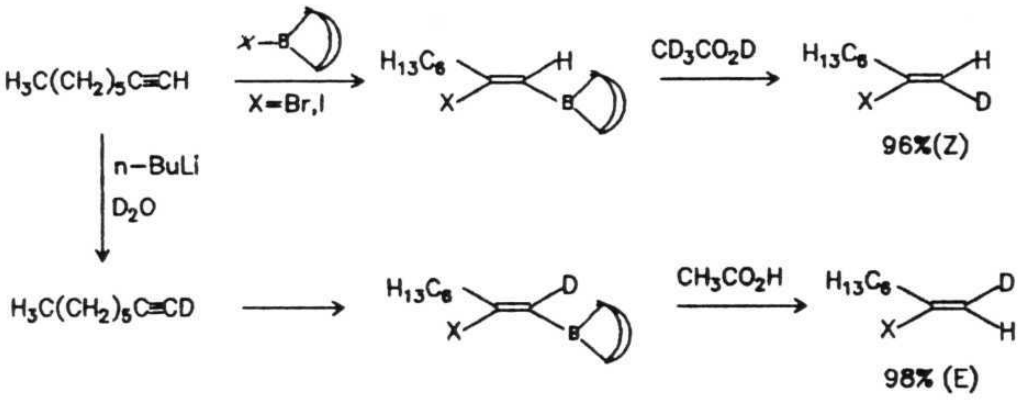


Boron halides as Haloborating Agents:

Boron halides are also useful as haloborating agents.[50] Haloboration reaction of 1-alkynes gives 2-halo-1-alkenyl boranes,

which are useful intermediates for the synthesis of a variety of organic compounds. B-bromo- or B-iodo-9-borabicyclo[3.3.1]nonane reacts readily with 1-alkynes. Such haloboration reactions proceed through Morkovnikov addition of the X-B moiety to -C≡C-bonds in *cis* fashion. The bromoboration reaction occurs chemoselectively at terminal -C≡C-bonds but not at internal -C≡C-, terminal and internal -C=C-bonds. The protonolysis of haloboration products with acetic acid gives the corresponding 2-bromo- or 2-iodo-1-alkenes in excellent yields (Scheme 10).[50]

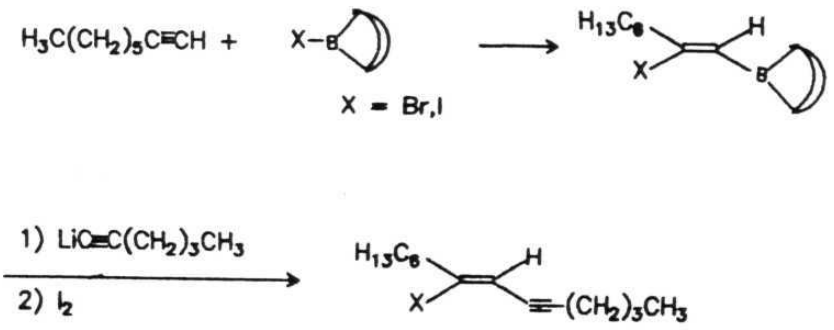
SCHEME 10



Under basic conditions the haloborated adducts are unstable.[51] 2-Haloalkenylboranes can be used for the selective synthesis of haloalkenyl derivatives under appropriate conditions without significant interference by competing β-elimination reactions.[52]

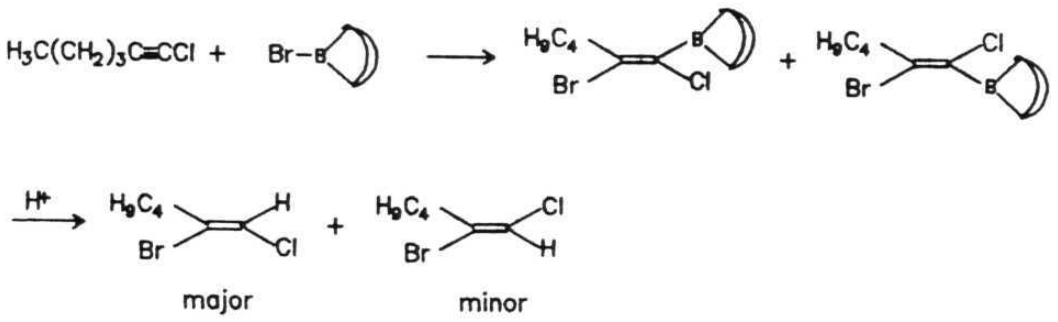
(Z)-1-Alkynyl-2-halo-1-alkenes can be stereo- and regioselectively synthesized in relatively good yields from 1-alkynes by the haloboration with B-halo-9-borabicyclo[3.3.1]nonane, and subsequent treatment with lithium acetylides and iodine (Scheme 11).[52]

SCHEME 11



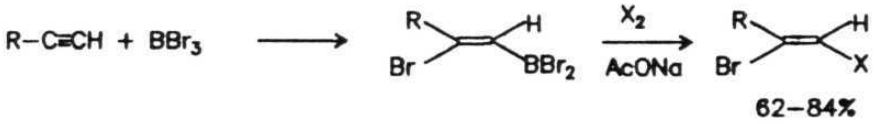
The reaction of 1-chloro-1-hexyne with B-bromo-9-borabicyclo-[3.3.1] nonane for 72h at room temperature, yields a mixture of 1-chloro- 2-bromo-1-hexenes after protonolysis (Scheme 12).[53]

SCHEME 12



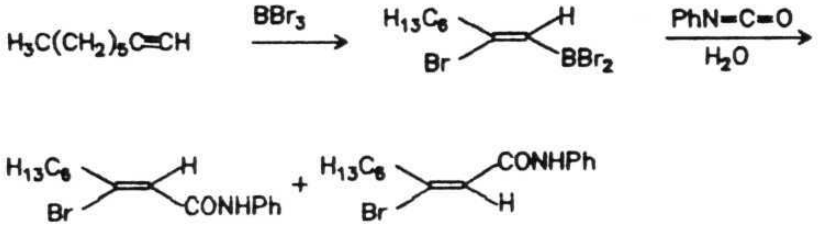
An attempt to synthesize (Z)-1,2-dihalo-1-alkenes from bromo-boration adducts of 1-alkynes with B-Br-9-BBN, has been unsuccessful. However, it has been found that the haloboration of 1-alkynes with tribromoborane, followed by the reaction with iodine or bromine in the presence of sodium acetate gives the expected (Z)-1,2-dihalo-1-alkenes stereospecifically (>98%) in good yields[54] (Scheme 13).

SCHEME 13



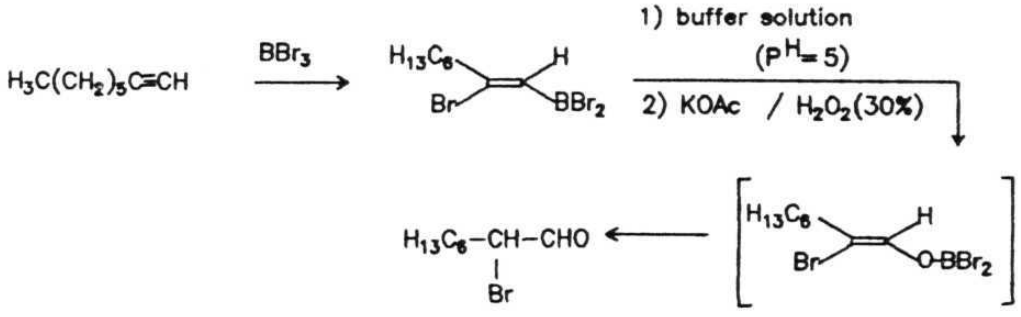
(Z)-2-Bromo-1-octenyldibromoborane, prepared by mixing an equimolar amount of BBr_3 and 1-octyne, readily undergoes 1,2 addition to phenyl isocyanate, to give two isomeric N-phenyl-3-bromo-2-nonenamides (Scheme 14).[55]

SCHEME 14

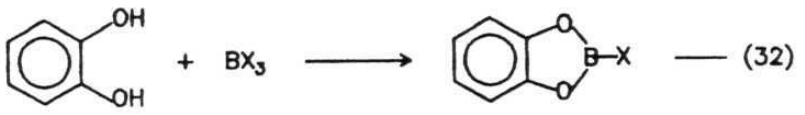


The reaction of BBr_3 with 1-alkynes gives 2-bromo alkenyl dibromoborane which on hydrogen peroxide oxidation yields 2-bromo alkanals (Scheme 15).[56]

SCHEME 15



Boron halides BX_3 (X = Cl, Br) can be also used for the preparation of halocatecholboranes. These are mild and selective reagents for cleavage of certain ether, ester and carbamate protecting groups (eq 32-35).



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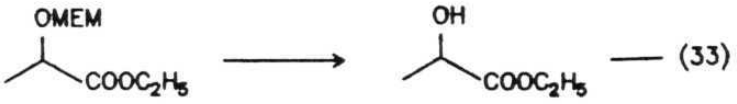


— (33)

—(34)

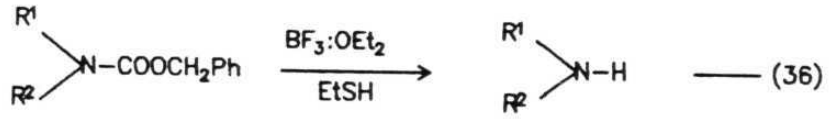
— (35)

Boron Halides for use in Ether Cleaving Reactions:

Boron trifluoride:

The addition complex of boron trifluoride with diethyl ether is the most readily accessible derivative. It can be distilled without decomposition (b.p. 124°C.760 torr).[58] Among the known Lewis acid complexes $BF_3.OEt_2$ is the most widely used reagent. Aliphatic and aromatic benzyl ethers have been easily cleaved on treatment with the hard acid, boron trifluoride etherate, and a soft nucleophile, EtSH or ethanedithiol to give the parent alcohols and phenols, respectively.[59]

Recently, the cleavage of benzyl carbamates was carried out using boron trifluoride etherate and ethanethiol (eq. 36).[60]



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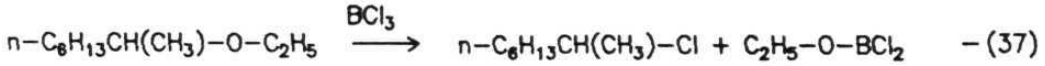
Boron trichloride:

Boron trichloride has been extensively used as a reagent for the cleavage of a wide variety of ethers such as alkyl aryl ethers, mixed aliphalic ethers, cyclic ethers and methoxy derivatives of carbohydrates. It also cleaves acetals and certain types of esters.[61]

Mixed dialkyl or alkyl alkenyl ethers are cleaved to give the alkyl chloride derived from the more electron releasing group (or the one leading to a the more stable carbenium ion) (eq 37 and 38)



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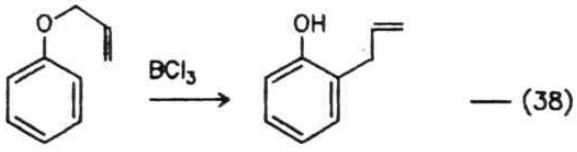
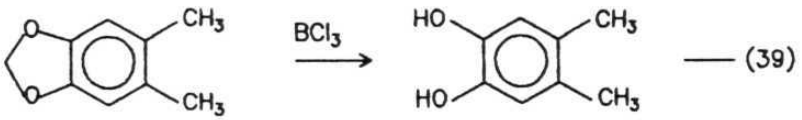


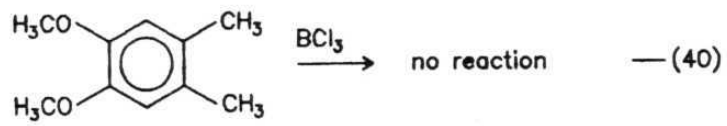
— (38)

It has been found that cleavage of ethers is easy with groups which form carbenium ions readily and also leads to facile carbenium ion rearrangements.[61,62]

The methylenedioxy group is cleaved selectively in the presence of methoxy groups in simple compounds as well as in multifunctional

natural products (eq 39 and 40).[63,64]



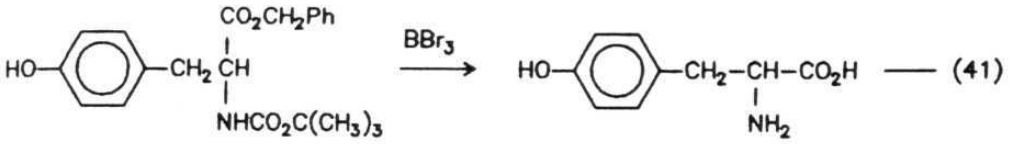


Boron tribromide:

The BBr_3 reagent has been used widely to cleave ether protecting groups under mild conditions without affecting a large number other functional groups. In the course of synthesis of complex natural products and biologically active materials, its usefulness has been widely exploited.[65,66]

Boron tribromide cleaves the ether function without affecting ester group or double bonds. When two or more ether functions are present, one of them could be cleaved without affecting the others.[67,68]

It has been well recognized that ordinarily an ester function could survive the reaction conditions needed for the cleavage of ether groups.[69,70] There are few quantitative data on the relative rates of cleavage of esters and ethers. However, protective groups like benzyl or benzyloxy carbonyl are cleaved at room temperature or below in 2 to 3h. The yields are 60–90% and, more importantly, the optical purity of the products is 99% (eq. 41).

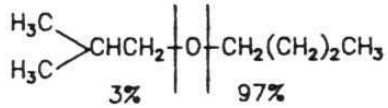


(41)

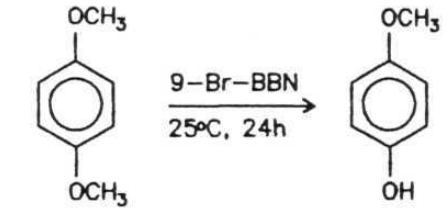
9-Bromo-9-borabicyclo[3.3.0]nonane, 9-Br-9BBN:

In a trifunctional reagent like boron tribromide, reactivity decreases sharply as each B-Br bond is replaced by a B-O bond. For example, dialkoxyboron bromide is very much less reactive than boron tribromide. As a sterically bulky reagent with a single B-Br bond, 9-Br-9BBN could be expected to have greater regioselectivity and a more uniform ether cleaving ability than BBr_3.[71]

The reagent distinguishes between two primary C-O bonds and cleaves only one of them with remarkable selectivity.



Refluxing a molar solution of each component in DCM is adequate for the cleavage of the common types of aryl-alkyl and alkyl-alkyl ethers. The reagent also displays selectivity in its ability to cleave one of the methoxy groups when more than one of the groups are present, *eg.* p-methoxyphenol is obtained in 87% from p-dimethoxy benzene. Also, a sensitive ether like allyl phenyl ether is cleaved to give allyl bromide and phenol. In contrast, BCl_3 brings about Claisen rearrangement (eq. 42-44).



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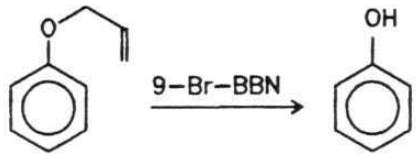

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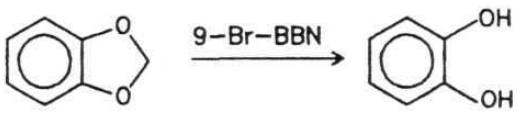


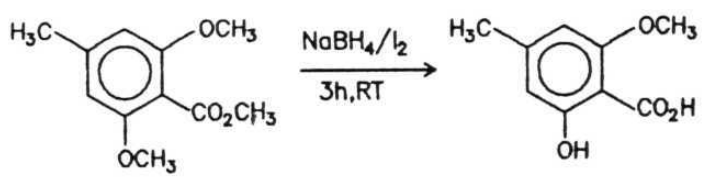
— (44)

Boron triiodide:

The strength of boron halides increases in the order.[71]

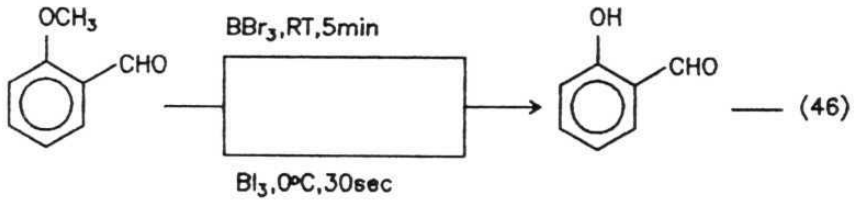
$$BF_3 < BCl_3 < BBr_3 < BI_3$$

It is therefore expected that boron triiodide should cleave ethers under milder conditions than those needed for boron tribromide. Only a few examples of the use of the reagent generated from sodium borohydride and iodine have been reported (eq. 45).[72]

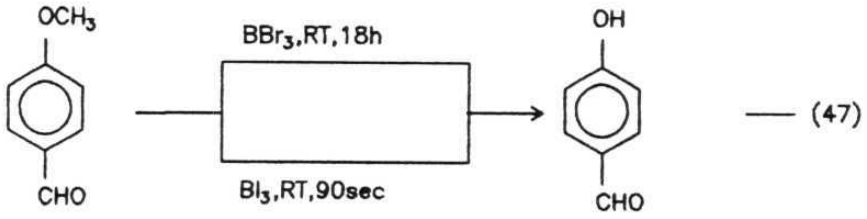


— (45)

Recently, Lansinger and Ronald, have studied the ether cleaving ability of pure boron triiodide and compared it with that of boron tribromide. As expected, they found boron triiodide to be a more powerful ether cleaving agent than boron tribromide (eq. 46 and 47).[73]



(46)

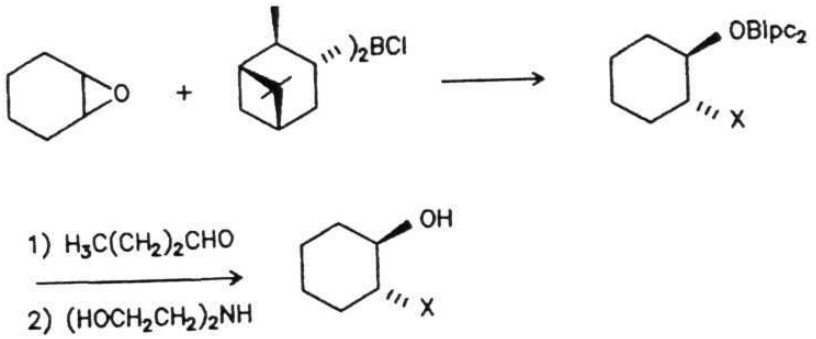


(47)

Diisopinocampheylchloroborane:

Diisopinocampheylchloroborane, can be used in enantioselective ring cleavage of meso epoxides to get halohydrins with excellent enantiomeric purity (Scheme 16).[74]

SCHEME 16



Our results of the investigations on the synthesis and utilization of iodoborane complexes are described in the next section.

RESULTS AND DISCUSSION

Synthesis and Reactions of Iodoborane–N,N-diethylaniline complex:

As outlined in the introductory section, the haloborane etherates or dimethyl sulfide complexes possess reactivities very much different from BH_3.THF or BH_3.SMe_2. Synthesis of chloroboranes and bromoboranes from the corresponding BH_3–Lewis base complexes require standardized solutions of HCl, BCl_3 or BBr_3 which make the synthesis and handling of such complexes somewhat difficult. It was of interest to examine the synthesis and reactivities of the iodoborane complexes.

The iodoborane Lewis base complexes have been prepared from the reaction of I_2 with the corresponding BH_3.Lewis base complexes[26,28] (eq. 48 and 49).

$$2H_3B{:}SMe_2 + X_2 \xrightarrow[X=Br,I]{CS_2} HX_2B{:}SMe_2 + H_2 \quad \text{— (48)}$$

$$(H_3C)_3N{:}BH_3 + I_2 \longrightarrow (H_3C)_3N{:}BHI_2 + H_2 \quad \text{— (49)}$$

We now have a convenient method for the synthesis of $BH_3{:}N(C_2H_5)_2Ph$, through the reaction of B_2H_6 generated using $I_2/NaBH_4$ reagent.[13] It was of interest to prepare the $Ph(C_2H_5)_2N{:}BH_2I$, $Ph(C_2H_5)_2N{:}BHI_2$ and $Ph(C_2H_5)_2{:}BI_3$ complexes and examine their reactivities towards organic functional groups.

It was found that the reaction of appropriate amounts of I_2 give the corresponding BH_2I, BHI_2 and BI_3 complexes (eq. 50–52).

$$2Ph(C_2H_5)_2N{:}BH_3 + I_2 \xrightarrow{\text{benzene}} 2Ph(C_2H_5)_2N{:}BH_2I + H_2 \quad \text{— (50)}$$

$$Ph(C_2H_5)_2N{:}BH_3 + I_2 \longrightarrow Ph(C_2H_5)_2N{:}BHI_2 + H_2 \quad \text{— (51)}$$

$$Ph(C_2H_5)_2N{:}BH_3 + 3/2I_2 \longrightarrow Ph(C_2H_5)_2N{:}BI_3 + 3/_2H_2 \quad \text{— (52)}$$

The infrared spectrum of the products in solution indicates the formation of these products as major species. However, presence of minor amounts of mixture of species cannot be ruled out (see experimental section for details).

Initially, we have examined the hydroboration characteristics of the $IBH_2{:}N(C_2H_5)_2Ph$ complex. The reagent is useful for hydroboration of alkenes and alkynes.

Hydroboration of 3-equivalents of 1-decene with $IBH_2{:}N(C_2H_5)_2Ph$ complex in benzene at room temperature for 14h, 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-diethylamiline-BH_3 complex is lost on reaction with iodine (eq. 53).

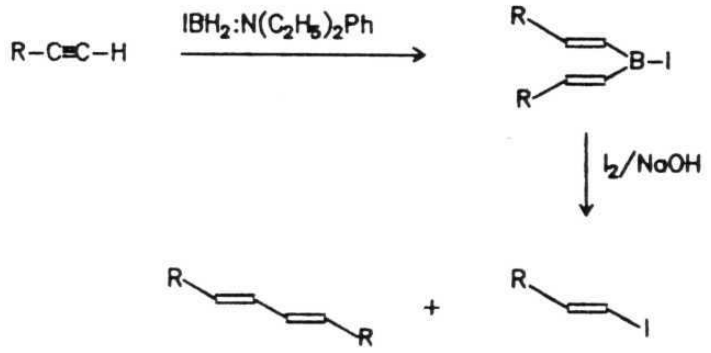
$$IH_2B{:}N(C_2H_5)_2Ph + H_3C(CH_2)_7CH{=}CH_2 \longrightarrow \xrightarrow{[O]} \begin{matrix} H_3C(CH_2)_8CH_2OH \\ + \\ H_3C(CH_2)_7CH{=}CH_2 \end{matrix} \quad \text{— (53)}$$

Hydroboration of 2-equivalents of 1-decene with $BH_2I{:}N(C_2H_5)_2Ph$ followed by carbenoidation-oxidation gave di-1-decylketone in 84% yield (eq. 54).

$$2H_3C(CH_2)_7CH{=}CH_2 + IH_2B{:}N(C_2H_5)_2Ph \longrightarrow [\ ] \xrightarrow{CHCl_3/NaOCH_3} \begin{matrix} O \\ \| \\ H_3C(CH_2)_9{-}C{-}(CH_2)_9CH_3 \end{matrix} \quad \text{— (54)}$$

As discussed in the introductory section, one of the most important applications of the monohaloborane (eg. $BH_2Cl:OEt_2$), is its use in the preparation of *cis, trans*-dienes from 1-alkynes.[16] We have found that application of the $BH_2I:N(C_2H_5)_2Ph$ complex for this purpose resulted in the formation of a mixture of the *trans, trans*-diene and the iodoolefin (Scheme 17).

SCHEME 17



Monovinylboranes give trans-iodoalkenes on reaction with I_2/NaOH.[75] Also, even divinylboranes give iodoalkenes as side products in the conversion of divinylborane to *cis, trans*-diene.[16] However, the formation of *trans, trans*-diene instead of *cis, trans*-diene is not understood. Accordingly, we have proceeded to investigate the synthetic utilities of the $BHI_2:N(C_2H_5)_2Ph$ complex. We have found that this $HBI_2:N(C_2H_5)_2Ph$ complex is useful for the hydroboration of alkenes, alkynes, reductive iodination of carboxylic acids, aldehydes and ketones, iodination of alcohols, reduction of amides and also in certain selective reactions.

Hydroboration of Alkenes and Alkynes with BHI_2:$N(C_2H_5)_2Ph$ complex:

The halo-boranes have an advantage over monoalkyl and dialkyl boranes for synthetic applications, since oxidations of organoboranes obtained using the alkylborane agents give products derived from the alkyl moieties, which might pose problems during workup. The reactivities of chloro and bromo borane - Lewis base complexes have been studied in some detail. Although, the $I_2BH.SMe_2$ complex is readily available through the reaction of $BH_3.SMe_2$ with I_2,[28] the reactivities of this reagent have not been examined in detail.

Hydroboration-oxidation of 1-decene with the diiodoborane-N,N-diethylaniline complex in 12h at room temperature gives 1-decanol in 81% yield. The reaction with styrene gives 2-phenylethanol in 83% yield. The ^1H NMR spectrum of the product indicates the absence of signals corresponding to 1-phenylethanol. These results are summarized in Table 1 (eq. 55 and 56).

$$H_3C(CH_2)_7CH{=}CH_2 \xrightarrow[2)\ {}^-OH/H_2O_2]{1)\ I_2HB{:}N(C_2H_5)_2Ph} H_3C(CH_2)_8CH_2OH \quad \text{—— (55)}$$

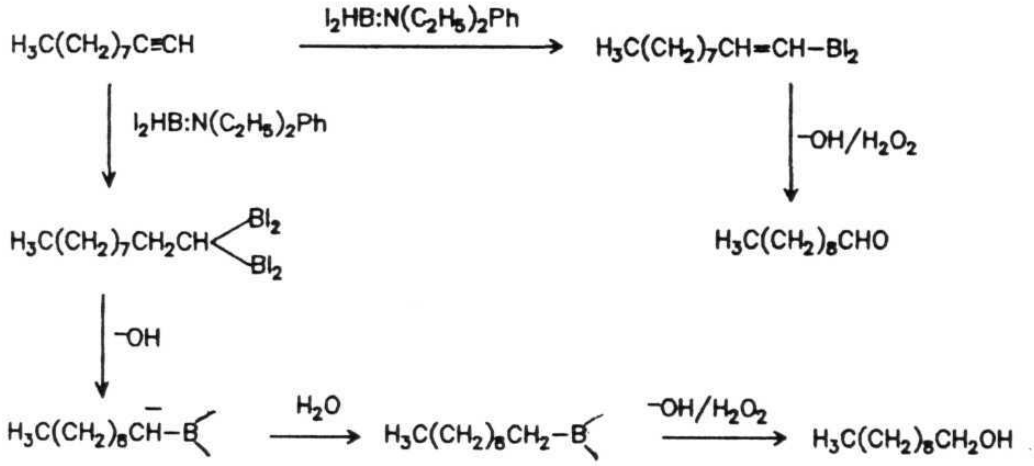
$$Ph{-}CH{=}CH_2 \xrightarrow[2)\ {}^-OH/H_2O_2]{1)\ I_2HB{:}N(C_2H_5)_2Ph} PhCH_2CH_2OH \quad \text{—— (56)}$$

With BH_3.THF, styrene undergoes hydroboration to place 81% of the boron on the terminal position with 19% at the internal position. In the case of $BHBr_2.SMe_2$ styrene undergoes hydroboration to place 97% of the boron on the terminal position with 3% at the 2-position.[2]

Hydroboration of 1-decyne for 12h followed by oxidation using

NaOAc/H_2O_2 yields 1-decanal 50% and 1-decanol 20% was isolated. These results are summarized in Table 1. The formation of 1-decanol indicates that a 1,1-dibora derivative is also formed in the hydroboration in addition to the alkenylborane (Scheme 18).

SCHEME 18



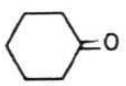
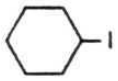
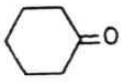
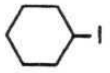
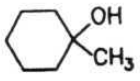
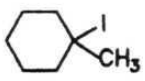
As outlined in the introductory section (eq. 24) hydroboration of 1-alkynes with a $BHCl_2$ complex yields gem-dibora derivative.

We have also carried out certain selective hydroboration studies with the BHI_2 amine complex which will be discussed later in this chapter.

Reductive iodination of carbonyl compounds:

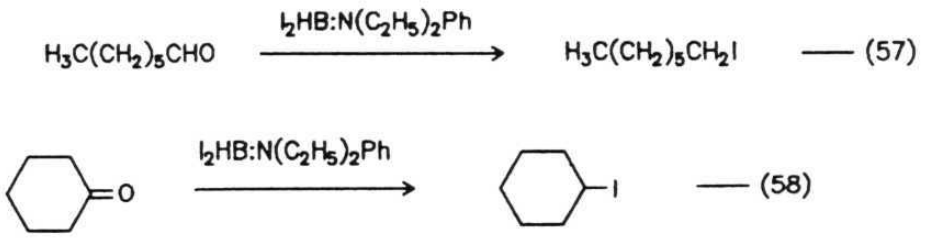
We have examined the reduction characteristics of the BHI_2:$N(C_2H_5)_2Ph$ complex in detail. It was found that the carbonyl compounds and carboxylic acids give the corresponding alkyl iodides in moderate to good yields, on reaction with BHI_2:$N(C_2H_5)_2Ph$ complex (Table 1).

TABLE 1: Hydroborations, Reductions, Iodination and Reductive Iodinations using BHI_2:$N(C_2H_5)_2Ph$ Complex:

Entry No.	Substrate	Reaction-Time	Product[d]	Yield(%)
1.	$H_3C(CH_2)_7CH = CH_2$	12h[a]	$H_3C(CH_2)_8CH_2$-OH	81
2.	$PhCH = CH_2$	12h[a]	$PhCH_2CH_2$-OH	83
3.	$H_3C(CH_2)_7CH \equiv CH$	12h[a]	$H_3C(CH_2)_8CHO$ + $H_3C(CH_2)_8CH_2$-OH	50 20
4.		11h[c]		75
5.	$H_3C(CH_2)_5CHO$	11h[c]	$H_3C(CH_2)_5CH_2$-I	82
6.	Ph-CH_2-COOH	11h[c]	$PhCH_2CH_2$-I	66
7.	$HOOC(CH_2)_8COOH$	11h[c]	I-$H_2C(CH_2)_8CH_2$-I	60
8.	$H_3C(CH_2)_{14}CH_2$-OH	12h[c]	$H_3C(CH_2)_{14}CH_2$-I	84
9.		6h[c]		82
10.		6h[c]		69
11.		12h[c]		86
12.		1h[c]		89
13.	$H_3C(CH_2)_8CON(CH_3)Ph$	12h[b]	$H_3C(CH_2)_8CH_2N(CH_3)Ph$	81
14.	$PhNHCOCH_3$	12h[b]	$PhNHCH_2CH_3$	41

(a) The experiments were carried out using organic substrate (5 mM), amine-borane (5 mM) and iodine (5 mM). The organoborane was oxidized using $NaOH/H_2O_2$. (b) Amides (5 mM), amine-borane (10 mM) and iodine (10 mM) were used. (c) For entires 8-12, alcoholic substrates (10 mM), amine-borane (10 mM) and iodine (10 mM) were utilized. For entries 4 and 5, the ketonic and aldehydic substrates (10 mM), amine-borane (10 mM) and iodine (10 mM),were utilized. For entry 6, the carboxylic acid substrate (10 mM), amine-borane (30 mM) and iodine (30 mM) were utilized. For entry 7, the carboxylic acid substrate (5 mM), amine-borane (30 mM) and iodine (30 mM) were utilized. For entry 8, the alcohol was added at 25^oC in 1h and then stirred for 12h at 80^oC. For entires 4-7, the substrates were added at 0^oC, the contents were brought to 25^oC in 1h and stirred for 11h at 25^oC. (d) The products were isolated by column chromatography, silica gel using (hexane:ethyl acetate) as an eluent and identified by spectral data (IR, ^1H & ^{13}C NMR) and comparison with data reported in the literature.

It was observed that reductive iodination of cyclohexanone and heptanaldehyde with diiodoborane-N,N-diethylaniline complex give the corresponding alkyl iodides in 75 and 82% yields (eq. 57 and 58).

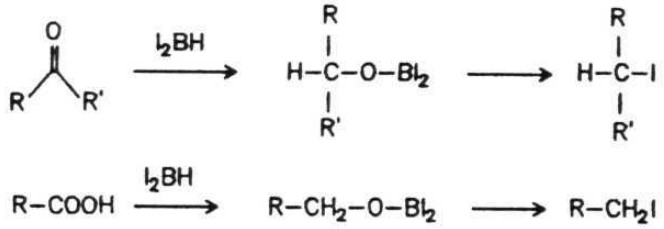


The reductive iodination of carboxylic acids with diiodoborane-N,N-diethylaniline complex gives the corresponding primary alkyl iodides in 60-66% yields. These results are summarized in Table 1 (eq. 59).

$$PhCH_2COOH \xrightarrow{I_2HB:N(C_2H_5)_2Ph} PhCH_2CH_2I \qquad (59)$$

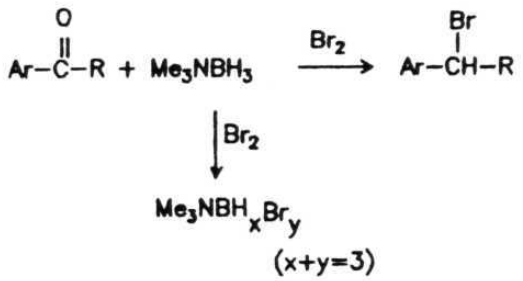
The reductive iodination of carbonyl compounds and carboxylic acids would go through the intermediacy of alkoxyboron compounds, since these substrates should readily undergo reduction by the boron hydride species present in the medium (Scheme 19).

SCHEME 19



Recently, it has been reported that reduction of aromatic ketones using Br_2-trimethylamine:BH_3 complex gives the corresponding bromo compounds. However, this reagent is not applicable to aliphatic carbonyl compounds.[76] The aliphatic aldehydes and ketones are reduced to corresponding alcohols under these conditions (Scheme 20).

SCHEME 20



The procedures developed here should serve as convenient methods for the direct conversion of carbonyl compounds and carboxylic acids to the corresponding alkyl iodides.

Conversion of Alcohols to Iodides:

Conversion of alcohols and ethers to iodides can be readily achieved utilizing B_2H_6 and I_2 or MBH_4 (M = LI, Na) and I_2[77-79] (eq. 60-62).

$$6MeOH + 3I_2 \xrightarrow{B_2H_6} 6MeI + 2H_3BO_3 + 3H_2 \qquad \text{——— (60)}$$

$$6PhOCH_3 + 3I_2 \xrightarrow{B_2H_6} 6MeI + 2B(OPh)_3 + 3H_2 \qquad \text{——— (61)}$$

$$3R-O-R' + 2I_2 + NaBH_4 \longrightarrow 3RI + B(OR') + NaI + H_2$$

(R'= alkyl,aryl,hydrogen) ——— (62)

However, these methods did not receive much attention. Presumably, this may be due to the non-availability of detailed procedures and also utilization of vacuum line techniques for handling these reactions.

The BHI_2:$N(C_2H_5)_2Ph$ should be useful for this purpose since it is likely to give the alkoxyboron derivative, which is the intermediate in the reduction of carbonyl compounds (Scheme 21).

SCHEME 21

$$RCH_2OH \xrightarrow{I_2HB:N(C_2H_5)Ph} RCH_2-O-BI_2 \longrightarrow R-I$$

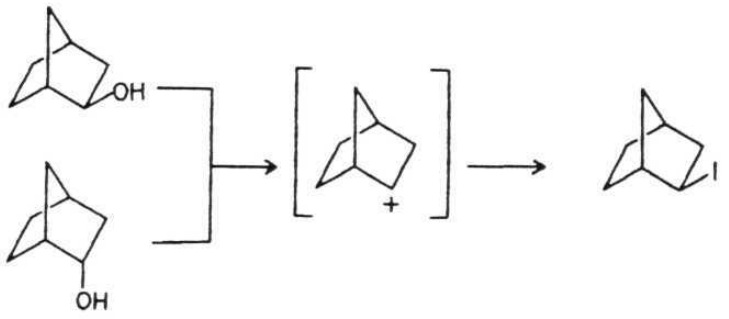
$$\uparrow$$

$$R-CHO \text{ or } R-COOH$$

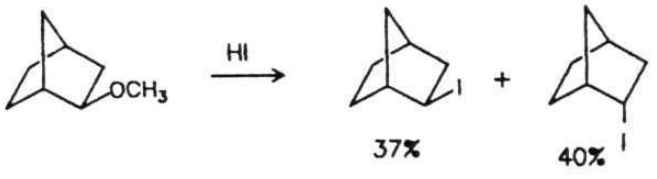
It was observed that the $BHI_2{:}N(C_2H_5)_2Ph$ complex converts alcohols to the corresponding iodides in moderate to good yields.

Cetyl alcohol is converted to cetyl iodide at 80°C in 12h. The *exo* and *endo*-2-norborneolswere converted to *exo*-2-norbornyl iodide at room temperature for 6h. The formation of *exo*-2-norbornyl iodide from both *exo*-2-norborneol and *endo*-2-norborneol indicates that the reactions in these cases go through a common intermediate, *i.e.*, the 2-norbornyl cation,[80] and the reactions may take a similar course with other substrates (Scheme 22).

SCHEME 22



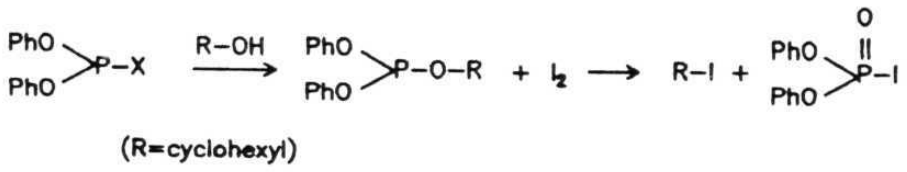
It is of interest to note that the HI rapidly cleaves *exo*-norbonyl methyl ether to a mixture of *exo*-2-norbornyl iodide and *endo*-norbornyl iodide (eq. 63).[81]



However, the ^{13}C NMR spectrum of the product obtained under the present reaction conditions indicates the absence of the *endo* iodide in the product.

In recent years, several new methods of conversion of alcohols to iodides which utilize phosphorous and silyl derivatives have appeared. For example, cyclohexyl iodide is formed upon treatment of cyclohexyl diphenylphosphite with iodine (Scheme 23).[82]

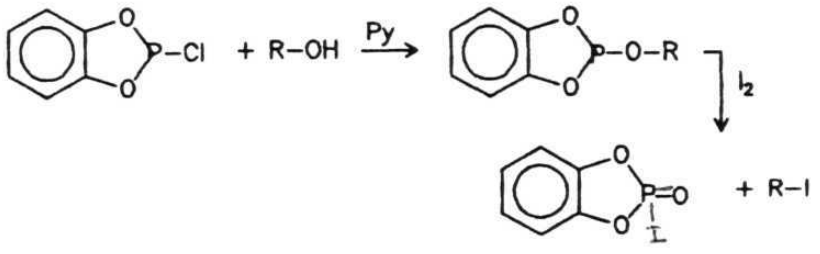
SCHEME 23



The utility of this reaction for the conversion of alcohols into iodides is limited by the tendency of the required reagent, diphenyl phosphorochloridite to disproportionate and by the necessity of purifying the intermediate phosphite in order to obtain the iodide in good yield, and also by the necessity of removing the difficultly hydrolyzable by product, diphenyliodophosphate, by ammonolysis.

Corey and Anderson have found that all of these problems can be avoided by employing the cyclic analog of diphenylphosphorochloridite, *o*-phenylene phosphorochloridite, a stable reagent which is easily prepared from catechol and phosphorous trichloride (Scheme 24).[83]

SCHEME 24



Krief *et al* found that primary, secondary and tertiary alkyl iodides are formed from the corresponding alcohol in high yields, using diphosphorous tetraiodide (eq. 64).[84]

$$4R\text{–}OH + P_2I_4 \xrightarrow{CS_2} [X] \longrightarrow 4R\text{–}I \qquad (64)$$

Iodotrimethylsilane has been used for the preparation of alkyl iodides from alcohols and ethers. A convenient method of synthesizing iodotrimethylsilane through the halogen exchange between chlorotrimethylsilane and magnesium iodide, has appeared which makes this reagent attractive.[85] The present boron based method is useful for the conversion of several functional groups to the corresponding iodides and hence is a good addition to these existing pool of reagents.

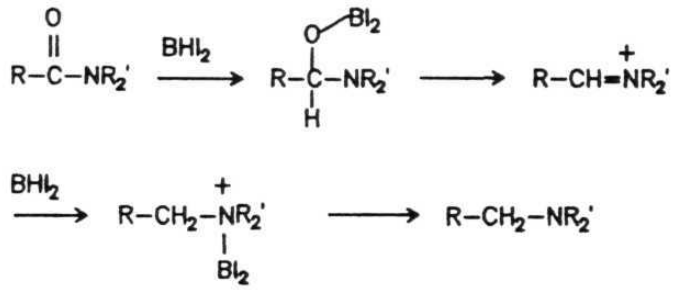
Reduction of Amides:

The diiodoborane–N,N–diethylaniline complex reduces amides to the corresponding amines in moderate yields. These results are summarized in Table 2 (eq. 65).

$$H_3C(CH_2)_8\text{–}CO\text{–}N(CH_3)Ph \xrightarrow{I_2HB:N(C_2H_5)_2Ph} H_3C(CH_2)_9N(CH_3)Ph \qquad (65)$$

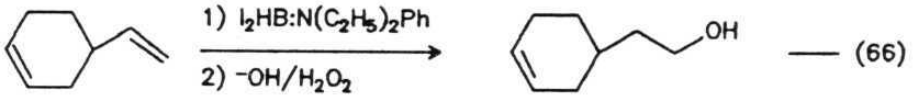
Presumably, in this case no iodination takes place due to a different course of the reaction (Scheme 25).

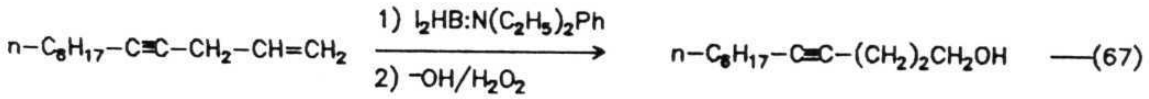
SCHEME 25



Selective reactions using BHI_2:$N(C_2H_5)_2Ph$ complex:

In order to examine the chemoselectivities of this reagent system, we have carried out several experiments, using bifunctional substrates or a mixture of two substrates. These results are summarized in Table 2. Hydroboration of 4-vinyl-1-cyclohexene for 12h followed by $NaOH/H_2O_2$ oxidation yields the corresponding cyclohexenyl ethanol (entry No.1, Table 2). This illustrates faster reaction of a terminal alkene over an internal cyclic olefinic moiety. The hydroboration of 1-allyldecyne followed by oxidation with $NaOAc/H_2O_2$ gives the corresponding alkynol (entry NO.2, Table 2) in 61% yield. This is surprising since the reaction of a similar enyne with $HBBr_2$. SMe_2 complex leads to preferential hydroboration of the acetylenic moiety.[31] This difference in the reactivity is not understood (eq. 66 and 67).





Nevertheless, the complementary result should be synthetically useful. It was found that both olefin and tertiary amide groups are attacked by the reagent (entry No.3, Table 2). Oxidation with $^{-}OH/H_2O_2$ gives the corresponding amino alcohol (eq. 68).

$$H_2C{=}CH(CH_2)_8{-}CO{-}N(CH_3)Ph \xrightarrow[2)\ ^{-}OH/H_2O_2]{1)\ I_2HB{:}N(C_2H_5)_2Ph} HOH_2C(CH_2)_9CH_2N(CH_3)Ph \quad \text{—(68)}$$

Hydroboration of methyl undecenoate for 12h followed by $NaOH/H_2O_2$ oxidation yields the corresponding methyl-11-hydroxyundecanoate. This illustrates that the ester group is not affected by this reagent (entry No.5, Table 2)(eq. 69).

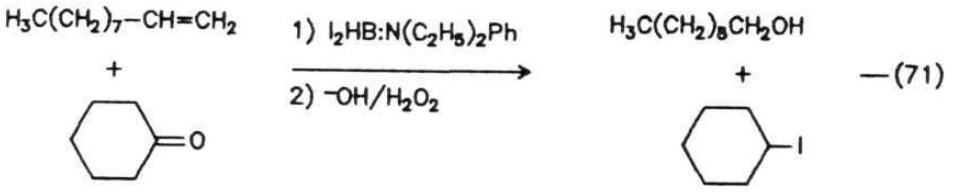
$$H_2C{=}CH(CH_2)_8COOCH_3 \xrightarrow[2)\ ^{-}OH/H_2O_2]{1)\ I_2HB{:}N(C_2H_5)_2Ph} HOH_2C(CH_2)_9COOCH_3 \quad \text{—(69)}$$

Also, hydroboration of 1-decene is successfully carried out in the presence of a nitrile group. This is interesting since both nitrile and olefinic moieties are attacked by reagents such as BH_3:THF[86] (eq. 70).

$$\begin{matrix} H_3C(CH_2)_7CH{=}CH_2 \\ + \\ H_3C(CH_2)_7C{\equiv}N \end{matrix} \xrightarrow[2)\ ^{-}OH/H_2O_2]{1)\ I_2HB{:}N(C_2H_5)_2Ph} \begin{matrix} H_3C(CH_2)_8CH_2OH \\ + \\ H_3C(CH_2)_7C{\equiv}N \end{matrix} \quad \text{— (70)}$$

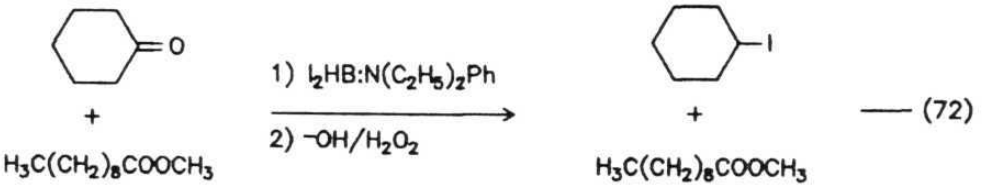
In order to examine whether reductive iodination of cyclohexanone can be carried out in the presence of other functional groups, we have

carried out experiments using cyclohexanone along with 1-decene, octyl cyanide and methyl-1-decanoate in individual runs. It was found that the 1-decene also undergoes hydroboration along with reductive iodination of cyclohexanone (entry No.7, Table 2) (eq 71).

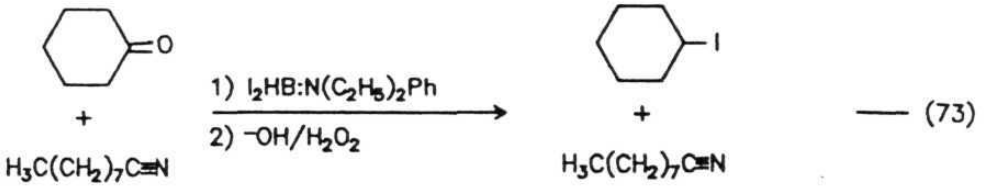


—(71)

However, the reductive iodination of cyclohexanone can be successfully carried out in the presence of carboxylic ester and nitrile groups (entries 8 and 9, Table 2) (eq. 72 and 73).

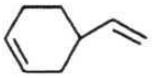
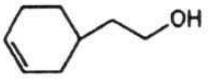
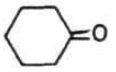
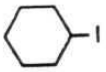
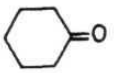
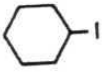
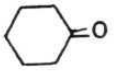
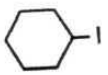


—— (72)



—— (73)

TABLE 2: **Hydroborations, reductions and reductive iodinations of bifunctional substrates:**

Entry No.	Substrate	Product	Yield(%)[a]
1.			76[b]
2.	$n\text{-}C_8H_{17}C{\equiv}CCH_2CH{=}CH_2$	$n\text{-}C_8H_{17}C{\equiv}C(CH_2)_2CH_2\text{-}OH$	61[b]
3.	$H_2C{=}CH(CH_2)_8CON(CH_3)Ph$	$HO\text{-}H_2C(CH_2)_9CH_2N(CH_3)Ph$	72[c]
4.	$H_3C(CH_2)_7CH{=}CH_2$	$H_3C(CH_2)_8CH_2\text{-}OH$	78[d]
	+	+	
	$H_3C(CH_2)_8COOCH_3$	$H_3C(CH_2)_8COOCH_3$	92
5.	$H_2C{=}CH(CH_2)_8COOCH_3$	$HOH_2C(CH_2)_9COOCH_3$	80[b]
6.	$H_3C(CH_2)_7CH{=}CH_2$	$H_3C(CH_2)_8CH_2\text{-}OH$	77[d]
	+	+	
	$H_3C(CH_2)_7C{\equiv}N$	$H_3C(CH_2)_7C{\equiv}N$	93
7.	$H_3C(CH_2)_7CH{=}CH_2$	$H_3C(CH_2)_8CH_2\text{-}OH$	40[e]
	+	+	
			46
8.			75[f]
	+	+	
	$H_3C(CH_2)_7C{\equiv}N$	$H_3C(CH_2)_7C{\equiv}N$	94
9.			71[f]
	+	+	
	$H_3C(CH_2)_8COOCH_3$	$H_3C(CH_2)_8COOCH_3$	92

(a)Products were isolated by column chromatography (silica gel, hexane:ethyl acetate) and identified by spectral data (IR, ^{1}H and ^{13}C NMR) and comparison with the data reported in the literature. (b) The experiments were carried out using amine-borane (5 mM), I_2 (5 mM) and organic substrates (5 mM). The organoborane was oxidized using $NaOH/H_2O_2$. (c) Amide (5 mM), amine-borane (15 mM) and I_2 (15 mM) were used. The organoborane was oxidized using $NaOH/H_2O_2$. (d) Amine-borane(5 mM), I_2 (5 mM) and 1-decene (5 mM), methyl-1-decanoate (5 mM) or octyl cyanide (5 mM) were used. The organoborane was oxidized using $NaOH/H_2O_2$. (e) To the reagent prepared from amine-borane (5 mM) and I_2 (5 mM), a mixture of 1-decene, (5 mM) and cyclohexanone (5 mM) was added at $0^{o}C$. The contents were brought to $25^{o}C$ in 1h and then stirred for 11h. The organoborane was oxidized using $NaOH/H_2O_2$. (f) To the reagent prepared from amine-borane (5 mM) and I_2 (5 mM), a mixture of cyclohexanone (5 mM) and methyl-1-decanoate (5 mM) or octyl cyanide (5 mM) was added at $0^{o}C$. The contents were brought to $25^{o}C$ in 1h and then stirred for 11h.

Generation of HI by the reaction of H_3CCOOH with $BI_3{:}N(C_2H_5)_2Ph$

Markovnikov addition of hydrogen halides to alkenes and alkynes is one of the most important reactions in organic chemistry. Electrophilic addition of hydrogen halides to unsaturated linkages is fraught with a number of experimental challenges.[87,88] It has often been found that anti-Markovnikov addition of HBr take place even when peroxides have not been added. This happens because of the substrate alkenes absorb oxygen from air, forming small amounts of peroxides. Markovnikov addition can be ensured by rigorous purification of the

substrate, but in practice this is not easy to achieve, and it is more common to add inhibitors, *e.g.* phenols or quinones, which suppress the free radical pathway.

It is also possible to add one or two moles of any of the four hydrogen halides to triple bonds (eq. 74).[87,88]

$$-C{\equiv}C- \xrightarrow{HX} -CH{-}CX- \xrightarrow{HX} -CH_2{-}CX_2- \quad \text{—— (74)}$$

Markovnikov's rule ensures that gem-dihalides and not vic-dihalides are the products of the addition of two moles of HX.

However. there is still interest on the development of more convenient procedures for this reaction. Recently, it has been reported that the reaction can be more advantageously accomplished by stirring a heterogeneous mixture of alkene, headecyltributylphosphonium bromide and aqueous hydrohalogenic acid at 115°C (eq. 75).[89]

$$R^1R^2C{=}CHR^3 + HX(aq) \xrightarrow[\Delta]{Q^+X^-} R^1R^2CXCH_2R^3 \quad \text{—— (75)}$$

R^1= alkyl,aryl; R^2= H,alkyl
R^3= alkyl,aryl; X= Cl,Br,I
Q= $(alkyl)_4N$, $(alkyl)_4P$

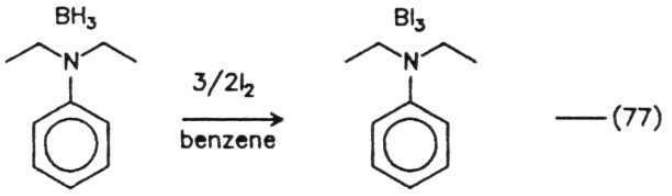
More recently, it has been reported that HI addition to some alkenes and 1-hexyne can be achieved using activated Al_2O_3-I_2 in refluxing petroleum ether (eq. 76).[90]

$$R\text{-}CH{=}CH_2 + I_2/Al_2O_3 \longrightarrow R\text{-}\underset{I}{CH}\text{-}CH_3 \quad \text{—(76)}$$

The boron-halogenation of amine-borane has been studied fairly extensively and a number of derivatives have reported.[91-94] Molecular halogens, hydrohalic acids or certain other halogen compounds substitute one or more halogen atoms on boron replacing hydrogen in the process (Scheme 26).

$$R_3N{:}BH_3 \xrightarrow[-H_2]{HX} R_3N{:}BH_2X \xrightarrow[-H_2]{HX} R_3N{:}BHX_2 \xrightarrow[-H_2]{HX} R_3N{:}BX_3$$

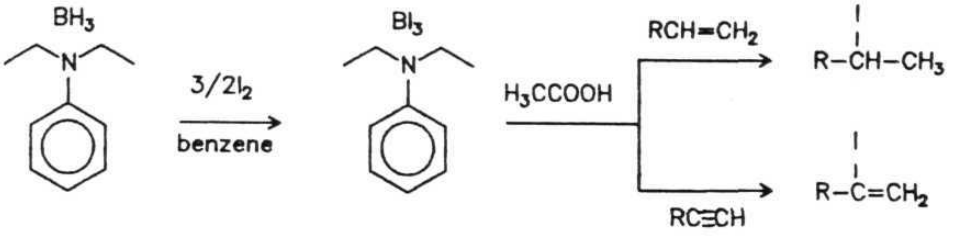
As outlined earlier, we have found that $H_3B{:}N(C_2H_5)_2Ph$ reacts with 1.5 mol eq. of I_2 to give $I_3B{:}N(C_2H_5)_2Ph$. The IR-spectrum of the solution exhibits no >B-H absorption, indicating that the species present in this case is the triiodoborane-N,N-diethylaniline complex (eq. 77).



—(77)

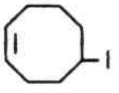
We have investigated the reactions of hydroiodic acid generated *in situ* from $BI_3{:}N(C_2H_5)_2Ph$ complex and acetic acid. It was found that it readily adds to alkenes and alkynes in Markovnikov fashion to form alkyl and alkenyl iodides in good yields under mild conditions (Scheme 27).[97]

SCHEME 27



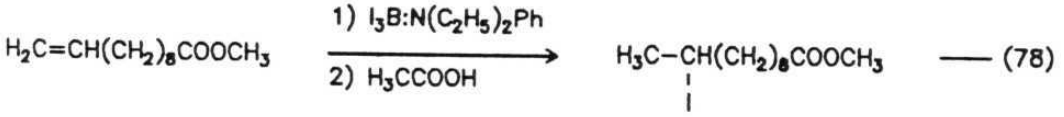
The alkenes and 1-alkynes give the corresponding Markovnikov alkyl and alkenyl iodides in good yields, on reaction with the reagent generated in this way in 12h at 25^{o}C (Table 3).

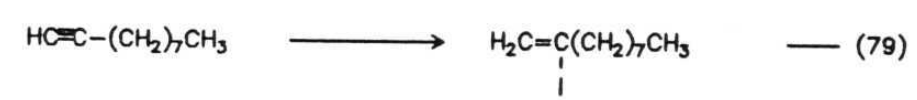
Table 3: Hydroiodination using BI_3:N,N-diethylaniline and acetic acid system.

Entry No.	Substrate	Product	Yield(%)[a]
1.	$H_3C(CH_2)_7CH=CH_2$	$H_3C(CH_2)_7\underset{I}{C}HCH_3$	82
2.	$H_3C(CH_2)_{13}CH=CH_2$	$H_3C(CH_2)_{13}\underset{I}{C}HCH_3$	83
3.	$H_2C=CH(CH_2)_8COOH$	$H_3C\underset{I}{C}H(CH_2)_8COOH$	76
4.	$H_3C=CH(CH_2)_8COOCH_3$	$H_3C\underset{I}{C}H(CH_2)_8COOCH_3$	80
5.			74
6.			82
7.	$HC\equiv C(CH_2)_7CH_3$	$H_2C=\underset{I}{C}(CH_2)_7CH_3$	84
8.	$HC\equiv C(CH_2)_9CH_3$	$H_2C=\underset{I}{C}(CH_2)_9CH_3$	84

(a) For entries 1-5, 7 and 8 the unsaturated hydrocarbons (10 mM), triiodoborane-amine complex (5 mM) and acetic acid (15 mM) were utilized. For entry 6, the unsaturated hydrocarbon (30 mM), triiodoborane-amine complex (5 mM) and acetic acid (15 mM) were utilized. After workup the product separated from the starting diene by fractional distillation under reduced pressure (0.5 mm/80^{o}C). Optimum results are obtained when 10 mM of alkenes or alkynes are utilized for 5 mM of BI_3:amine complex and the yields are based on this ratio of reagents. (b) Products were isolated by column chromatography (silica gel/hexane) and identified by spectral data (IR, ^{1}H & ^{13}C NMR) and comparison with the data reported in the literature.

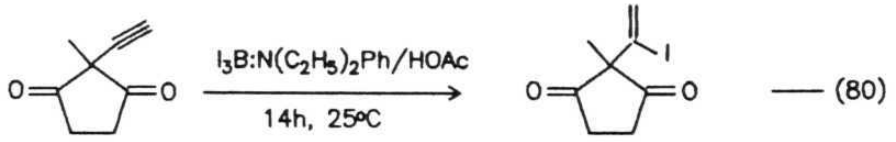
The reagent system tolerates an ester group (entry 4), and the 1-alkynes give only the mono hydroiodination products (entries 7 and 8). These features should make this reagent system attractive in transformations in which a mild reagent is required for hydroiodination (eq. 78 and 79).





Several reports have appeared on the utilization of the BI_3:N,N-diethylaniline complex following our initial report on the preparation and utilization of the complex.[95]

Shibasaki *et al* utilized the BI_3:N,N-diethylaniline complex and acetic acid for the regiospecific transformation of an acetylenic diketone into the alkenyl iodide[96] (eq. 80).



— (80)

The BI_3:$N(C_2H_5)_2Ph$ complex has been also used for cleavage of ethers and geminal diacetates. The ester group was found to be unaffected at room temperature (eq. 81-83).[97]

$$Ph-O-CH_3 \xrightarrow[2)\ H_3CCOOH]{1)\ I_3B:N(C_2H_5)_2Ph} Ph-OH \quad \text{— (81)}$$

$$Ph-CH_2-O-CH_2-Ph \longrightarrow Ph-CH_2-I \quad \text{— (82)}$$

$$4-CH_3C_6H_4CH(OAC)_2 \longrightarrow 4-CH_3C_6H_4CHO \quad \text{— (83)}$$

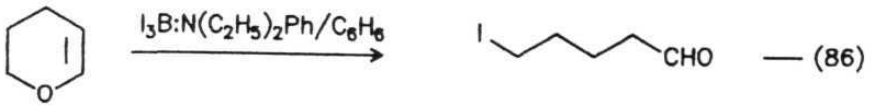
Kabalka *et al* have found that the alkane/arene-sulfonic acid derivatives and sulfoxides are converted to disulfides and sulfides respectively, using the BI_3:$N(C_2H_5)_2Ph$ reagent (eq. 84 and 85).[98]

$$RSO_nX \xrightarrow[22-95\%]{I_3B:N(C_2H_5)_2Ph/C_6H_6} RSSR \quad \text{— (84)}$$

n=1; X=Cl
n=2; X=Cl,OH,OCH_3

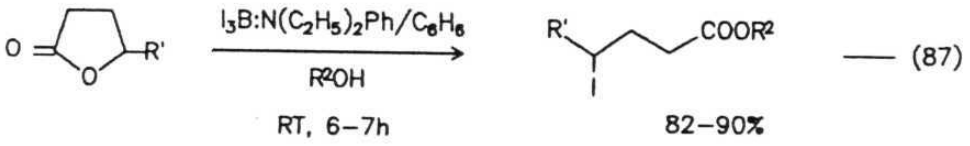
$$RSOR \xrightarrow[77-80\%]{I_3B:N(C_2H_5)_2Ph/C_6H_6} RSR \quad \text{— (85)}$$

We found that the BI_3:$N(C_2H_5)_2Ph$ complex readily cleaves 3,4-dihydro-2H-pyran to give 4-iodopentanal in 80% yield (eq. 86).



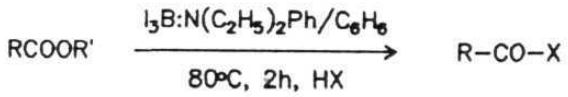
— (86)

Kabalka *et al* utilized the $BI_3N(C_2H_5)_2Ph$ complex for the cleavage of lactones to the corresponding ω-iodocarboxylic acids and esters which are isolated in good yields (eq. 87).[99]



— (87)

The BI_3:$N(C_2H_5)_2Ph$ has been also used for the hydrolysis, transesterfication and aminolysis of esters at 80°C for 2h (eq. 88).[100]



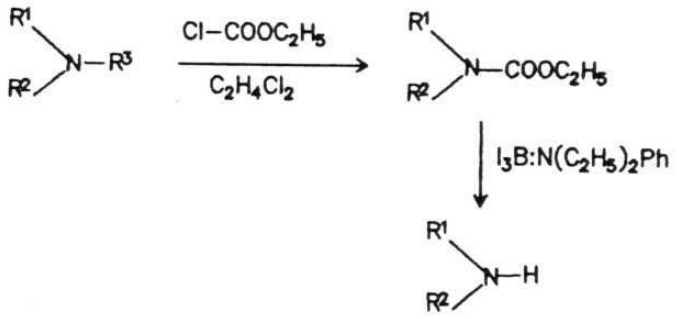
— (88)

R= alkyl (aryl); R'= alkyl

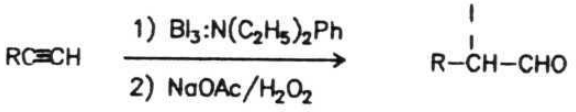
X= OH,OR,NHC_6H_5,$NHCH_2C_6H_5$

It was found in this laboratory that this reagent is useful for cleavage of some N-carbamates at room temperature. The corresponding secondary amines are obtained in good yields (Scheme 28).[101]

SCHEME 28



We have also attempted iodoboration of 1-decyne using $I_3B{:}N(C_2H_5)_2Ph$. However, the iodo aldehyde was obtained in low yield after $NaOAc/H_2O_2$ oxidation.



CONCLUSIONS

Convenient methods for the preparation of $IBH_2{:}N(C_2H_5)_2Ph$, $I_2BH{:}N(C_2H_5)_2Ph$ and $I_3B{:}N(C_2H_5)_2Ph$ complexes have been developed by the reaction of borane-N,N-diethylaniline complex with appropriate amounts of iodine. The $BHI_2{:}N(C_2H_5)_2Ph$ reagent has been found to a useful reagent for iodination of alcohols and reductive iodination of carbonyl compounds and carboxylic acids under mild conditions. This reagent is also useful for hydroboration of alkenes and reduction of tertiary amides. A new, convenient procedure for the generation of HI *in situ* from $BI_3{:}N(C_2H_5)_2Ph$ complex and acetic acid, for addition to alkenes and alkynes in Markovnikov fashion to form alkyl and alkenyl iodides under mild conditions, has been developed. The reagent system tolerates an ester group and the 1-alkynes give only the mono hydroiodination product.

EXPERIMENTAL SECTION

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 IR Spectrometer Model-257 with polystyrene as reference. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-FX-100 Spectrometer with chloroform-d as a solvent and TMS as reference (δ = 0 ppm). Elemental analysis were perfomed on a Perkin Elmer elemental analyzer Model-240 C. Gas chromatography analyses were carried out on a Chemeto-2 instrument equipped with a flame ionisation detector on an SE-30 or carbowax column using nitrogen as carrier gas. Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 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 out using Acme's silica gel (100-200 mesh). Catalytic hydrogenations were carried out on parr hydrogenation apparatus in 250 mL pressure bottle.

All the glassware were pre-dried at 140^{o}C in an air oven, for atleast 4h, assembled hot and cooled under a stream of dry nitrogen. Unless, otherwise mentioned, all the operations/transformations of reagents/reactions were carried out using standard syringe, septum techniques recommended for handling air sensitive organometallic compounds.[2] Reagents prepared *in situ* in solvents were transformed using double ended stainless stell (Aldrich) needle under a stream of nitrogen whenever required.

In all experiments, round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected by a long tube to the atmosphere.

All dry solvents and reagents (liquids) used were distilled from appropriate drying agents just before use. As a routine all organic extracts were washed with saturated sodium chloride and dried over anhydrous $MgSO_4$ and concentrated on a Buchi-EL-rotary evaporator. All yields reported are isolated yields of materials judged homogeneous by TLC, IR and NMR spectroscopy.

Benzene, diglyme and THF were distilled over benzophenone sodium. All alkenes utilized were commercial samples, supplied by Fluka, Switzerland. N,N-Diethylaniline and iodine were supplied by SDs India. 1-Decyne and 1-dodecyne were prepared following a reported procedure.[101a] N-Methyl-N-phenyldecanamide and N-methyl-N-phenyl-undecenamide were prepared using the corresponding acids and N-methyl aniline. Trideca-4-yn-1-ene was prepared using 1-decyne and alkyl bromide following a reported procedure.[101b]

Reaction of I_2 with N,N-diethylanilne-borane complex:preparation of monoiodoborane N,N-diethylaniline complex (MIBDA):

Borane-N,N-diethylaniline complex (10 mM) was prepared *in situ* by bubbling diborane, generated by dropwise addition of iodine (10 mM) in diglyme (10 mL) to $NaBH_4$ (20 mM) in diglyme (5 ml) at 25°C, into a solution of N,N-diethylaniline (10 mM) in dry benzene (60 ml) for 1h.[13] Iodine (5 mM) in benzene (20 ml) was added at 10°C in order to convert borane-amine complex into monoiodoborane-amine complex

(evolution of H_2 gas was observed). The contents of the flask were stirred at room temperature till the reaction mixture becomes colourless (45 min). The monoiodoborane-N,N-diethylaniline complex thus prepared was utilized 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}.[102,103]

Reaction of MIBDA with 1-decyne:

To the MIBDA complex (10 mM) in benzene (60 ml), 1-decyne (2.76 g, 20 mM) was added and the contents were stirred for 12h at room temperature. The reaction mixture was brought to $10^{o}C$ and iodine (2.54 g, 10 mM) was added and stirred for 2h at room temperature. 3N NaOH (20 ml) was added at room temperature and further stirred for 4h. The reaction mixture was quenched with water and the organic layer was separated. The aqueous layer was extracted with ether (2 x 20 ml) and the combined organic extract was washed with 3N HCl (2 x 20 ml), water, sodiumthiosulphate, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), the product which eluted first was identified as (E, E)-9,11-eicosadiene (0.83 g, 60%) and the fraction (0.53 g, 20%) which eluted next was identified as E-1-iodo-1-decene from the ^{13}C NMR spectral data

Fraction - 1:

IR (neat) ν_{max} : 2910, 2840, 950 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.99 (t, 6H), 1.3-2.0 (m, 28H), 4.0 (m, 2H), 5.30-6.20 (m, 4H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.2, 22.8, 29.2, 29.5, 29.7, 32.1, 32.8, 130.6, 132.2.

Spectral data of this product showed 1:1 correspondence with the data of this compound reported in the literature.[104]

Fraction - 2:

IR (neat) ν_{max} : 1620, 940, 720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, 3H), 1.2-1.9 (m, 14H), 5.8-6.6 (m, 3H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 28.5, 29.0, 29.5, 29.8, 32.1, 36.2, 74.4, 146.5

This product is reported in the literature.[105]

Reaction of I_2 with N,N-diethylaniline-borane complex: Preparation of diiodoborane:N,N-diethylaniline complex:

To the N,N-diethylaniline:borane complex (10 mM) in benzene (40 ml), iodine (2.54 g, 10 mM) in dry benzene (20 ml) was added with the aid of a double ended needle at $10^{o}C$ (evolution of H_2 gas was observed). The contents of the flask were stirred at room temperature till the reaction mixture becomes colourless (2h). The diiodoborane: N,N-diethylaniline complex thus prepared was utilized for further reactions.

IR (benzene) ν_{max} : 2500 cm^{-1}. Reported IR absorption (B-H, stretching) for $BHBr_2:SMe_2$: ν_{max} : 2500 cm^{-1}.[106]

Hydroboration of 4-vinyl-1-cyclohexene using BHI_2:$N(C_2H_5)_2Ph$ complex:

I_2BH:N,N-diethylaniline complex (5 mM) was prepared *in situ* as above. The 4-vinyl-1-cyclohexene (0.540 g, 5 mM) was added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml) H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 2-(4-cyclohexenyl)ethanol was isolated.

Yield : 76% (0.48 g)

IR (neat) ν_{max} : 3275, 3050, 1040, 920, 650 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.20–2.20 (m, 10H), 3.64 (t, 2H), 5.60 (s, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.7, 28.6, 29.7, 31.4, 39.0, 60.1, 126.1, 126.8.

The data are identical with the data of this product reported in the literature.[107]

The above procedure for hydroboration was followed for the conversion of a few other olefins and alkynes.

$H_3C(CH_2)_7CH=CH_2 \longrightarrow H_3C(CH_2)_8CH_2OH$

Yield : 81% (1.27 g)

IR (neat) ν_{max} : 3350, 2950, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, 3H), 1.2 (m, 16H), 3.6 (t, 2H), 5.30 (s, 1H). (Spectrum Number 1)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.9, 22.6, 25.8, 29.3, 29.6, 31.9, 32.5, 62.5. (Spectrum Number 2)

The data are identical with the data of this compound reported in the literature.[108]

$$PhCH{=}CH_2 \longrightarrow PhCH_2CH_2OH$$

Yield : 83% (1.0 g)

IR (neat) ν_{max} : 3300, 1020 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.60 (s, 1H), 2.60–2.88 (t, 2H), 3.60–3.88 (t, 2H), 7.00–7.40 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 38.9, 63.2, 126.1, 128.4, 128.8, 138.7.

The data are identical with the data of this compound reported in the literature.[109]

$$H_3C(CH_2)_7C{\equiv}CH \longrightarrow H_3C(CH_2)_8CHO \ (I) + H_3C(CH_2)_8CH_2OH \ (II)$$

Fraction - I:

Yield : 50% (0.78 g)

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

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80 (t, 3H), 1.20–2.30 (m, 18H), 9.2 (br s, 1H).

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

The data are identical with the data of this compound reported in the literature.[110]

Fraction - II:

Yield : 20% (0.31 g)

Spectral data of the product showed 1:1 correspondence with the data of the product obtained in the previous experiment.[110]

Hydroboration of trideca-4-yn-1-ene using BHI_2:$N(C_2H_5)_2Ph$ complex:

I_2BH:N,N-diethylaniline complex (5 mM) was prepared *in situ* as above. The trideca-4-yn-1-ene (0.90 g, 5 mM) was added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated. The aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/ 90:10), trideca-4-yn-1-ol was isolated.

Yield : 61% (0.60 g)

IR (neat) ν_{max} : 330, 2300, 1500, 1125 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.72–0.92 (t, 3H), 1.12–1.84 (m, 15H), 2.00–2.32 (m, 4H), 3.60–3.76 (t, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.9, 15.2, 18.5, 28.5, 29.0, 29.4, 31.7, 61.6, 79.2, 80.8. (Spectrum Number 3)

Mass (m/e) : 195 (M^{+}-1, 5%), 97 (100%) (Spectrum Number 4)

Analysis : C% ; H%

Calculated : 79.53; 12.32

Found : 79.45; 12.33

Reaction of diiodoborane:N,N-diethylaniline complex with n-heptanaldehyde:

I_2BH:N,N-diethylaniline complex (10 mM) was prepared *in situ* as above. n-Heptanaldehyde (1.14 g, 10 mM) was added to this reagent at $0^{o}C$ and in 1h it was brought to $25^{o}C$. The contents were stirred further for 11h at $25^{o}C$. The reaction mixture was quenched with water (10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), n-heptyl iodide was isolated.

Yield : 82% (1.88 g)

IR (neat) ν_{max} : 2950, 1480, 720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.88 (t, 3H), 1.08–2.00 (m, 10H), 3.00–3.26 (t, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 6.8, 13.9, 22.5, 28.1, 30.4, 31.5, 33.5.

The data are identical with the data of this product reported in the literature.[83]

The reaction with cyclohexanone (10 mM) was also carried out following the procedure outlined above.

Yield : 75% (1.58 g)

Spectral data of the product showed 1:1 correspondence with the data of this product reported in the literature.[84]

Reaction of diiodoborane:N,N-diethylaniline complex with sebacic acid:

I_2BH:N,N-diethylaniline complex (30 mM) was prepared *in situ* as above. Sebacic acid (1.00 g, 5 mM) was added to this reagent at 0^oC and in 1h it was brought to 25^oC. The contents were further stirred for 11h at 25^oC. The reaction was quenched with water (10 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane), 1,10-diiododecane was isolated.

Yield : 60% (1.12 g)

IR (neat) ν_{max} : 2950, 1480, 720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.16-2.00 (m, 16H), 3.04-3.25 (t, 4H). (Spectrum Number 5)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 7.3, 28.4, 29.2, 30.4, 33.5. (Spectrum Number 6)

The data are identical with the data of this compound reported in the literature.[111]

The reaction with phenylacetic acid (10 mM) was also carried out following the procedure outlined above.

$PhCH_2CO_2H \longrightarrow PhCH_2CH_2I$

Yield : 66% (15.3 g)

IR (neat) ν_{max} : 3050, 3000, 2950, 1600, 740 700 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 3.00–3.40 (m, 4H), 7.00–7.36 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 6.1, 40.5, 127.2, 128.2, 129.0, 141.0.

The data are identical with the data of this compound reported in the literature.[84]

Reaction of diiodoborane:N,N-diethylaniline complex with cetyl alcohol:

I_2BH-N,N-diethylaniline complex (10 mM) was prepared *in situ* as above. The cetyl alcohol (2.42 g, 10 mM) was added to this reagent at 25^oC, stirred for 1h and then stirred for 12h at 80^oC. The reaction mixture was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the

solvent and purification by chromatography on silica gel column (hexane), cetyl iodide was isolated.

Yield : 84% (2.95 g)

IR (neat) ν_{max} : 2950, 1480, 720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.88 (t, 3H), 1.00–2.00 (m, 28H), 3.00–3.28 (t, 2H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 6.0, 14.0, 22.6, 28.6, 29.5, 29.7, 30.6, 31.9, 33.6.

This product is reported in the literature.[112]

Reaction of diiodoborane:N,N-diethylaniline complex with *endo* norborneol:

I_2BH-N,N-diethylaniline complex (10 mM) was prepared *in situ* as above. The *endo*-norborneol (1.10 g, 10 mM) was added to this reagent at 25°C, stirred for 6h. The reaction mixture was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane), *exo*-norbornyl iodide was isolated.

Yield : 69% (1.54 g)

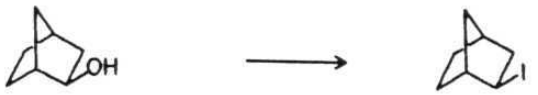
IR (neat) ν_{max} : 2950, 1440, 740 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.00–2.60 (m, 10H), 3.80–4.00 (m, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 28.3, 28.6, 29.8, 36.2, 37.8, 45.0, 47.8.

The data are identical with the data of this compound reported in the literature.[81]

The reaction was also carried out using *exo*-norborneol (10 mM), cyclohexanol (10 mM) and 1-methylcyclohexanol (10 mM) following the procedure outlined above.



Yield : 82 % (1.83 g)

Spectral data of the product showed 1:1 correspondence with the data of the product obtained in the previous experiment.[81]

Yield : 86% (1.82 g)

IR (neat) ν_{max} : 2950, 1440, 700, 640 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.00–2.50 (m, 10H), 4.10–4.60 (m, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 25.1, 27.5, 32.5, 39.5.

The data are identical with the data of this compound reported in the literature.[84]

Yield : 89% (19.9 g)

IR (neat) ν_{max} : 2950, 1440, 740 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–1.88 (m, 10H), 2.08 (s, 3H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.8, 25.0, 38.9, 45.7, 58.9.

The data are identical with the data of this compound reported in the literature.[84]

Reduction and hydroboration of N-methyl-N-phenylundecenamide using BHI_2:N,N-diethylaniline complex:

I_2BH:N,N-diethylaniline complex (15 mM) was prepared *in situ* as above. The N-methyl-N-phenylundecanamide (1.30 g, 5 mM) was added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml)/H_2O_2 (30%, 10ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), N-methyl-N-phenylundecanol was isolated.

Yield : 81% (1.00 g)

IR (neat) ν_{max} : 3300, 3025, 2900, 1600, 740, 680 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.04–1.68 (m, 19H), 2.88 (s, 3H), 3.08–3.32 (t, 2H), 3.48–3.68 (t, 2H),

6.48–7.24 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 25.5, 26.3, 26.9, 29.3, 32.4, 37.2, 52.3, 62.0, 111.9, 115.7, 128.8, 149.1.

Mass (m/e) : 277 (M, 20%), 120 (100%)

Analysis	: C% ;	H% ;	N%
Calculated	: 77.92;	11.26;	5.04
Found	: 77.75;	11.28;	4.95

The above procedure for reduction was followed for the conversion of a few other amides.

$H_3C(CH_2)_8CON(CH_3)Ph \longrightarrow H_3C(CH_2)_8CH_2N(CH_3)Ph$

Yield : 81% (10.0 g)

IR (neat) ν_{max} : 3050, 2950, 1600, 1450, 740, 690 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.64–0.96 (t, 3H), 1.00–1.68 (m, 16H), 2.84 (s, 3H), 3.00–3.40 (t, 2H), 6.40–6.76 (m, 3H), 7.00–7.28 (m, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 26.7, 27.1, 29.6, 31.9, 38.1, 52.8, 112.1, 115.9, 129.1, 149.5.

The data are identical with the data of this compound reported in the literature.[113]

$PhNHCOCH_3 \longrightarrow PhNHCH_2CH_3$

Yield : 41% (2.6 g)

IR (neat) ν_{max} : 3020, 2950, 1600, 1450, 740, 690 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.00–1.28 (t, 3H), 2.88–3.20 (Q, 2H), 3.28 (s, 1H), 6.40–6.72 (m, 3H), 6.96–7.20 (m, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 15.0, 38.6, 113.0, 117.4, 129.5, 148.8.

The data are identical with the data of this compound reported in the literature.[114]

Hydroboration of methyl undecenoate using BHI_2:$N(C_2H_5)_2Ph$ complex:

I_2BH:N,N-diethylaniline complex (5 mM) was prepared *in situ* as above. Methyl undecenoate (0.99 g, 5 mM) was added to this reagent at 25°C and stirred for 12h. The reaction was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), methyl-11-hydroxyundecanoate was isolated.

Yield 80% (0.80 g)

IR (neat) ν_{max} : 3300, 2900, 1720, 1440, 1160, 1040 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.00–1.64 (m, 18H), 1.76 (s, 1H) 2.04–2.32 (t, 2H), 3.36–3.64 (m, 5H). (Spectrum Number 8)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.8, 25.6, 29.0, 29.3, 32.5, 33.9, 51.3, 62.4, 174.4. (Spectrum Number 7)

The data are identical with the data of this product reported in the literature.[115]

Reaction of a 1:1 mixture of 1-decene and cyclohexanone with HBI_2:$N(C_2H_5)_2Ph$ complex:

I_2BH:N,N-diethylaniline complex (5 mM) was prepared *in situ* as above. 1-Decene (0.70 g, 5 mM) and cyclohexanone (0.49 g, 5 mM) were added to this reagent at 10°C and in 1h it was brought to 25°C. The contents were stirred further for 11h at 25°C. The reaction was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-decanol (0.32 g, 40%) and cyclohexyl iodide (0.46 g, 46%) were isolated.

The spectral data showed 1:1 correspondence with the data of these products obtained in the previous experiments.

Reaction of a 1:1 mixture of 1-decene and octyl cyanide with HBI_2:$N(C_2H_5)_2Ph$ complex:

I_2BH:N,N-diethylaniline complex (5 mM) was prepared *in situ* as above. 1-Decene (0.70 g, 5 mM) and octyl cyanide (0.69 g, 5 mM) were added to this reagent at 25°C, stirred for 12h. The reaction was

quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with water, brine and dried over anhydrous $MgSO_4$. Evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-decanol (0.62 g, 77%) was isolated and octyl cyanide (0.65 g, 93%) was recovered.

The spectral data showed 1:1 correspondence with the data of these products obtained in earlier experiments.

Similar experiments were carried out by taking 1:1 mixtures of cyclohexanone (5 mM) and 1-methyldecanoate (5 mM) or octyl cyamide (5 mM) and the results are summarized in Table 2.

Preparation of triiodoborane:$N(C_2H_5)_2Ph$ complex:

To the N,N-diethylaniline:borane complex (5 mM) in benzene (40 ml), iodine (I_2) (1.90 g, 7.5 mM) in dry benzene (20 ml) was added with the aid of a double ended neddle at 10^oC (evolution of H_2 gas was observed). The contents of the flask were stirred at room temperature for 3h. The IR-spectrum of the solution exhibits no >B-H absorption at 2500 cm^{-1}, indicating that the species present in the case is the triiodoborane:N,N-diethylaniline complex. The triiodoborane:N,N-diethylaniline complex thus prepared was utilized for further reactions.

Hydroiodination of 1-decene using N,N-diethylaniline:BH_3, I_2 and acetic acid system:

I_3B:N,N-diethylaniline complex (5 mM) was prepared *in situ* as above. Acetic acid (0.9 g, 15 mM) was added to this reagent at 10^oC. The 1-decene (1.40 g, 10 mM) was added under nitrogen and the contents were stirred for 12h, at 25^oC. The reaction was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane), 2-iododecane was isolated.

Yield : 82% (2.19 g)

IR (neat) ν_{max} : 2950, 1460, 720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–0.96 (t, 3H), 1.08–1.52 (m, 14H), 1.80–2.00 (d, 3H), 4.00–4.20 (m, 1H). (Spectrum Number 10)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.6, 28.8, 28.9, 29.2, 29.4, 29.7, 29.8, 31.8, 42.9. (Spectrum Number 9)

This product is reported in the literature.[116]

The above procedure for hydroiodination was followed for the conversion of a few other olefins.

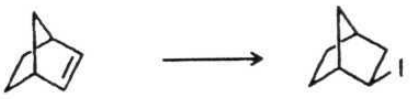
$$H_3C(CH_2)_{13}CH{=}CH_2 \longrightarrow H_3C(CH_2)_{13}{-}\underset{\displaystyle I}{\underset{|}{CH}}{-}CH_3$$

Yield : 83% (2.92 g)

IR (neat) ν_{max} : 2950, 1460, 720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–0.96 (t, 3H), 1.20–1.40 (m, 26H), 1.84–2.00 (d, 3H), 4.00–4.36 (m, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 27.8, 28.7, 28.9, 29.3, 29.7, 30.7, 31.9, 43.0.



Yield : 74% (1.65 g)

Spectral data of this compound showed 1:1 correspondence with the data of this product obtained in earlier experiments.

$H_2C{=}CH(CH_2)_8CO_2H \longrightarrow H_3C{-}\underset{\underset{I}{|}}{CH}{-}(CH_2)_8CO_2H$

Yield : 76% (2.37 g)

IR (neat) ν_{max} : 3300, 2950, 1710, 930, 720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.20–1.80 (m, 16H), 1.84–2.00 (d, 3H), 2.20–2.48 (t, 2H), 4.00–4.36 (t, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.3, 28.4, 28.8, 28.9, 29.4, 30.2, 33.9, 42.7, 180.5.

$H_2C{=}CH(CH_2)_8CO_2CH_3 \longrightarrow H_3C{-}\underset{\underset{I}{|}}{CH}{-}(CH_2)_8CO_2CH_3$

Yield : 80% (2.60 g)

IR (neat) ν_{max} : 2950, 1740, 720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.04-1.68 (m, 16H), 1.80-1.96 (d, 3H), 2.08-2.40 (t, 2H), 3.48-3.68 (s, 3H), 3.92-4.36 (m, 1H).(Spectrum Number 14)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.8, 28.5, 29.0, 29.6, 30.6, 34.0, 42.8, 51.4, 174.3. (Spectrum Number 13)

Hydroiodination of 1,5-cyclooctadiene using BI_3:N,N-diethylaniline and acetic acid system:

BI_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. Acetic acid (0.90 g, 15 mM) was added at 10^oC. The 1,5-cyclooctadiene (30 mM) was added under nitrogen and the contents were stirred for 12h at 25^oC. The reaction was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), 5-iodo cyclooctene was isolated.

Yield : 82% (1.93 g)

IR (neat) ν_{max} : 3025, 2950, 900, 700 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.28-2.24 (m, 10H), 4.24-4.60 (m, 1H), 5.40-5.80 (m, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 25.0, 27.0, 28.8, 34.8, 38.3, 42.0, 129.2, 129.6.

The data are identical with the data of this product reported in the literature.[117]

Hydroiodination of 1-decyne using BI_3:N,N-diethylaniline and acetic acid system:

BI_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. Acetic acid (0.90 g, 15 mM) was added at 10^oC. 1-Decyne (1.38 g, 10 mM) was added under nitrogen and the contents were stirred for 12h at 25^oC. The reaction was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), 2-iododec-1-ene was isolated.

Yield : 84% (2.23 g)

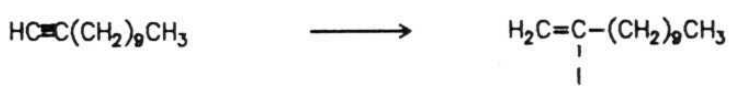
IR (neat) ν_{max} : 3050, 2950, 1620, 900, 720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80-1.00 (t, 3H), 1.08-1.64 (m, 12H), 2.20-2.56 (t, 2H), 5.60-5.72 (s, 1H), 6.00-6.12 (s, 1H). (Spectrum Number 12)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 28.1, 29.1, 29.2, 31.9, 45.4, 112.8, 125.0. (Spectrum Number 11)

This product is reported in the literature.[50]

The reaction with 1-dodecyne (10 mM) was also carried out following the procedure outlined above.



Yield : 84% (2.46 g)

IR (neat) ν_{max} : 3050, 2950, 1620, 900, 720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–0.96 (t, 3H), 1.08–1.64 (m, 16H), 2.20–2.56 (t, 2H), 5.60–5.72 (s, 1H), 6.00–6.12 (s, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.2, 22.8, 28.2, 29.2, 29.4, 29.6, 32.0, 45.4, 112.9, 125.1.

This product is reported in the literature.[118]

Cleavage of 3,4-dihydro-2H-pyran using BI_3:$N(C_2H_5)_2Ph$ complex:

BI_3:$N(C_2H_5)_2Ph$ complex (10 mM was prepared *in situ* as above. 3,4-dihydro-2H-pyran (10 mM, 0.84 g) was added under nitrogen and the contents were stirred for 12h at 25°C. The reaction was quenched with water (10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), sodium thiosulphate (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 5-iodo-1-pentnal was isolated.

yield :76% (1.61 g)

IR (neat) ν_{max} : 2950, 2750, 1720, 740 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 8.0, 24.0, 33.8, 43.7, 203.0.

This product is reported in the literature.[119]

Attempted iodoboration of 1-Decyne using BI_3:N,N-diethylaniline complex:

BI_3:$N(C_2H_5)_2Ph$ complex (10 mM) was prepared *in situ* as above.1-Decyne (1.38 g, 10 mM) was added under nitrogen and the contents were stirred for 12h at 25°C. The reaction was quenched with water (10 ml) and oxidized using NaOAc (6N, 10 ml)/H_2O_2 (16%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5),2-iodo-1-decanal was isolated.

Yield : 30% (0.85 g)

IR (neat) ν_{max} : 2850, 1710, 720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.86–0.90 (t, 3H), 1.00–1.96 (m, 14H), 4.20–4.60 (m, 1H), 9.2 (d, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.0, 28.2, 28.5, 28.7, 31.2, 31.5, 36.3, 191.0

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CHAPTER 2

Synthesis and utilization of gem-diboryl derivatives

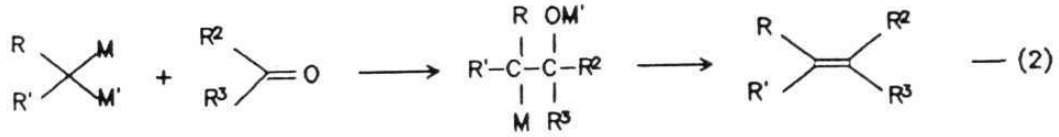
INTRODUCTION

Organometallic compounds having two metal atoms bonded to the same carbon atom are an interesting class of compounds. The first compound of this class, methylene mercuric iodide has been known for a long time.[1] It was found that methylene iodide and elemental mercury react under the influence of sunlight to give bis(iodomercuri) methane (eq. 1).

$$CH_2I_2 + 2Hg \longrightarrow CH_2(HgI)_2 \quad \text{—— (1)}$$

The gem-dimetallic compounds such as methylene dilithium,[2,3] and methylene magnesium, methylene magnesium halide,[4] diphosphorous,[5] α-metalosilicon,[6] disilicon compounds[6] and ditrialkylstannylmethane[7] have been proved to be useful in organic synthesis. Other compounds of this kind are the gem-diboron[8,9] and dialuminium compounds[10] arising from dihydroboration and dihydroalumination of teriminal acetylenes.

These derivatives readily react with benzaldehyde and ketones to give olefins, probably, through an addition-elimination sequence[11] (eq. 2).



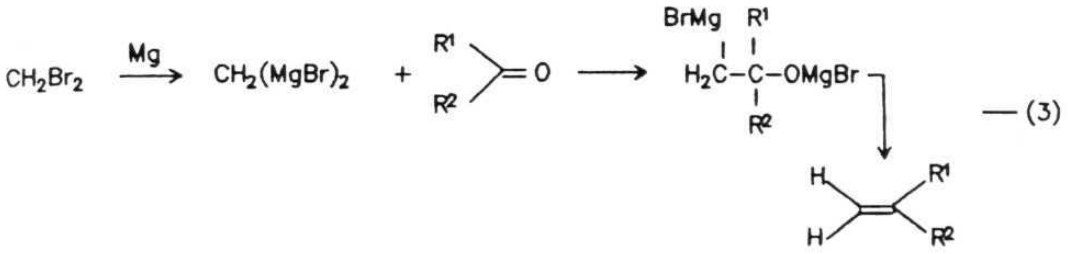
— (2)

(M and M'= metals)

The type of mechanism involved in the elimination, its rate and stereochemistry and the possible side reactions depend on the nature

of the metal and the reaction conditions.

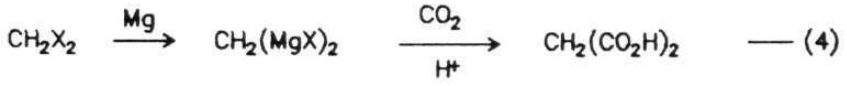
The gem-disubstituted magnesium compounds formed from CH_2Br_2 or CH_2I_2, react with aldehydes or ketones to give olefins in moderate to good yields (eq. 3).[12,13]



— (3)

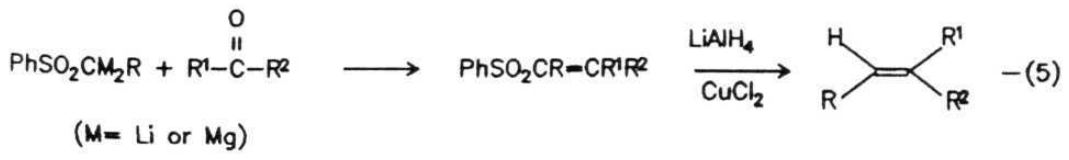
The reaction could not be extended to other gem-dihalides. Similar reactions with gem-dimetallic compounds prepared using some other metals give olefins.[13a]

The geminal dimetallic nature of the magnesium reagent has been confirmed by carbonation which gives malonic acid in substantial yields (eq.4).



— (4)

The α,α-dimetallic derivatives of phenyl sulfones $PhSO_2CM_2R$ (M = Li or Mg) react with aldehydes or ketones (R^1COR^2) to give good yields of the α,β-unsaturated sulfones,[14] which can be reduced with aluminium amalgam or with LAH-$CuCl_2$ to give the olefins[15] (eq.5).

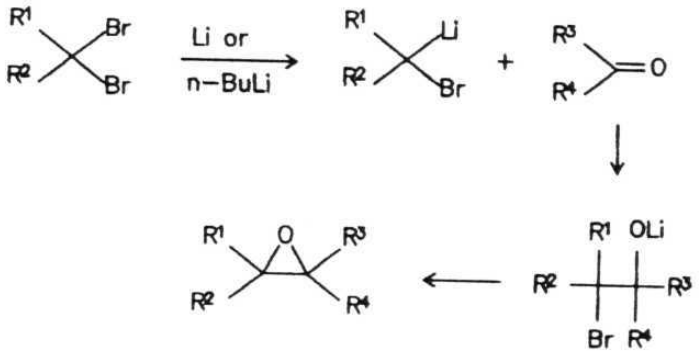


(M= Li or Mg)

— (5)

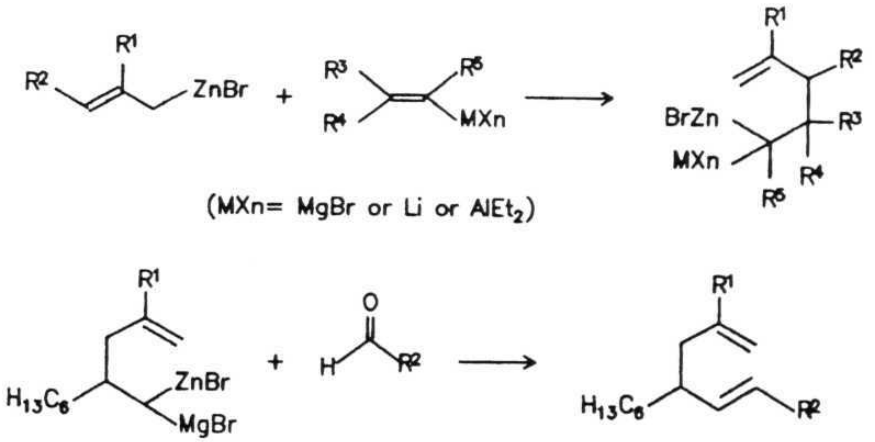
On the other hand, gem-dihalides on reaction with Li or n-BuLi and a carbonyl compound give epoxides (Scheme 1).[16-19]

SCHEME 1

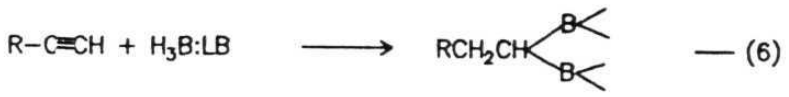


Recently, 1-magnesia-1-zincalkenes have been conveniently prepared by the reaction of allyl zinc bromide with alkenyl-magnesium bromide.[20] 1-Magnesia-1-zincalkenes react smoothly with various aldehydes in the presence of BF_3:OEt_2 to furnish (E)-1,5-dienes in high yields and high isomeric purity.[21] 1-Magnesia-1-zincalkenes are less reactive than Grignard reagents; thus 1-magnesia-1-zincalkenes do not react with ketones, esters, anhydrides or various iodo derivatives (Scheme 2).

SCHEME 2

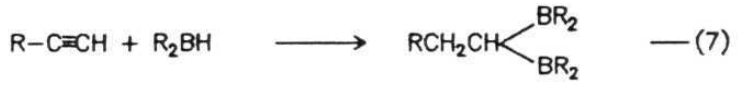


The discovery of the hydroalumination and hydroboration reactions has opened a new route for the prepartion of difunctional organometallic compounds.[22,23] These difunctional organometallic compounds, in which the two metal-carbon bonds exhibit large differences in reactivity, should also be useful in organic synthesis. 1,1-Diborylalkanes can be readily prepared by hydroboration of 1-alkynes with BH_3:LB complexes (eq. 6).[8,24,25]



— (6)

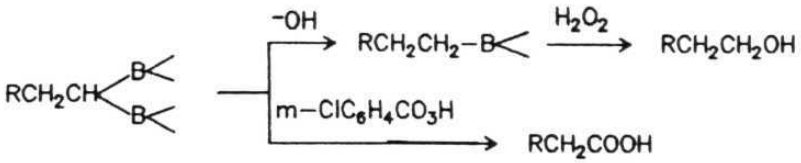
The use of certain dialkylboranes as hydroborating agents results in essentially quantitative yields of the geminal diboron compound (eq.7).[26-29]



— (7)

The structure of the geminal dihydroboration product was established by its oxidation with alkaline hydrogen peroxide to the corresponding primary alcohol. This point to an initial rapid hydrolysis of the dihydroboration intermediate. Examination of the product from deuterioboration of 1-alkyne, followed by alkaline hydrogen peroxide oxidation, revealed that the 1-hexanol orginates from a 1,1-dibora compound. Confirmatory evidence for the predominant formation of geminal diboron derivative was obtained by its oxidation with m-chloroperbenzoic acid to the corresponding carboxylic acid (Scheme 3).[24]

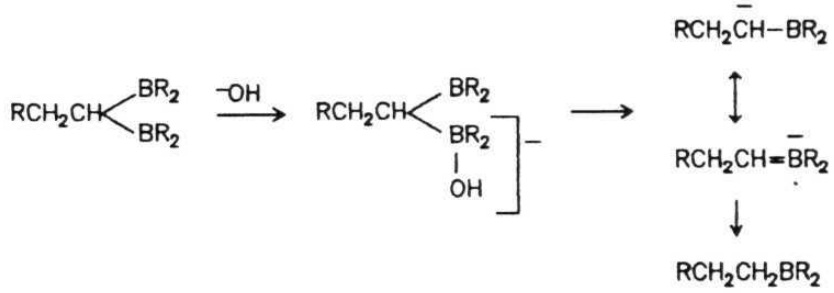
SCHEME 3



The results indicate that the dihydroboration of 1-hexyne proceeds with addition of approximately 80% of the boron atoms at the terminal carbon. The use of either 2,3-dimethyl-2-butylborane or dicyclohexylborane or 9-BBN as the hydroborating agent gives the 1,1-diboro derivative in 90-96% yields.[24]

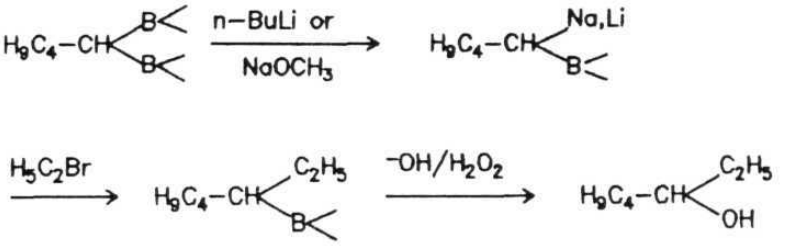
It is known, that the 1,1-diboro derivatives, which are easily obtained from acetylenic compounds on hydroboration, are unstable to hydrolytic cleavage, being converted into the corresponding alkylborane. This fact could be understood in terms of stability of the carbanion which is formed by attack of the base on the electrophilic boron atom, the stability being reached through the resonance with the vacant orbital of the second boron atom (Scheme 4)[8]

SCHEME 4



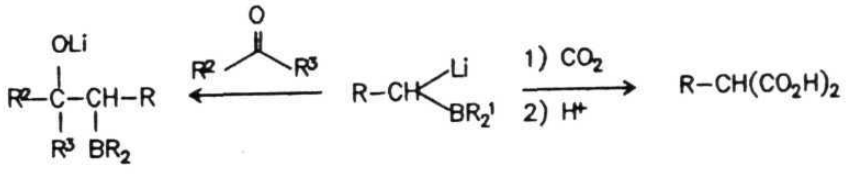
It has been reported that 1,1-diborylpentane, undergoes a similar facile cleavage with sodium methoxide, lithium methoxide, butyl lithium and methyl lithium to give the 1-boro-1-sodio and 1-boro-1-lithio derivatives, respectively. The structures of these intermediates have shown by their conversion to 3-heptylborane when treated with ethyl bromide. The organoborane was not isolated but oxidized using $^{-}OH/H_2O_2$ to give 3-heptanol (Scheme 5).[25]

SCHEME 5

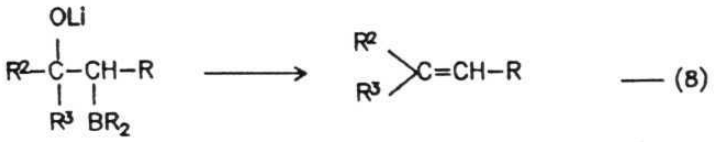


The structure of the 1-bora-1-lithio alkane derivative was established by carbonation and carbonylation to obtain the corresponding malonic acid derivative and olefins, respectively (Scheme 6).[27,28] The gem-organoboron compounds themselves do not react with carbon dioxide and carbonyl compounds.

SCHEME 6



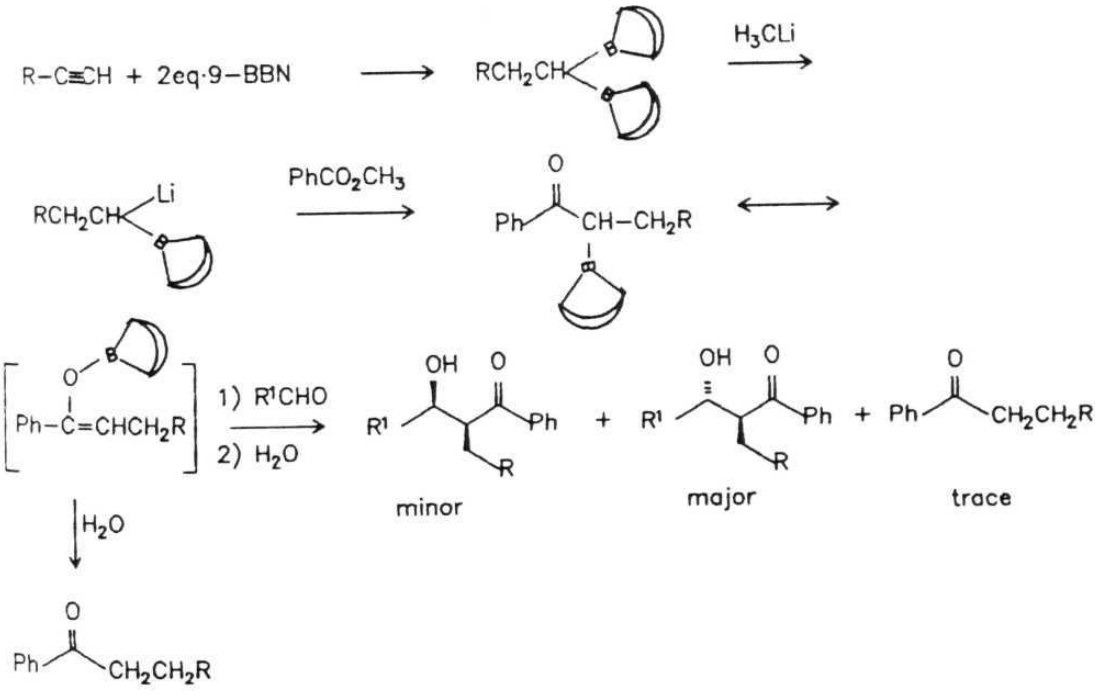
An organometallic compound of this kind could successively undergo an 1:2 elimination to form the corresponding olefins (eq. 8).



— (8)

In recent years, there has been immense interest in the cross-aldol reactions, one of the most useful means for the stereoselective construction of acyclic compounds containing multiple chiral centers. It has been demonstrated that an excellent diastereoselection can be attained in the formation of erythro and threo aldols by the utilization of vinyloxyboranes. A novel and useful procedure for the generation of phenylsubstituted vinyloxyboranes by the acylation of boron-stabilized carbanion, prepared from 1-alkynes with methyl benzoate has been reported. The vinyloxyboranes thus generated further react with aldehydes to give the corresponding cross-aldols in good yields (Scheme 7).[29]

SCHEME 7



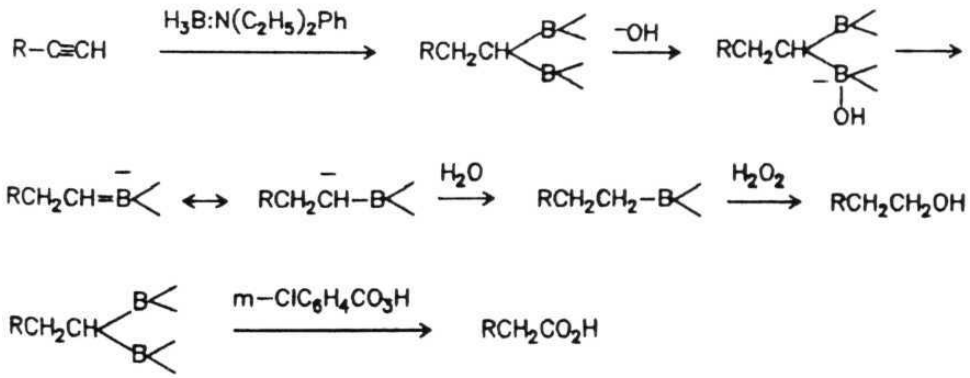
We have undertaken this work in order to examine the development of convenient methods of preparation and utilization of gem-dibora derivative through hydroboration of alkynes using the readily accessible $H_3B{:}N(C_2H_5)_2Ph$ complex.

RESULTS AND DISCUSSION

Synthesis and utilization of gem-diboryl derivatives:

In continuation of our efforts towards the applications of the N,N-diethylaniline–borane complex prepared from diborane generated using $I_2/NaBH_4$ system,[30–34] we became interested in the preparation and utilization of 1,1-diborylalkanes through hydroboration of 1-alkynes with the $BH_3{:}N(C_2H_5)_2Ph$ complex. In order to ascertain the formation of a 1,1-dibora derivative, we have first carried out the hydroboration of 1-decyne (7.5 mM) using $BH_3{:}N(C_2H_5)_2Ph$ complex (5 mM) in benzene. Oxidation of the intermediate boron compound with $H_2O_2/^{-}OH$ gives 1-decanol in 82% yield and oxidation with m-chloroperbenzoic acid gives 1-decanoic acid in 80% yield, indicating the formation of the 1,1-dibora compound in good yields in the hydroboration step (Scheme 8).[24]

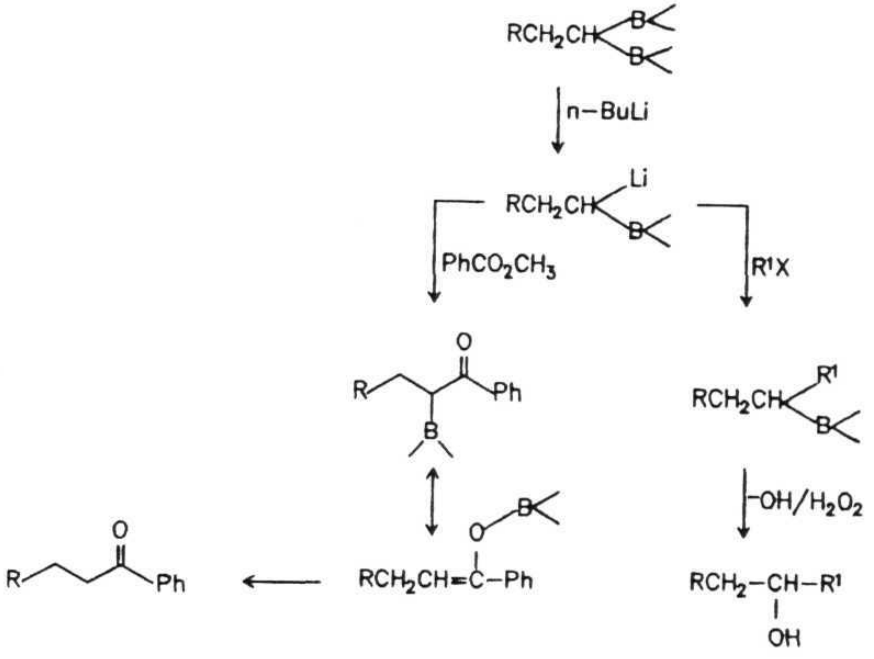
SCHEME 8



We have also observed that the reaction of n-butyllithium with 1,1-diboryldecane prepared in this way affords boron-stabilized carbanions which upon treatment with certain alkyl bromides and esters

followed by oxidation give secondary alcohols and carbonyl compounds respectively. These results are summarized in Table 1. The yields are comparable to the yields reported with methods utilizing BH_3:THF for hydroboration (Scheme 9).[29]

SCHEME 9



Although, the reactions described in Schemes 8 and 9 have been known for a long time, the 1,1-diboryl compounds have not received much attention. It was envisaged that the α-boramagnesium halide formed through the addition of Grignard reagent to 1,1-diboryl compound on treatment with $I_2/\ ^-OH$ would lead to rearrangement of the alkyl group through α-iodoboron intermediates, resulting in the formation of secondary alkyl boron compounds as shown in Scheme 10.

Table 1: **Synthesis of secondary alcohols and carbonyl compounds through reaction of boron stabilized carbanion.**

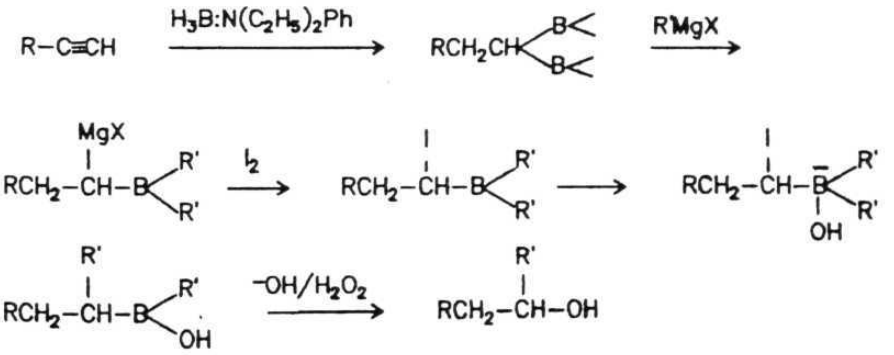
Entry[a]	Substrate	Product[b]	Yield[c](%)
1.	$PhCH_2Br$	$PhCH_2CH(OH)(CH_2)_8CH_3$	62
2.	$H_2C{=}CH{-}CH_2Br$	$H_2C{=}CHCH_2CH(OH)(CH_2)_8CH_3$	60
3.	$H_3C(CH_2)_2CH_2Br$	$H_3C(CH_2)_3CH(OH)(CH_2)_8CH_3$	59
4.	$PhCOOCH_3$	$PhCOCH_2(CH_2)_8CH_3$	61

a) For entries 1-3, alkyl bromides (10 mM), 1,1-diboryldecane (7.5 mM) and n-BuLi (8 ml, 1.2 M) were utilized. The organoborane was oxidized using $^{-}OH/H_2O_2$. For entry 4, methyl benzoate (10 mM), 1,1-diboryldecane (7.5 mM) and n-BuLi (8 ml, 1.2 M) were utilized.

b) Products were isolated by column chromatography [(silica gel/ hexane:ethyl acetate (95:5)] and identified by spectral data (IR, ^1H & ^{13}C NMR).

c) Yields based on 1-alkyne utilized.

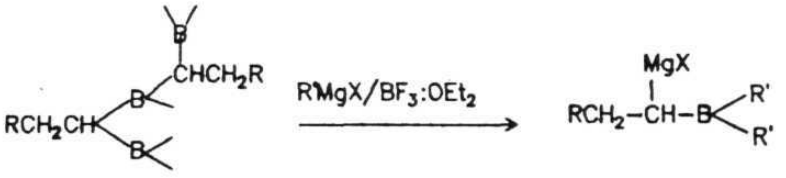
SCHEME 10



It was found that this is indeed the case when the reaction was carried out with 1-decyne (7.5 mM), BH_3:$N(C_2H_5)_2Ph$ (5 mM), PhMgBr (10 mM) and I_2 (10 mM). The corresponding secondary alcohol has been obtained in moderate yield (~50%) after $H_2O_2/\ ^-OH$ oxidation.

It is assumed that the 1,1-diboryl polymers breakdown to the α-boraalkylmagnesium bromide (Scheme 10) on reaction with RMgX. However, the alkyne and BH_3:$N(C_2H_5)_2Ph$ complex are used in 3:2 ratio and the stoichiometry (Scheme 10) requires involvement of alkyne and boron in 1:1 ratio. It was thought that the use of BF_3:OEt_2 and equivalent amount of RMgX to form BR_3 *in situ* would be helpful for the breakdown of the 1,1-diboryl polymers (Scheme 11).

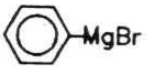
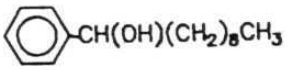
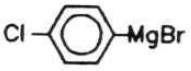
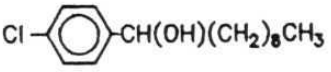
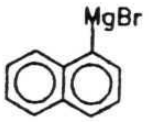
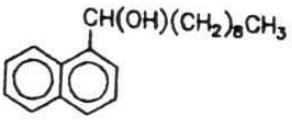
SCHEME 11



We have observed that the yield of the secondary alcohol is increased by about 10% when the reaction was carried out using 1-decyne (7.5 mM), BH_3:$N(C_2H_5)_2Ph$ (5 mM), PhMgX (30 mM) and BF_3:OEt_2 (2.5 mM). Hence, we have carried out all transformations outlined in Table 2 in this way. Several mixed alkyl carbinols have been synthesized following this procedure. These results are summarized in Table 2

In order to further examine the intermediacy of α-boraalkyl-magnesium bromide, we have examined the alkylation-carbonylation process (Scheme 12). However, the expected trialkyl carbinol was not formed and the corresponding secondary alcohol, resulting from

Table 2: Synthesis of secondary alcohols through reacation of 1,1-diboryldecane with $RMgX/I_2$ followed by oxidation.

Entry[a]	Grinard reagent	Product[b]	Yield[c](%)
1.			60
2.			59
3.			57
4.	$H_3C(CH_2)_2CH_2MgBr$	$H_3C(CH_2)_3CH(OH)(CH_2)_8CH_3$	59
5.	$(H_3C)_2CHMgBr$	$(H_3C)_2CHCH(OH)(CH_2)_8CH_3$	52
6.	$H_2C=CHCH_2MgBr$	$H_2C=CHCH_2CH(OH)(CH_2)_8CH_3$	50
7.	$H_3C(CH_2)_4C\equiv CMgBr$	$H_3C(CH_2)_4C\equiv CCH(OH)(CH_2)_8CH_3$	32

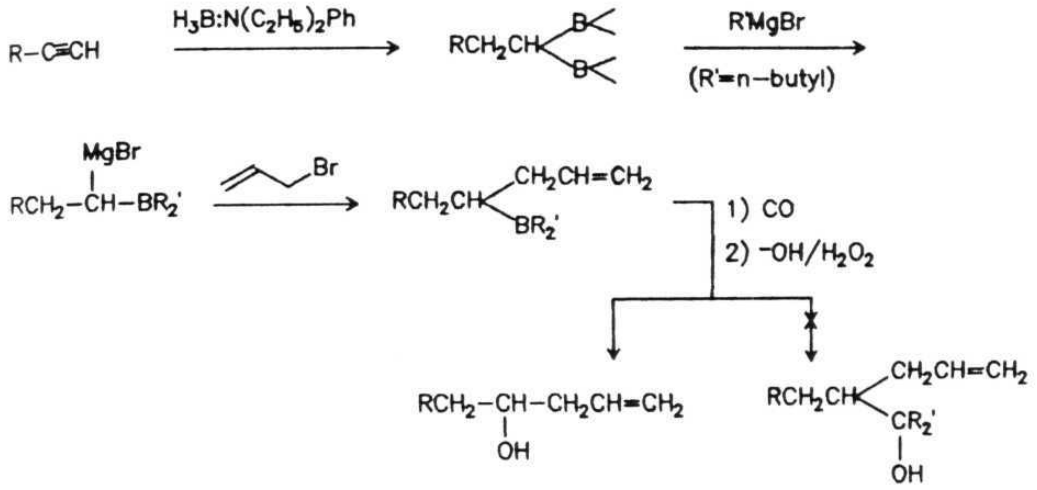
a) For entries 1-7, 1,1-diboryldecane (7.5 mM) and Grignard reagent prepared using RBr (30 mM) and Mg (35 mM) in THF (30 ml) were utilized.

b) Products were isolated by column chromatography [silica gel/ hexane:ethyl acetate (95:5)] and identified by spectral data (IR, ^1H & ^{13}C NMR).

c) Yield based on 1-alkyne utilized.

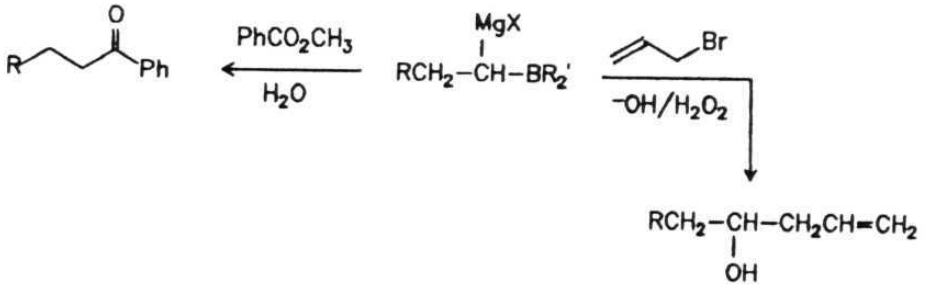
alkylation of the intermediate α-boraalkylmagnesium bromide, was obtained in 30% yield.

SCHEME 12



This observation indicates that although the intermediate has the property expected for α-boraalkylmagnesium bromide, it may not be precisely the $RCH_2CH(MgX)BR_2^1$ species. The intermediacy of α-boraalkylmagnesium bromide was further ascertained by carrying out the alkylation with alkyl bromide and the reaction with methyl benzoate (Scheme 13).

SCHEME 13



The mixed dialkyl carbinols and dialkyl ketones can be prepared through carbonylation[35] and cyanidation[36] of trialkyl boranes under certain conditions. The present transformation is a good alternative

to these methods, although in the present case three out of the four alkyl groups derived from the Grignard reagent are not utilized. Since one of the alkyl/aryl groups is prepared through a method not involving hydroboration, it is possible to prepare carbinols containing unsaturated moieties following the method reported here. Also, the zinc-boron organometallic species, structurally similar to the magnesium-boron derivatives suggested in Scheme 10, have been proved to be useful synthetic intermediates.[37] Although, precise structure of the intermediate α-boraalkylmagnesium species is not understood, the reagent system should be useful for synthetic applications.

CONCLUSIONS

1,1-Diboryldecyl derivative was synthesized by the reaction of the 1-decyne with $H_3B{:}N(C_2H_5)_2Ph$ complex. It was observed that the reaction of in butyllithium with the 1,1-diboryl compound prepared in this way affords boron stabilized carbanion which upon treatment with certain alkylbromides and esters followed by oxidation gives secondary alcohols and carbonyl compounds, respectively, in good yields. It was also observed that the addition of Grignard reagent/$BF_3{:}OEt_2$ to 1,1-diboryl compound followed by $I_2/^{-}OH$ treatment leads to rearrangement of the alkyl group through α-iodoboron intermediates. Oxidation of the resulting secondary alkyl boron compound gives the mixed alkyl secondary alcohols in moderate yields.

EXPERIMENTAL SECTION

General Information:

Several items given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. 1-Decyne was prepared following a reported procedure.[38] The n-butyllithium was commercial sample supplied by E-Merck, Germany. All alkyl bromides utilized are commerical samples supplied by Fluka, Switzerland. Methyl benzoate was commercial sample supplied by SD's, India.

Oxidation of 1,1-diboryldecane with alkaline hydrogen peroxide:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* by bubbling diborane, generated by dropwise addition of iodine (1.27 g, 5 mM) in diglyme (10 ml) to $NaBH_4$ (0.4 g, 10 mM) in diglyme (5 ml) at 25°C, into a solution of N,N-diethylaniline (0.75 g, 5 mM) in dry benzene (50 ml) for 1h. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h and refluxed for 6h. The reaction mixture was cooled to 10°C. The organoborane was oxidized by the addition of 3N NaOH (10 ml) followed by dropwise addition of H_2O_2 (16%, 15 ml). The reaction mixture was stirred for 2h at 25°C. The organic layer was separated and the aqueous layer was washed with ether (2 x 20 ml). The combined organic layer was washed with 3N HCl (2 x 10 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 1-decanol was isolated.

Yield : 82% (0.86 g)

IR (neat) ν_{max} : 3350, 1060 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm o,9 (t, 3H), 1.2 (m, 16H), 3.6 (t, 2H), 5.3 (s, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.9, 22.6, 25.8, 29.3, 29.6, 31.9, 32.5, 62.5.

The spectral data of this product showed 1:1 correspondence with data reported in the literature.[39]

Oxidation of 1,1-diboryldecane with m-chloroperbenzoic acid:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h and refluxed for 6h. The reaction mixture was coold to 10°C. The organoborane was oxidized by adding dropwise 25 ml of a solution of m-chloroperbenzoic acid (2.58 g, 25 mM) in tetrahydrofuran. After stirring an additional hour at 25°C, the reaction mixture was made basic by adding 3N sodium hydroxide. The organic phase was decanted from the aqueous phase, and washed once with water. The combined aqueous phase was acidified with dil.HCl, then extracted with ether (3 x 20 ml). The combined organic extract was dried over anhydrous $MgSO_4$. On evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-decanoic acid (1.03 g, 80%) was isolated.

The sample showed 1:1 correpondence (TLC & IR) with an authentic sample.[40]

Reaction of 1,1-diboryldecane with n-BuLi/$PhCH_2Br$:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h and refluxed for 6h. The reaction mixture was cooled to 10°C and n-butyllithium (8 ml, 1.2 M) was added slowly, the contents were further stirred for 2h at 25°C. Benzyl bromide (1.71 g, 10 mM) was added at 25°C and further stirred for 6h. The reaction mixture was quenched with water (5 ml) and oxidized using 3N NaOH (10 ml) and H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was washed with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (2 x 10 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-phenylundecan-2-ol was isolated.

Yield : 62% (1.15 g)

IR (neat) ν_{max} : 3350, 3050, 2950, 1600, 740, 700 cm^{-1}

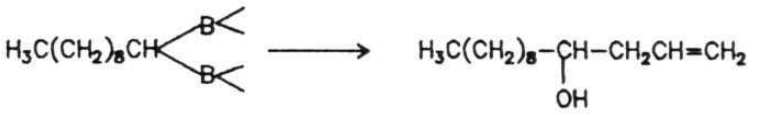
^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–0.95 (t, 3H), 1.2–1.72 (m, 16H), 2.30 (s, 1H), 2.60–2.90 (m, 2H), 3.80–3.90 (m, 1H), 7.15–7.40 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 25.7, 29.3, 31.8, 36.8, 44.0, 72.7, 126.5, 128.6, 129.6, 138.9.

Analysis	: C% ; H%
Calculated	: 82.20; 11.36
Found	: 82.15; 11.41

This compound has been reported in the literature.[41]

The reactions with allylbromide (1.20 g, 10 mM) and n-butyl bromide (1.37 g, 10 mM) were also carried out following the procedure oulined above.



Yield : 60% (0.89 g)

IR (neat) ν_{max} : 3360, 3080, 2935, 2860, 1645, 900 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–0.90 (t, 3H), 1.20–1.50 (m, 16H), 1.80 (s, 1H), 2.08–2,35 (m, 2H), 3.61 (br m, 1H), 5.10–5.17 (m, 2H), 5.73–5.89 (m, 1H). (Spectrum Number 16)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.7, 22.4, 25.4, 29.3, 31.7, 36.6, 41.7, 70.6, 117.7, 135.1.(Spectrum Number 15) 44.0, 72.7, 126.5, 128.6, 129.6, 138.9.

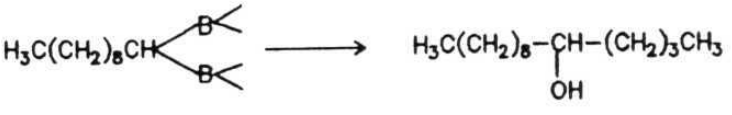
Mass (m/e) : 197 (M^{+}-1)

Analysis : C% ; H%

Calculated : 78.72; 13.21

Found : 78.65; 13.19

This compound has been reported in the literature.[42]



Yield : 59% (0.94 g)

IR (neat) ν_{max} : 3350, 2900, 1460 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–1.05 (t, 6H), 1.15–1.65 (m, 23H), 3.60 (m, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 25.6, 29.4, 29.6, 31.9, 37.5, 72.0.

This compound has been reported in the literature.[43]

Reaction of 1,1-diboryldecane with n-BuLi/$PhCOOCH_3$:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h and refluxed for 6h. The reaction mixture was cooled to 10°C and n-butyllithium (8 ml, 1.2 M) was added slowly. The contents were further stirred for 2h at 25°C. Methyl benzoate (1.36 g, 10 mM) was added at 25°C and further stirred for 6h. The reaction mixture was quenched with water (5 ml). The organic layer was separated and the aqueous layer was washed with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (2 x 10 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-phenyl-1-undecanone was isolated.

Yield : 61% (1.1 g)

IR (neat) ν_{max} : 3050, 2950, 1700, 1600, 700 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.80–0.95 (t, 3H), 1.15–1.80 (m, 16H), 2.90–3.00 (t, 2H), 7.40–7.60 (m, 3H), 7.90–8.0 (d, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 24.3, 29.3, 29.5, 31.8, 38.5, 128.0, 128.6, 132.8, 137.2, 200.5.

Analysis	: C% ;	H%
Calculated	: 82.87;	10.64
Found	: 82.78;	10.80

This compound has been reported in the literature.[44]

Reaction of 1,1-diboryldecane with PhMgBr/I_2-NaOH:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C . BF_3:OEt_2 (0.35 g, 2.5 mM) was added and the contents were brought to 25°C and stirred further for 1h. The PhMgBr, prepared using PhBr (30 mM) and Mg (35 mM) in THF (30 ml), was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Iodine (5 g, 20 mM) in benzene (20 ml) was added dropwise to the reaction mixture at 10°C and further stirred for 2h at 25°C. NaOH (3N, 30 ml) solution was added dropwise to the reaction mixture and stirred further for 2h. The reaction mixture was oxidized using H_2O_2 (30%, 20 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 1-phenyl-1-decanol was isolated.

Yield : 60% (1.05 g)

IR (neat) ν_{max} : 3300, 3050, 2950, 1600, 760, 700 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.84 (t, 3H), 1.00–1.68 (m, 16H), 3.64 (t, 1H), 3.84 (s, 1H), 6.66–7.32 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.9, 22.5, 25.6, 29.2, 29.5, 31.8, 32.2, 62.8, 115.5, 120.2, 129.6, 156.0.

This compound has been reported in the literature.[45]

Reactions of 1,1-diboryldecane with other Grignard reagents were also carried out following the procedure outlined above.

Yield : 59% (1.18 g)

IR (neat) ν_{max} : 3300, 3050, 2950, 1600, 780 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.88–0.94 (t, 3H), 1.20–1.63 (m, 16H), 2.64 (b s, 1H), 3.66–3.72 (t, 1H), 6.75–7.63 (m, 4H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 25.6, 29.3, 29.5, 31.8, 32.4, 63.0, 116.8, 125.0, 129.4, 154.9.

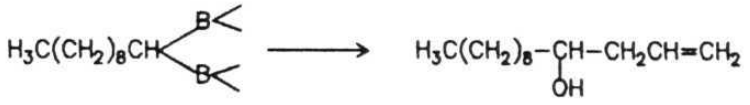
Yield : 57% (1.21 g)

IR (neat) ν_{max} : 3250, 3050, 2900, 1600, 780, 760 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.70–0.90 (t, 3H), 1.00–1.45 (m, 16H), 3.50 (b s, 1H), 4.00–4.10 (t, 1H), 6.70–814 (m, 7H).

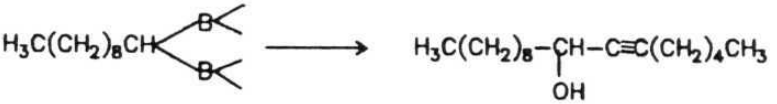
^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 25.6, 27.8, 29.4, 29.6, 31.9, 36.9, 37.2, 72.8, 108.7, 115.6, 120.2, 120.5, 122.0, 124.9, 125.1, 126.0, 126.4, 127.7, 129.4, 134.6, 152.3, 154.1.

Analysis	: C% ;	H%
Calculated	: 84.45;	9.92
Found	: 84.30;	9.98



Yield : 50% (0.74 g)

Spectral data of this product showed 1:1 correspondence to the data of the product obtained in an earlier experiment.[42]



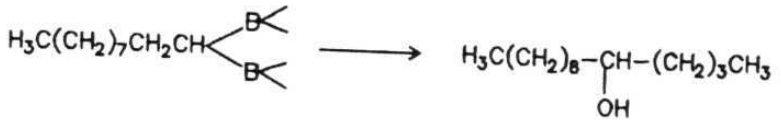
Yield : 32% (0.6 g)

IR (neat) ν_{max} : 3300, 2900, 2250, 1460 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.64–0.96 (m, 6H), 1.00–2.20 (m, 25H), 4.24 (t, 1H).

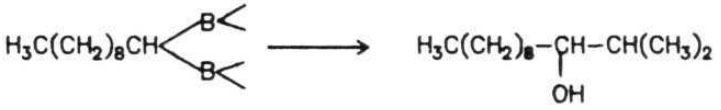
^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.8, 14.0, 18.6, 22.2, 22.6, 25.2, 28.4, 29.3, 29.5, 31.0, 31.9, 38.2, 62.7, 81.5, 85.4. (Spectrum Number 17)

Analysis	:	C% ;	H%
Calculated	:	80.88;	12.78
Found	:	80.75;	12.82



Yield : 59% (0.94 g)

Spectral data of this product showed 1:1 correspondence to the data of the product obtained in an earlier experiment.[43]



Yield : 52% (0.78 g)

IR (neat) ν_{max} : 3300, 2900, 1440 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.60–0.88 (m, 9H), 0.92–1.64 (m, 17H), 3.24 (m, 1H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.9, 17.0, 18.8, 22.6, 26.0, 29.2, 29.6, 31.9, 33.4, 34.1, 76.7.(Spectrum Number 18)

Mass (m/e) : 199 (M^{+}-1)

Reaction of 1,1-diboryldecane with $H_3C(CH_2)_2CH_2MgBr/H_2C{=}CHCH_2Br$:

The $BH_3{:}N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C . $BF_3{:}OEt_2$ (0.35 g,

2.5 mM) was added and the contents were brought to 25°C and stirred further for 1h. The $H_3C(CH_2)_2CH_2MgBr$, prepared using $H_3C(CH_2)_2CH_2Br$ (30 mM) and Mg (35 mM) in THF (30 ml), was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Allyl bromide (1..20 g, 10 mM) was added dropwise to the reaction mixture at 25°C and further stirred for 3h at 25°C. The organoborane was oxidized by the addition of 3N NaOH (10 ml) followed by dropwise addition of H_2O_2 (16%, 15 ml). The reaction mixture was stirred further for 2h at 25°C. The organic layer was washed with 3N HCl (2 x 10 ml), water, brine and dried over anhydrous $MgSO_4$.After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), tridec-1-en-4-ol (0.47 g, 32%) was isolated.

Spectral data of this product showed 1:1 correspondence to the data obtained in the earlier experiments.[42]

Reaction of 1,1-diboryldecane with $H_3C(CH_2)_2CH_2MgBr/PhCOOH_3$:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C . BF_3:OEt_2 (0.35 g, 2.5 mM) was added and the contents were brought to 25°C and stirred further for 1h. The $H_3C(CH_2)_2CH_2MgBr$, prepared uisng $H_3C(CH_2)_2CH_2Br$ (30 mM) and Mg (35 mM) in THF (30 ml), was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Methyl benzoate (1.36 g, 10 mM) was added dropwise to the reaction mixture at 25°C and further stirred for 3h at 25°C.

The reaction mixture was quenched with water (5 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-phenyl-1-undecanone (0.68 g, 38%) was isolated.

Spectra data of this product showed 1:1 correspondence with the data of the product obtained in an earlier experiment.[44]

Attempted carbonylation reaction with alkylated α-boraalkylmagmesium bromide:

The BH_3:$N(C_2H_5)_2Ph$ complex (5 mM) was prepared *in situ* as above. 1-Decyne (1.04 g, 7.5 mM) was added at 25°C, stirred for 0.5h. The contents were refluxed for 6h and cooled to 10°C . BF_3:OEt_2 (0.35 g, 2.5 mM) was added and the contents were brought to 25°C and stirred further for 1h. The $H_3C(CH_2)_2CH_2MgBr$, prepared uisng $H_3C(CH_2)_2CH_2Br$ (30 mM) and Mg (35 mM) in THF (30 ml), was added to the reaction mixture at 10°C. The reaction mixture was stirred for 1h at 25°C and refluxed for 2h. Allyl bromide (1.20 g, 10 mM) was added dropwise to the reaction mixture at 25°C and further stirred for 3h at 25°C, ethylene glycol (10 ml) was added and the reaction mixture was brought to 100°C. It was stirred further for 6h at 100°C while bubbling carbon- monoxide through it. The reaction mixture was then brought to 25°C, 3N NaOH (20ml) was added and the oxidation was carried out by the dropwise addition of H_2O_2 (16%, 10ml). The organic layer was

separated and the aqueous layer was washed with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (2x20 ml),3N NaOH (2x20ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), tridec-1-en-4-ol (0.44 g, 30%) was isolated. The spectral data showed 1:1 correspondence with data of the product obtained in an earlier experiment.[42]

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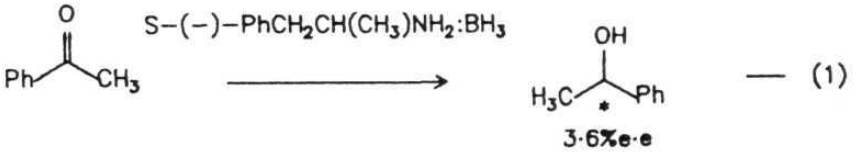
CHAPTER 3

Synthesis and Utilization of Chiral Amine-Boranes

INTRODUCTION

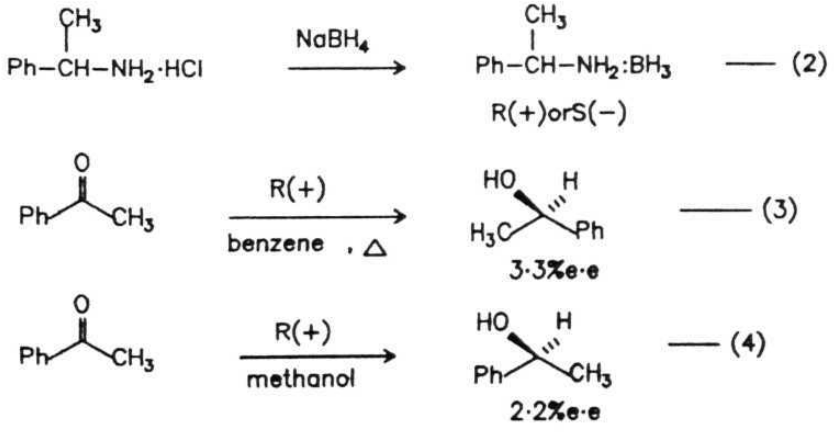
Synthesis and Utilization of Chiral Amine-Boranes:

Chiral amine-borane complexes are promising reagents for asymmetric reduction of prochiral carbonyl compounds. Fiand and Kagan[1] prepared amine-boranes from S-(-)-1-methyl-2-phenylethylamine and its N-methyl and N,N-dimethyl derivatives, and showed that acetophenone was reduced to optically active 1-phenylethanol with these reagents, but the optical yields 3.6-5.0% were disappointingly low (eq. 1).



— (1)

Borch and Levitan,[2] studied the asymmetric reduction of acetophenone with R-(+)-1-phenylethylamine-borane and the reduction of heptan-2-one in various solvents. It was found that the reduction is incomplete even after reaction periods of 4h at 25°C. The optical yields of the resultant alcohols were found to be only 1.5-3.3% e.e (eq. 2-4).

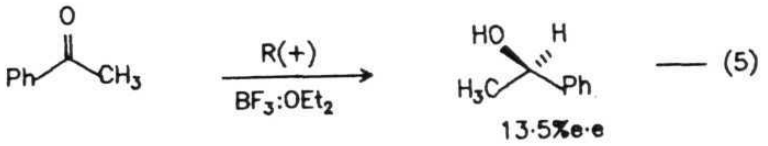


— (2)

— (3)

— (4)

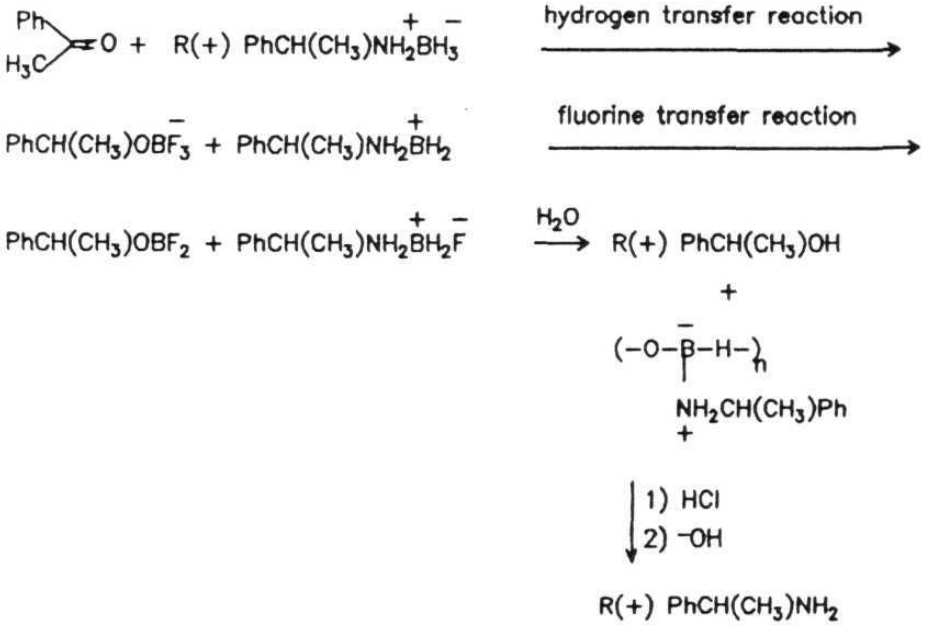
Grundon *et al*[3] reported that when the asymmetric reduction of acetophenone was carried out with equimolar quantities of the R-(+)-1-phenylethylamine-borane and boron trifluoride etherate in tetrahydrofuran at $0^{o}C$, the reaction was complete after 0.5h to give R-(+)-1-phenylethanol with 13.5% e.e (eq. 5).



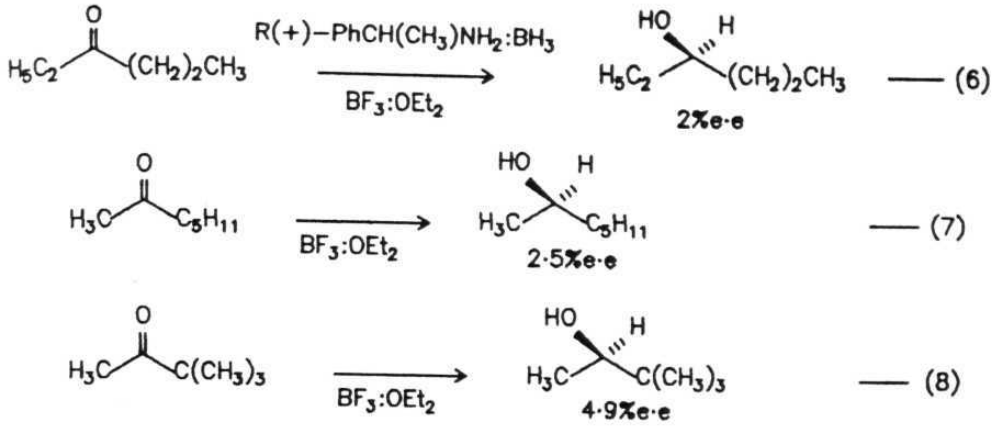
— (5)

The mechanism suggested for the reduction of ketones with 1-phenylethylamine-borane and boron trifluoride is shown in Scheme 1.

SCHEME 1



It was found that heptan-2-one, methyl t-butyl ketone and ethyl isopropyl ketone were also reduced rapidly and quantitatively to give the corresponding alcohols, but the optical induction was much less than that observed in reaction with acetophenone (eq. 6-8).

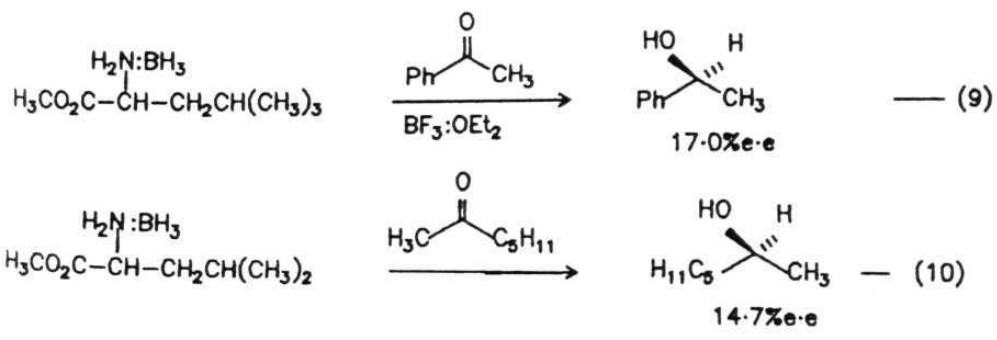


— (6)

— (7)

— (8)

Grundon *et al* also reported that the asymmetric reduction of acetophenone using stoichiometric quantities of L-leucine methyl ester-borane in tetrahydrofuran gave 1-phenylethanol in 48% yield after 5h at ambient temperature.[3] When the reaction mixture was treated with 1 equivalent of BF_3:OEt_2 at 0^oC immediately after the addition of acetophenone, the reduction was complete in 30 minutes. 1-Phenylethanol was isolated in almost quantitative yield. L-Leucine methyl ester-borane reacted similarly with 3,3-dimethylbutan-2-one and heptan-2-one. Asymmetric reduction of acetophenone was also carried out with the amine-boranes derived from L-phenylalanine methyl ester and L-valine methyl ester. The results show that the S-enantiomers of the alcohols are present in excess with optical purities of 14-22% (eq. 9-11).



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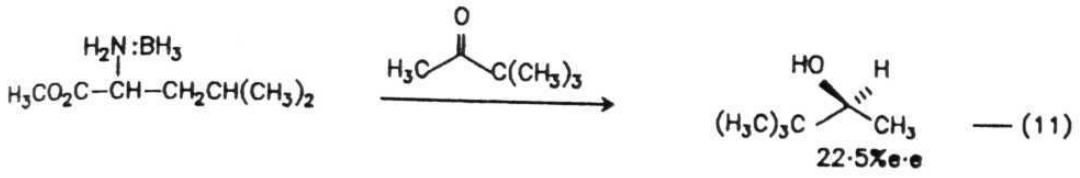
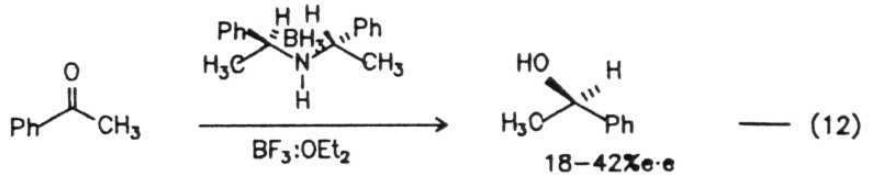


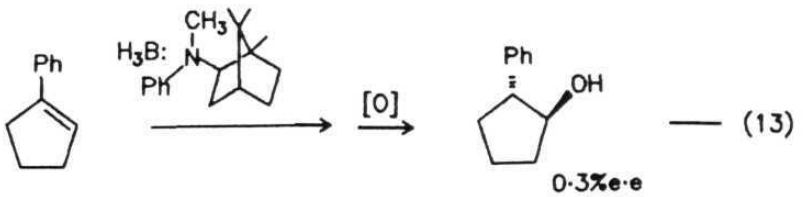
— (11)

Eleveld and Hogeveen studied the asymmetric reduction of acetophenone with stoichiometric quantities of the (S,S), α,α'-dimethyldibenzylamine-BH_3 and BF_3:OEt_2 in THF.[4] It was found that the 1-phenylethanol was obtained in 18-42% e.e. Reduction of acetophenone using BF_3:OEt_2 and the (S,S)-α,α'-dimethyldibenzylamine-borane give 1-phenylethanol with 42% e.e and 78% chemical yield (eq. 12).



— (12)

In this laboratory, it was found that the hydroboration/ oxidation of representative prochiral olefins using N-isobornyl-N-methylaniline-borane and N-benzyl-N-isopropyl-α-methylbenzylamine-borane gives corresponding alcohols with 0.3 to 19% enantiomeric excess (eq. 13,14).[5] These results may have some interesting mechanistic implications Scheme 2.



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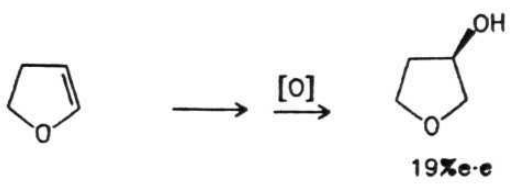

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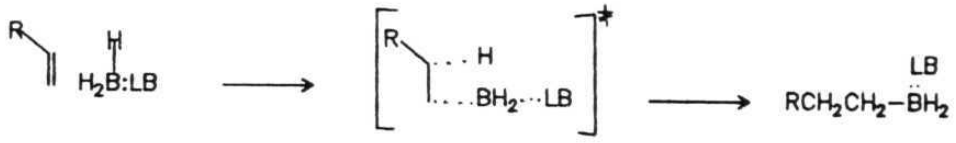
SCHEME 2



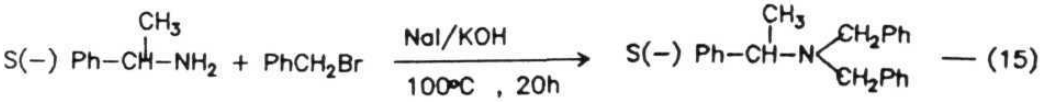
In an effort to further examine the utilization of amine–boranes in reductions and hydroborations, we have undertaken this investigation.

RESULTS AND DISCUSSION

Synthesis of Chiral Amines:

a) Synthesis of S-(-)-N,N-dibenzyl-α-methylbenzylamine:

This tertiary amine was prepared through benzylation of S-(-)-α-methylbenzylamine in the presence of KOH powder, benzyl bromide and sodium iodide[6] (eq. 15).

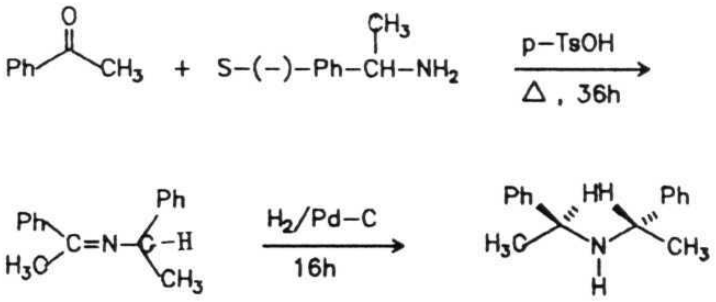


— (15)

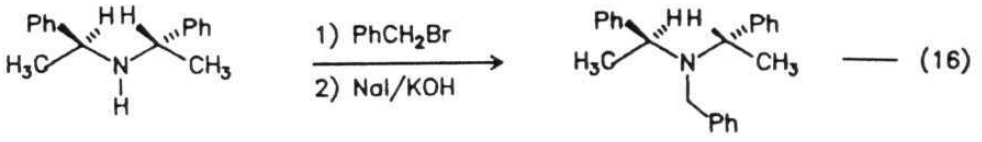
b) Synthesis of S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine:

It was thought that the S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine-BH_3 complex would give better results in the reduction and hydroboration. Although, this compound has not been reported, the synthesis of the corresponding secondary amine has been reported. We have followed procedures available in the literature starting from acetophenone and S-(-)-α-methylbenzylamine, for the synthesis. The corresponding imine was obtained in 90% yield through condensation with acetophenone in the presence of p-toluenesulfonic acid. Catalytic hydrogenation of this imine over Pd/C in ethyl acetate afforded the S,S -α,α'-dimethyl dibenzylamine in 70% yield (Scheme 3).

SCHEME 3

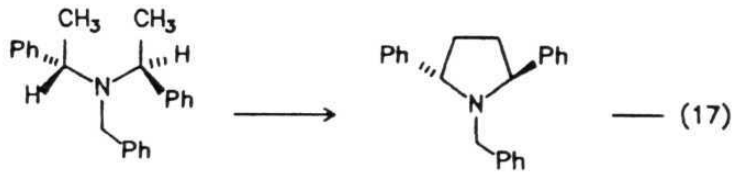


The S,S -α,α'-dimethyldibenzylamine was converted to the corresponding N-benzyl derivative (80%) by benzylation in the presence of sodium iodide, powdered KOH and benzyl bromide at 100°C for 14h (eq.16).



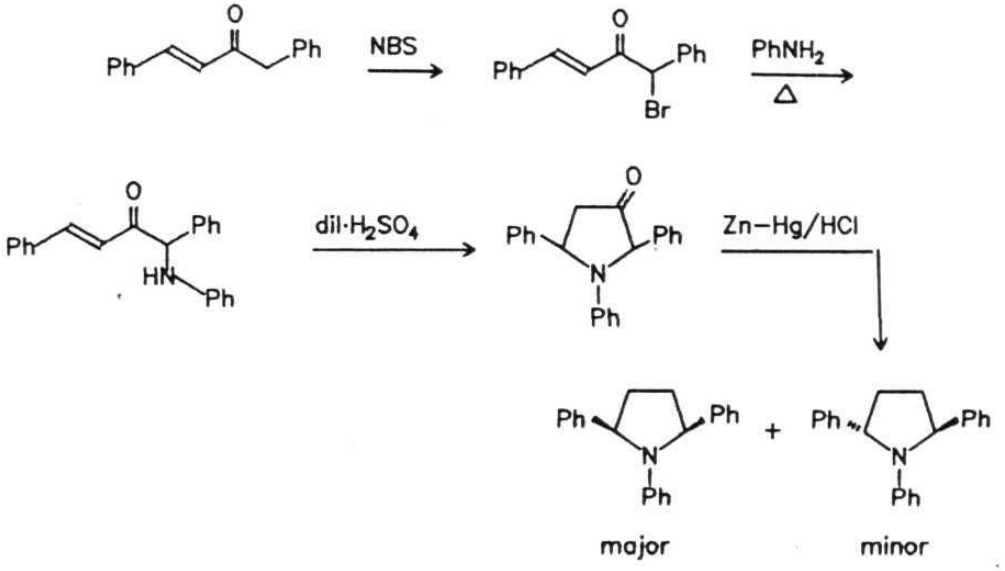
c) **Synthesis of trans-2,5-diphenylpyrrolidine:**

In the S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine, the chiral groups around nitrogen are free to adopt several conformations. It was thought that the chiral recognition will be greater if the nitrogen is fixed in a ring (eq.17).



The corresponding N-phenyl derivatives have been prepared[7] as outlined in Scheme 4.

SCHEME 4



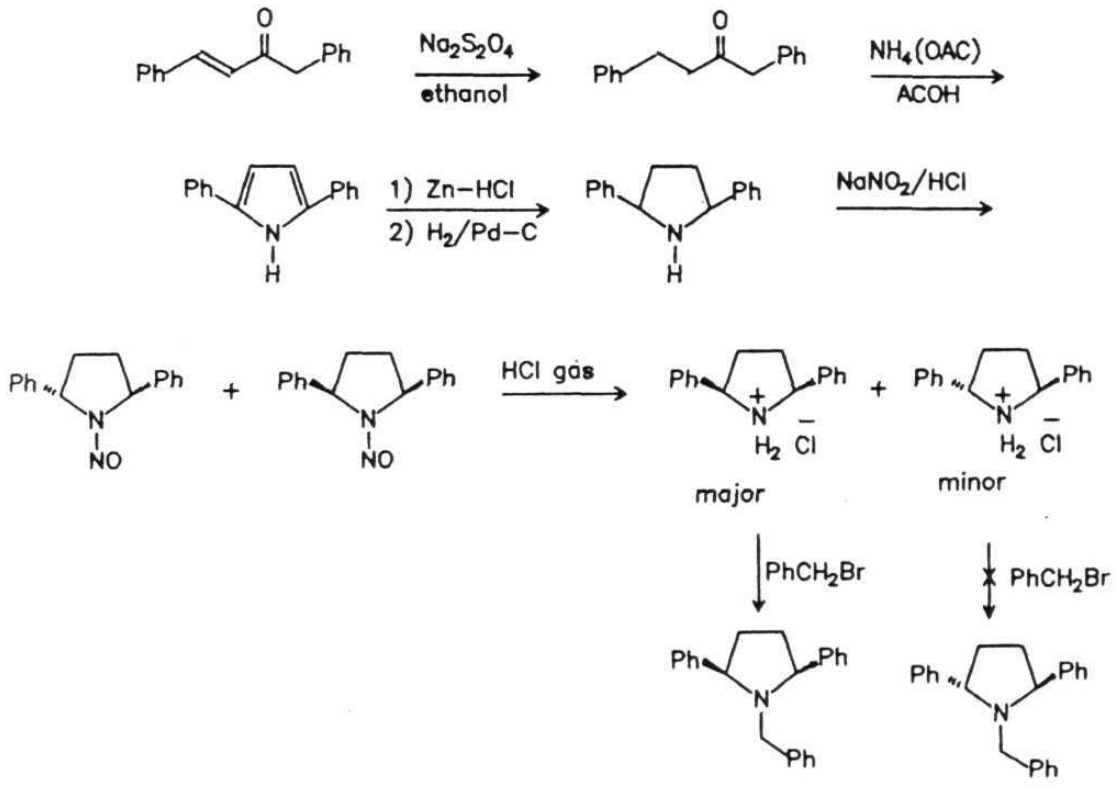
Unfortunately, the cis-derivative is formed more amount than the trans-N-phenyl derivative. We have not attempted the preparation of this material since it is some what difficult to resolve the aniline derivatives. Hence, we decided to concentrate on the synthesis of the corresponding N-benzyl derivative.

Overberger *et al* reported the synthesis of cis- and trans- 2,5-diphenylpyrrolidines as well as that of their N-nitrosamine derivatives[8] (Scheme 5).

The N-benzyl derivative was prepared from the major hydrochloride isomer. The nmr spectrum of this N-benzyl derivative showed a singlet absorption at δ 3.41 (benzylic protons). It has been reported that singlet signals in the benzylic region of α,α'-disubstituted pyrrolidines or piperidines is an evidence for cis-configuration since trans disubstitution gives rise to quartets.[9] On the basis of this, both N-benzyl derivative and its pyrrolidine precursor have been assigned a

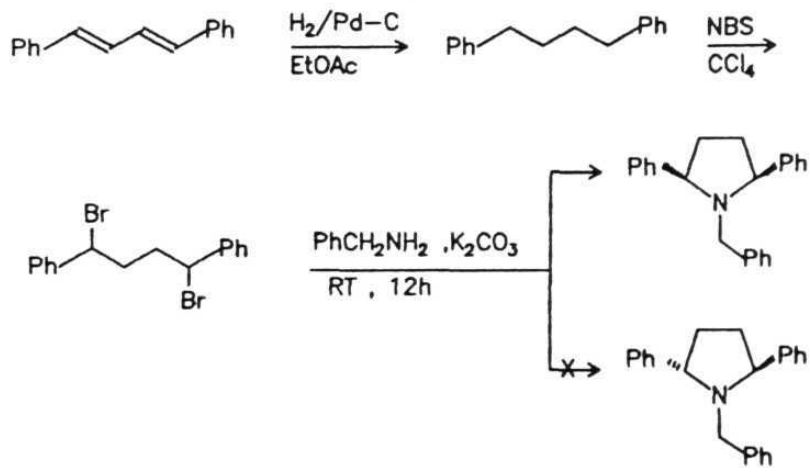
cis-configuration. The minor hydrochloride was therefore assigned the trans configuration. However, this isomer failed to react with benzyl bromides.

SCHEME 5

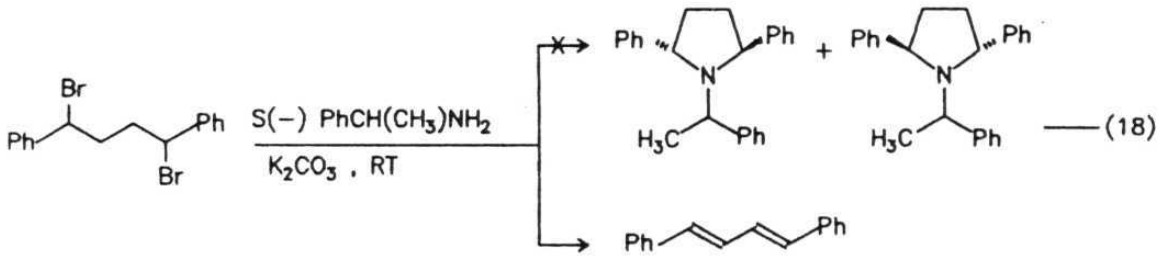


We have envisaged the synthesis of N-benzyl-2,5-diphenylpyrrolidine following the steps outlined in Scheme 6.

SCHEME 6



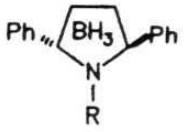
The product obtained was found to have characteristics (mp, NMR) reported for the cis-N-benzyl-2,5-diphenylpyrrolidine. However, in order to further ascertain the nature of this compound, we made a salt of this product with (+) camphor-10-sulphonic acid. It was found that repeated crystallization of this salt failed to give any optically active N-benzyl-2,5-diphenylpyrrolidine upon decomposition. So, we concluded that the product at hand is most probably the cis-derivative (meso). It was also attempted to prepare the N-α-methylbenzyl derivative of the 2,5-diphenylpyrrolidine. Unfortunately, the reaction failed in this case and only the corresponding elimination product was obtained (eq. 18).



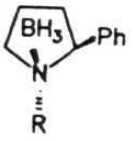
(18)

d) Synthesis of 2-phenylpyrrolidine:

As outlined earlier, we wanted to prepare the chiral trans-2,5-diphenyl system as the corresponding BH_3 complex would help in differentiating the diastereomeric transitation states in asymmetric reductions and hydroborations.

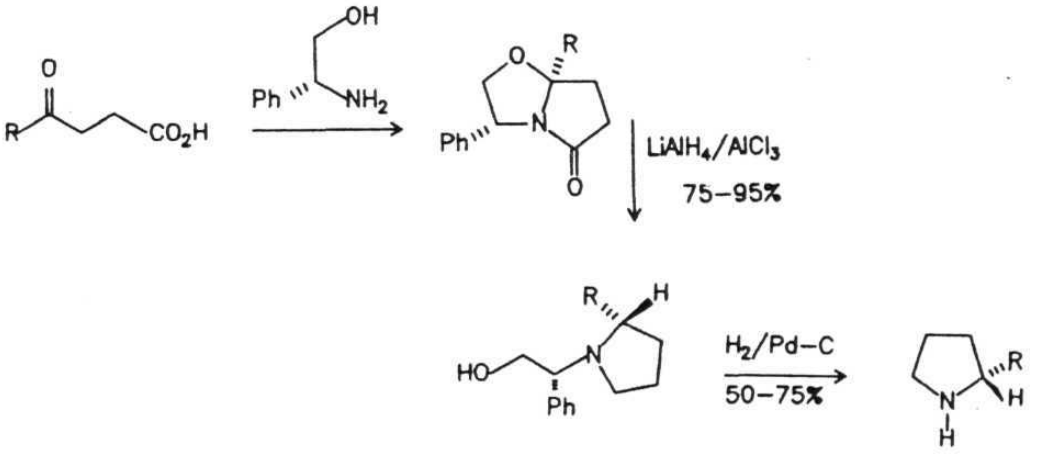


The BH_3 moiety would be always cis to the phenyl in such a situation. It was thought that even in 2-phenylpyrrolidine system, the situation would be similar to this in the case of bulky N-alkyl groups.



Recently, Meyers and Burgess reported the preparation of 2-substituted pyrrolidines from 3-arylpropanoic acids,[10] following the sequence of reactions outlined in Scheme 7.

SCHEME 7

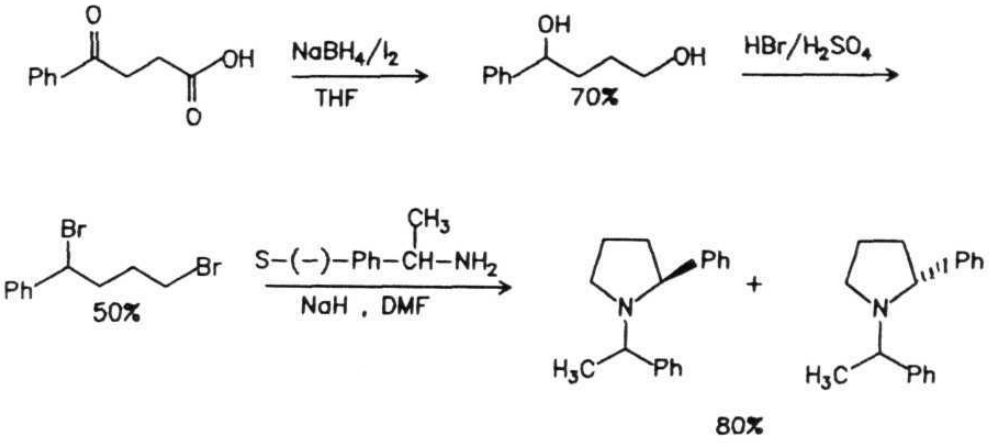


We have envisaged the synthesis starting from the chiral α-methyl benzylamine (Scheme 8).

It was identified that the 1-phenyl-1,4-dibromobutane is the crucial intermediate for the synthesis (Scheme 8). This was prepared in two steps from β-benzoylpropanoic acid, through reduction using $NaBH_4/I_2$ system, developed in this laboratory.[10a,10b] The dibromide on reaction with S-(-)-α-methylbenzylamine in the presence of NaH in DMF at room temperature for 12h, gave a mixture of the required diastereomeric amines in 80% yield. The isomers have been separated

by column chromatography (Alumina, hexane). The (-) isomer, $[\alpha]_D^{25}$ = -120^o (C 1.3, $CHCl_3$) was obtained in 40% yield, the (+) isomer, $[\alpha]_D^{25}$ $+37^o$ (C 0.5, $CHCl_3$) was obtained in 38% yield.

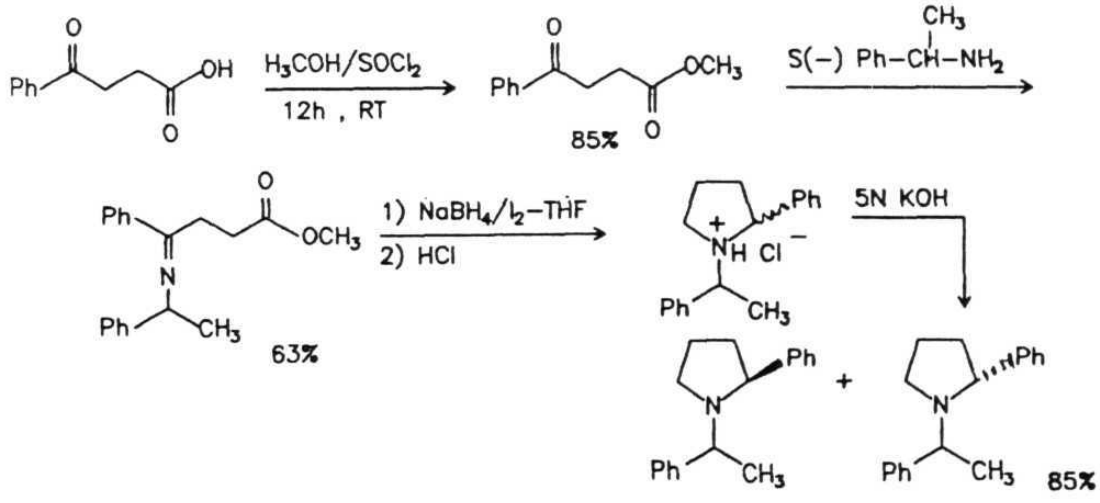
SCHEME 8



We have found that it is more convenient to obtain pure (-) isomer in adequate quantities, which is eluted first from the chromatography column (Alumina, hexane). So, we have carried out our studies using this isomer.

In the above procedure, the dibromo compound was obtained only in 50% yield from the corresponding diol. So, another synthesis, without going through this intermediate has been also developed (Scheme 9).

SCHEME 9

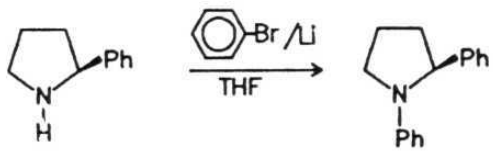


A mixture of methyl β-benzoylpropionate and S-(-)-α-methylbenzyl amine in benzene was refluxed for 12h, under nitrogen atmosphere using Dean-Stark apparatus to obtain the corresponding imine in 65% yield. This imine on reduction with $NaBH_4/I_2$ in THF followed by 6N HCl treatment gave the amine hydrochlorides. The diastereomeric amines were readily regenerated using 5N KOH (phenolphthalein indicator). The diastereomers were readily separated by column chromatography on alumina using hexane as a solvent as described above.

We find the latter method (Scheme 9) is better than the previous method and hence we followed this for accumulation of the chiral amines for our studies.

e) **Attempts towards the synthesis of 1,2-diphenylpyrrolidine:**

Hydroborations of olefins utilizing the N-alkyl derivatives are relatively slow. However, the N-phenyl derivatives undergoes faster reaction. So, we attempted to synthesize the 1,2-diphenylpyrrolidine derivative. It was thought that this compound can be readily prepared from the corresponding secondary amine following an N-phenylation procedure developed in this laboratory (eq. 19).[10c]

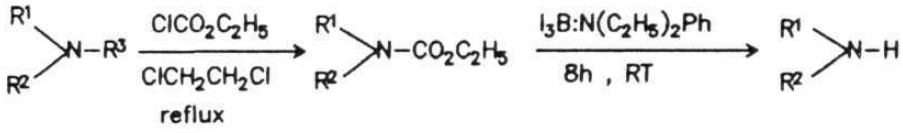


——(19)

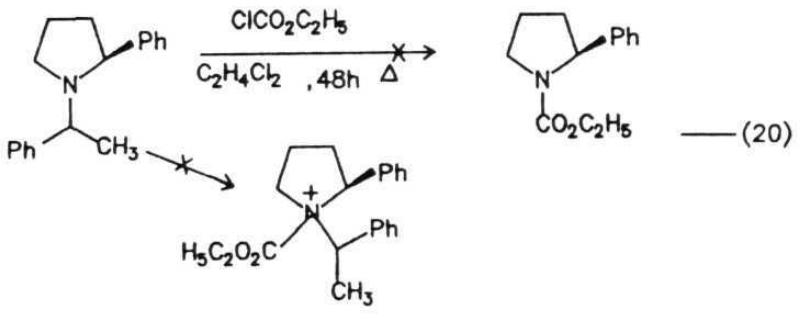
This method requires the corresponding secondary amine. We have attempted the conversion of the (-) isomer obtained previously (Scheme 9) to the secondary amine in several ways. The N-debenzylation of

tertiary amines is usually carried out using H2/Pd-C or under catalytic transfer hydrogen conditions ($Pd/C/NH_4^+COO^-$). We attempted the reaction of N-debenzylation of S-(-)-N-α-methylbenzyl-2-phenyl pyrrolidine with H_2/10% Pd/C catalyst under 40 Lbs per.sq inch hydrogen pressure. It was found that even after 12h the starting material remained intact. In this laboratory, a convenient method for N-debenzylation of tertiary amines has been developed.[10d] The N-benzyl-and N-α-methylbenzylamine derivatives are readily converted to the corresponding N-carbamates by adding chloroformate to the amine in dichloroethane at 25°C then refluxing for 6h. The N-carbamate derivative on treatment with BI_3:$N(C_2H_5)_2Ph$ complex gives the corresponding secondary amine (Scheme 10).

SCHEME 10



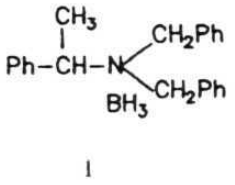
Unfortunately, the (-)-α-methylbenzyl-2-phenylpyrrolidine did not react with ethyl chloroformate even after refluxing 48h in dichloroethane. Presumably, the formation of the intermediate salt is difficult in this case (eq. 20).



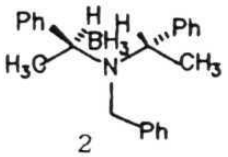
—(20)

We did not pursue the synthesis of the N-phenyl derivative further.

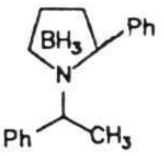
Asymmetric Reduction of Ketones Using Chiral Amine-Boranes:



1

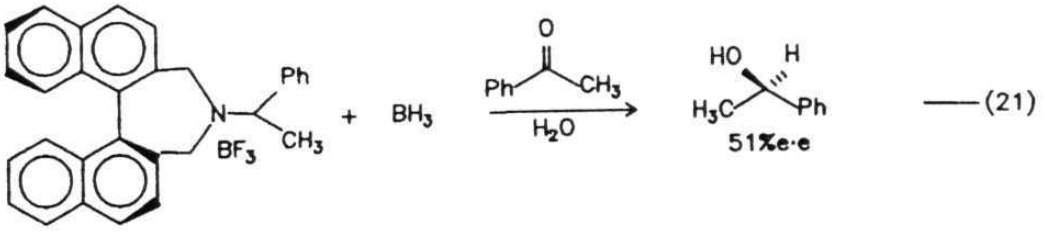


2



3

As discussed in the introductory section, reduction of prochiral ketones with chiral amine boranes with or without BF_3:OEt_2 catalysis gives asymmetric inductions in the range 2.2- 42%. Initially, we have been interested in understanding the mechanism of the BF_3 catalysis. An investigation undertaken in this laboratory, utilizing the binaphthyl system revealed that the reduction of prochiral ketones utilizing the chiral amine borane-BF_3 catalyst in combination with achiral reagent such as $H_3B{:}N(C_2H_5)_2Ph$, $H_3B{:}N(C_2H_5)_3$ or B_2H_6 itself, leads to similar results with 51% e.e.[11] (eq. 21).



——(21)

The results can be explained by considering a cyclic transition state outlined below.

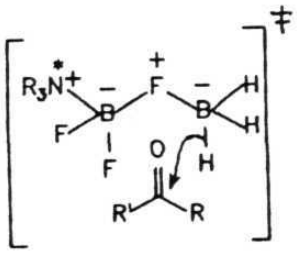
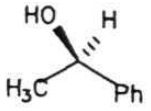
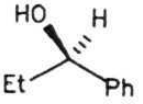
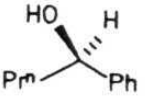
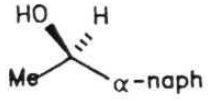


Table 1: Reduction of prochiral ketones using borane-S-(-)-N,N-dibenzyl-α-methylbenzylamine complex.

Entry[a]	Substrate	Product[b]	Yield[c]	$[\alpha]_D^{25}$(C, solvent)[d]	% e.e.[i]
1.	$PhCOCH_3$		80	$+11^o$ (C2, CH_3OH)[e]	24
2.	PhCOEt		87	$+10^o$ (C1.5, $CHCl_3$)[f]	22
3.	$PhCOPr^n$		80	$+2.5^o$(C4, Benzene)[g]	6
4.	α-naphCOMe		75	$+31.4^o$ (C1.75, CH_3OH)[h]	39

a) Reactions were carried out at room temperature for 6h, with 10 mM of amine-borane, 10 mM of ketone and 10 mM of BF_3:OEt_2 in benzene. The experiments were run at least twice in each case, α-naph= α-naphthyl.

b) Products were identified by analysis of spectral data (IR and ^1H & ^{13}C NMR) and comparison with the reported data.

c) Yields are isolated, chromatographed, and distilled products.

d) Optical rotations were measured with on Autopol-II automatic polarimeter (accuracy ± 0.01^o).

e) Based on the maximum $[\alpha]_D^{20}$ -45.5^o (C3, MeOH)[3]

f) Based on the maximum $[\alpha]_D^{20}$ -45.45^o (C5.15, $CHCl_3$)[12]

g) Based on the maximum $[\alpha]^{25}$ $+45.2^o$ (C3, benzene)[13]

h) Based on the maximum $[\alpha]_D^{25}$ -78.9^o (C3, MeOH)[12]

i) Enantiomeric excess.

We have decided to further investigate the synthetic utilities of the amine boranes prepared here using the chiral α-methylbenzylamine.

The N,N-dibenzyl-α-methylbenzylamine-BH_3 (1) was prepared in benzene by passing B_2H_6 generated using the $I_2/NaBH_4$ system. It was found that this amine-borane reduces acetophenone in the presence of BF_3:OEt_2 to 1-phenylethanol with 24% ee. Reduction of a few other ketones were also carried out using this amine-borane in the presence of BF_3:OEt_2, and the results are summarized in Table 1. The configurations of the products are consistently R. The optical inductions decreases on increasing the chain length of the alkyl moiety.

It was thought that replacement of another benzyl group with α-methylbenzyl group would lead to better results. Accordingly, we prepared the N-benzyl-α,α'-dimethyldibenzylamine as outlined earlier in this section. The corresponding amine-borane (2) was prepared in benzene and the reduction of acetophenone was carried in the absence and presence of BF_3:OEt_2 (Table 2). It was found that the asymmetric inductions obtained are better than the N,N-dibenzyl-α-methylbenzylamine system but still it is only up to 52% ee.

It was thought that the amine-boranes with nitrogen atom in a ring would give better inductions. The 2,5-diphenyl system would be a good choice for examining this.

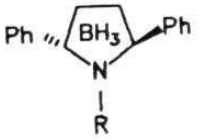
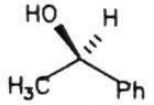
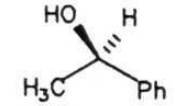
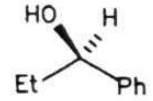
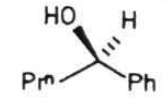
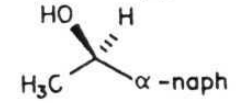


Table 2: Reduction of prochiral ketones using borane S,S-(-)-N-benzyl-α,α'-dimethyldibenzylamine complex:

Entry[a]	Substrate	Product[b]	Yield[c]	$[\alpha]_D^{25}$(C, solvent)[d]	% e.e.[i]
1.	$PhCOCH_3$		65	$+7^{o}$(C2, CH_3OH)[e]	15
2.	$PhCOCH_3$		82	$+22^{o}$(C1.5, CH_3OH)[e]	48
3.	PhCOEt		78	$+16.8^{o}$(C2.2, $CHCl_3$)[f]	37
4.	$PhCOPr^n$		75	$+4.6^{o}$(C3.2, Benzene)[g]	10
5.	α-naphCOMe		70	$+41^{o}$(C1, CH_3OH)[h]	52

a) For entry 1, was carried out at RT for 12h, with 10 mM of amine-borane and 10 mM of ketone in benzene. For entries 2-5, were carried out at room temperature for 6h, with 10 mM of amine-borane, 10 mM of ketone and 10 mM of BF_3:OEt_2 in benzene. The experiments were run at least twice in each case, α-naph= α-naphthyl.

b) Products were identified by analysis of spectral data (IR and ^1H & ^{13}C NMR) and comparison with the reported data.

c) Yields are isolated, chromatographed, and distilled products.

d) Optical rotations were measured with on Autopol-II automatic polarimeter (accuracy ± 0.01^{o}).

e) Based on the maximum $[\alpha]_D^{20}$ -45.5^{o} (C3, MeOH)[3]

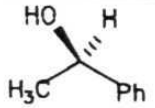
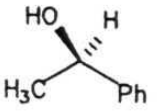
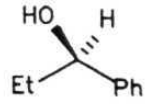
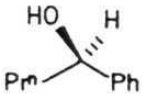
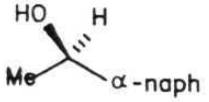
f) Based on the maximum $[\alpha]_D^{25}$ -45.45^{o} (C5.15, $CHCl_3$)[12]

g) Based on the maximum $[\alpha]_D^{25}$ $+45.2^{o}$ (C3, benzene)[13]

h) Based on the maximum $[\alpha]_D^{25}$ -78.9^{o} (C3, MeOH)[12]

i) Enantiomeric excess.

Table 3: Reduction of prochiral ketones using borane (-)-N-α-methylbenzyl-2-phenylpyrrolidine complex:

Entry[a]	Substrate	Product[b]	Yield[c]	$[\alpha]_D^{25}$(C, solvent)[d]	% e.e.[i]
1.	$PhCOCH_3$		72	$+7.6^o$ (C2, CH_3OH)[e]	16.20
2.	$PhCOCH_3$		73	$+24.3^o$(C3, CH_3OH)[e]	53.40
3.	PhCOEt		70	$+18.7^o$(C2.4, $CHCl_3$)[f]	41.00
4.	$PhCOPr^n$		65	$+ 7^o$(C3.4, Benzene)[g]	15.00
5.	α-naphCOMe		71	$+44.3^o$(C1.2, CH_3OH)[h]	56.00

a) For entry 1, was carried out at RT for 12h, with 10 mM of amine-borane and 10 mM of ketone in benzene. For entries 2-5, were carried out at room temperature for 6h, with 10 mM of amine-borane, 10 mM of ketone and 10 mM of BF_3:OEt_2 in benzene. The experiments were run at least twice in each case, α-naph= α-naphthyl.

b) Products were identified by analysis of spectral data (IR and ^1H & ^{13}C NMR) and comparison with the reported data.

c) Yields are isolated, chromatographed, and distilled products.

d) Optical rotations were measured with on Autopol-II automatic polarimeter (accuracy ± 0.01^o).

e) Based on the maximum $[\alpha]_D^{25}$ -45.5^o (C3, MeOH)[3]

f) Based on the maximum $[\alpha]_D^{20}$ -45.45^o (C5.15, $CHCl_3$)[12]

g) Based on the maximum $[\alpha]_D^{15}$ $+45.2^o$ (C3, benzene)[13]

h) Based on the maximum $[\alpha]_D^{25}$ -78.9^o (C3, MeOH)[12]

i) Enantiomeric excess.

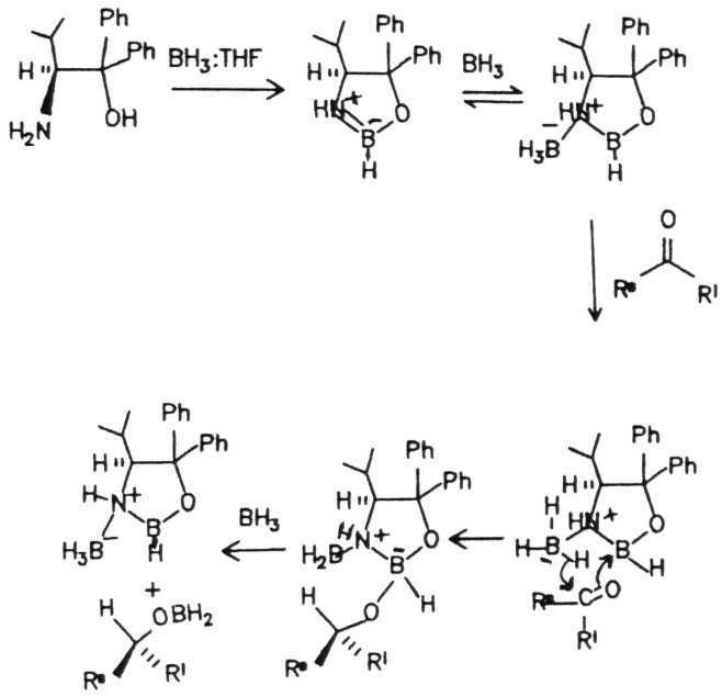
Unfortunately, our efforts to prepare this amine (4) were not successful. We decided to prepare the 2-phenylpyrrolidine system since it could be expected that in the resulting complex (3) the BH_3 (or BF_3) would be *cis* to the chiral discriminating 2-phenyl substituent.

This amine was prepared as described earlier in this section. It was found that this amine-borane reduces acetophenone to 1-phenyl ethanol with 16.2% e.e in the absence of $F_3B{:}OEt_2$. It was also found that it reduces acetophenone to 1-phenylethanol with 53% e.e in the presence of $F_3B{:}OEt_2$. Reduction of a few other ketones were also carried out using this amine-borane in the presence of $BF_3{:}OEt_2$. The results are summarized in Table 3. The configurations of the products are consistently R. The optical inductions decreases with increasing the chain length of the alkyl moiety. These features have been also observed with the other α-methylbenzyl amine derivatives.

Unfortunately, the asymmetric inductions obtained in these BF_3 catalyzed chiral amine-borane reductions are only modest. In recent years, several reports have appeared, describing the catalysis of chiral reduction by the Itsuno and Corey reagent systems[13-19] (Scheme 11).

In this laboratory, more convenient methods have been developed for the synthesis of such amino alcohols and oxazaborolidines, which can be utilized for asymmetric reductions to obtain alcohols with >90% ee.[20,21] Accordingly, we did not pursue the catalysis of amine-borane reductions of ketones by BF_3 further.

SCHEME 11



Hydroboration of Olefins using Chiral Amine–Boranes:

The hydroboration of alkenes and alkynes is one of the most useful reactions in synthetic organic chemistry (eq. 22 and 23).

$$R-CH=CH_2 + H_3B:LB \longrightarrow RCH_2CH_2-B< \quad (22)$$

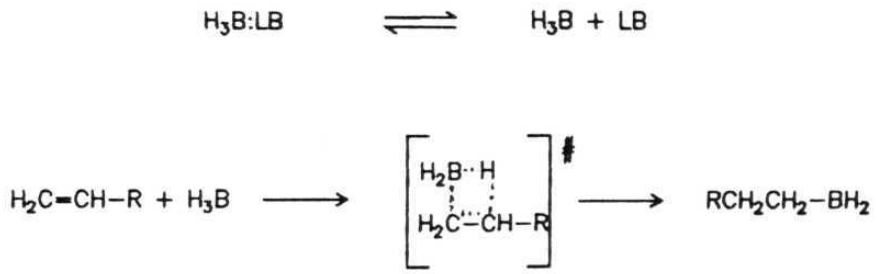
$$R-C\equiv CH + H_3B:LB \longrightarrow R-CH=CH-B< \quad (23)$$

Several alkyl, alkoxy and haloborane reagents have been developed and the subject has been extensively reviewed.[24] However, the mechanism of the this important reaction is not clearly

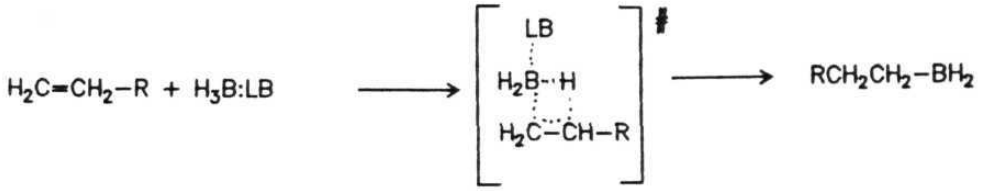
understood.[22-36] The question is the role of the Lewis base in the reaction of BH_3:Lewis base complex with olefin. From the data available in the literature, three mechanistic pictures can be visualized for the reaction (Scheme 12).

SCHEME 12

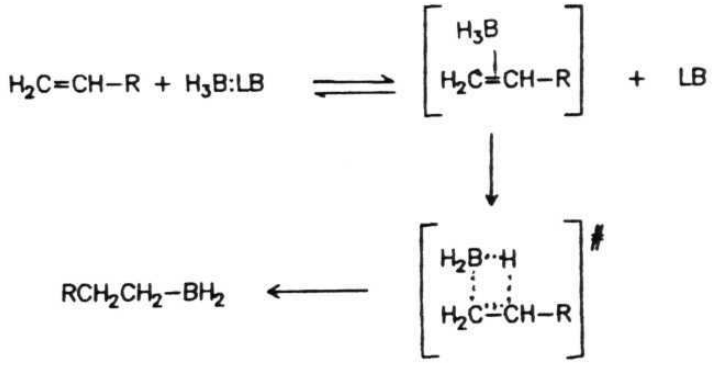
1. S_N1 like mechanism: Involving free 'BH_3' monomer formation in an equilibrium step.[25]



2. S_N2 like mechanism: Without any intermediate.[27,30]



3. Mechanism with Π-complex intermediate.[34,36]

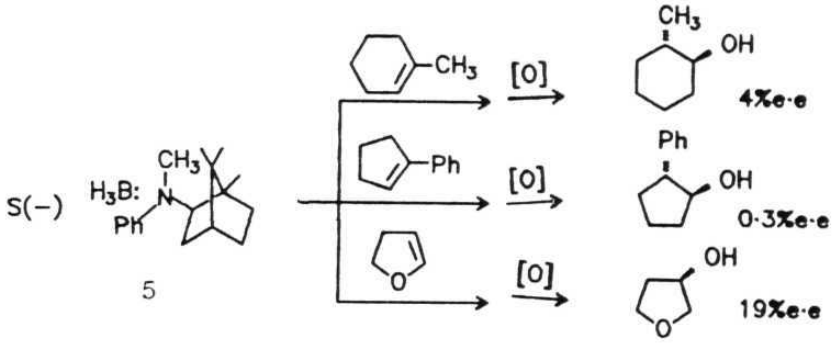


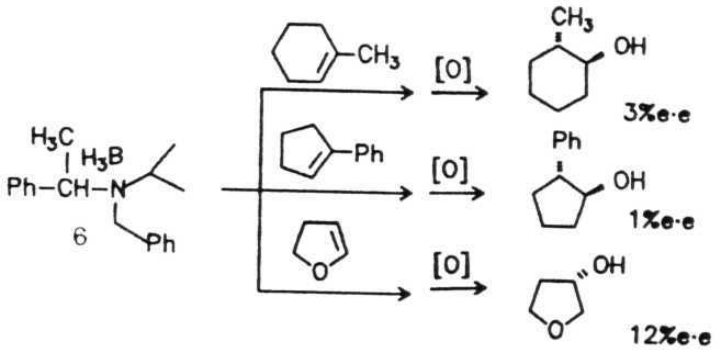
Kinetic evidence was presented for the S_N1 type mechanism.[25] Kinetic evidence was also presented for the S_N2 type mechanism.[27] It was also supported on theoretical grounds.[30] The mechanism involving the Π-complex intermediate was invoked for explaining the dehydroboration reaction in certain cases.[34] Also, the Π-complex intermediates have been invoked for explaining the results of asymmetric hydroboration of certain alkenes by Ipc_2BH[36a]

Although in all three mechanisms the Lewis base gets detached from the boron to some extent, it is only in the case of S_N2 type mechanism, it is still attached to some extent in the transition state of >B-H addition to the alkene. Accordingly, it was thought that the results of hydroboration of prochiral alkenes utilizing chiral-amine borane complexes would help in understanding the mechanism of this reaction.

Preliminary results obtained utilizing the readily accessible amines 5 and 6 indicated that hydroboration oxidation of certain alkenes leads to the formation of alcohols with 0.3-19% e.e (Scheme 13).[5]

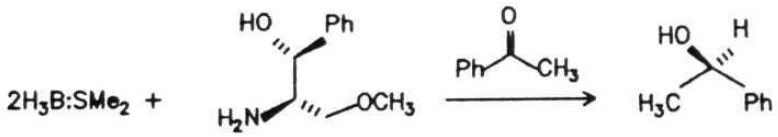
SCHEME 13



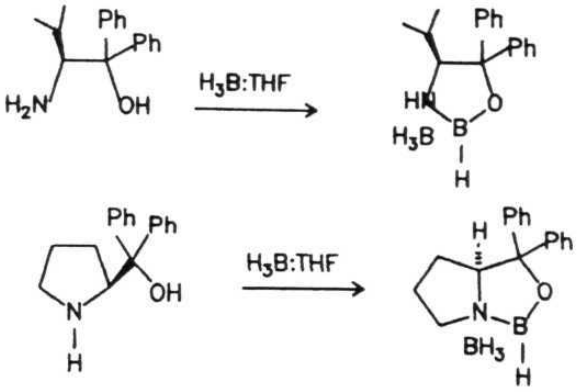


Initially, it was thought that the reaction gives better induction in the case of 2,3-dihydrofuran as it is a more reactive alkene and the results may indicate spectrum of mechanism for the reaction.

However, Mandal *et al* prepared a mixture of reagent using (1S,2S)-(+)-2-amino-3-methoxy-1-propanol and BH_3:SMe_2 and obtained 49% e.e in the reduction of acetophenone (eq. 24).[37]



More importantly, it was observed that the hydroboration of α-methylstyrene by this system leads to asymmetric inductions up to 37% e.e.[37] Mandal *et al* did not specify the structure of the hydroborating species. However, the species may resemble the intermediates obtained using other amino alcohols (*eg.*, Itsuno and Corey reagents).[13-19]

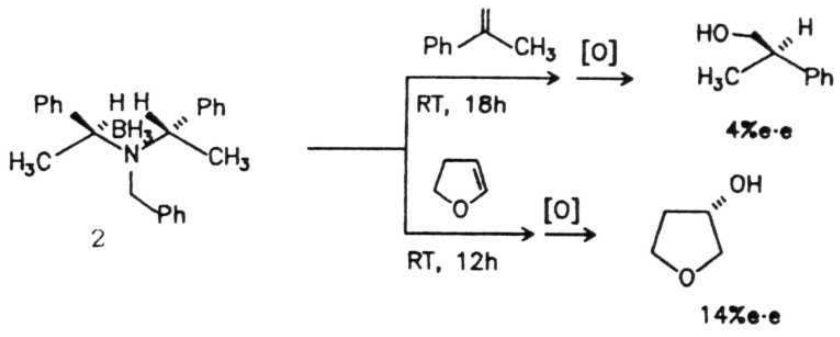


We have decided to examine this problem utilizing amine-boranes prepared from S,S -(-)-N-benzyl-α,α'-dimethyl dibenzylamine and (-)-N-α-methylbenzyl-2-phenylpyrrolidine, for the hydroboration of α-methylstyrene and 2,3-dihydrofuran in benzene.

Hydroboration-oxidation of prochiral olefins using borane-S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine:

It was observed that the hydroboration of α-methylstyrene with S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine-borane (2) in 18h at room temperature, followed by oxidation with $NaOH/H_2O_2$ gives 2-phenyl-1-propanol in 65% yield and 4.0% e.e. Hydroboration of 2,3-dihydrofuran was also carried out following the same procedure. Here, the corresponding alcohol is obtained in 72% yield and 13.8% e.e (Scheme 14).

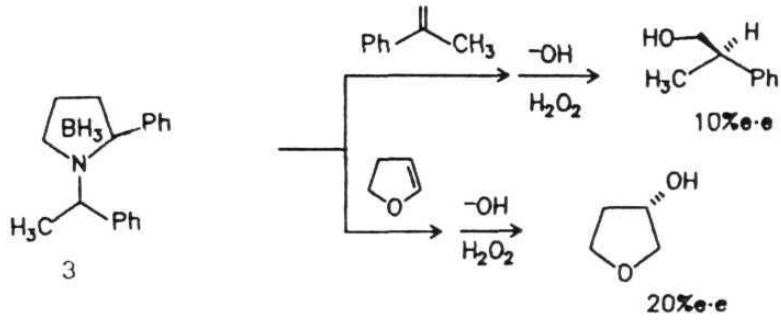
SCHEME 14



Hydroboration-oxidation of prochiral olefins using borane- (-)-N-α-methylbenzyl-2-phenylpyrrolidine:

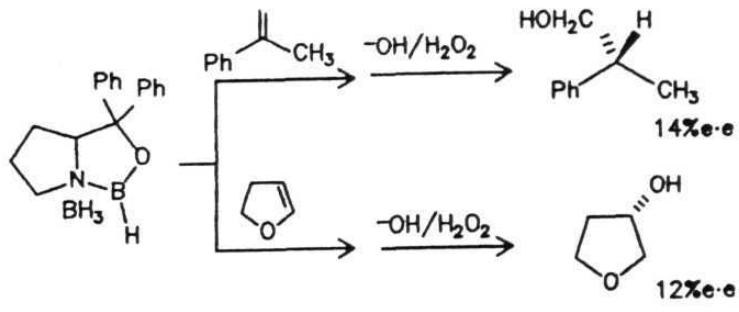
Hydroboration of α-methylstyrene with (-)-N-α-methylbenzyl-2-phenylpyrrolidine-borane (3) in 12h at room temperature, followed by oxidation with $NaOH/H_2O_2$ gives 2-phenyl-1-propanol in 72% yield and 9.8% e.e. Hydroboration of 2,3-dihydrofuran was also carried out following same procedure. Here, the corresponding alcohol is obtained in 75% yield and 19.6% e.e (Scheme 15).

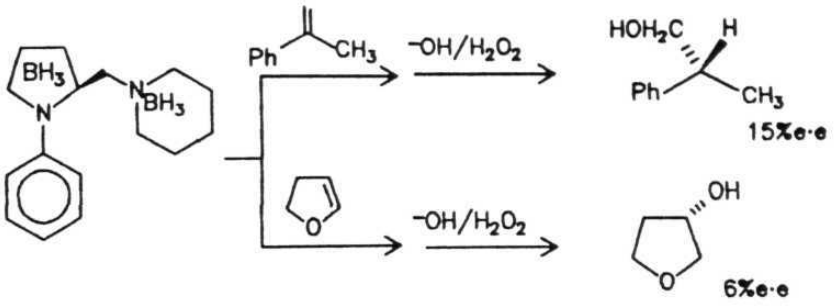
SCHEME 15



In this laboratory, it was found that hydroboration of α-methyl styrene and 2,3-dihydrofuran by the Corey's system and S(-)-N--phenyl-α-methylpyrrolydylpipirediene also give similar results (Scheme 16).[38]

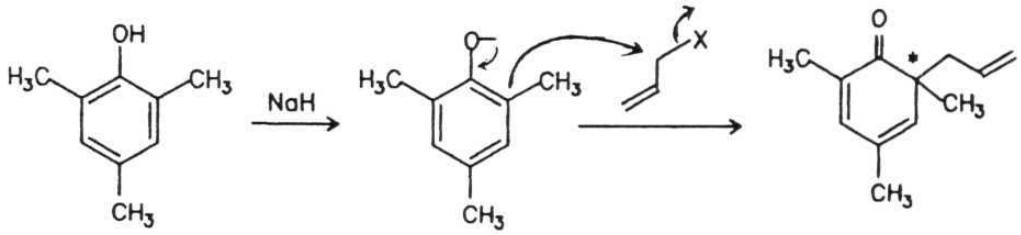
SCHEME 16





All these results indicate that the Lewis-base does play a role in the transition state of the hydroboration reaction. The asymmetric inductions are poor in all experiments. However, it is of interest to note that in a typical S_N2 displacement reaction, a chiral leaving group is known to give asymmetric induction up to 8.4% e.e. This indicates that the presence of a chiral leaving group in the transition state leads to asymmetric induction (Scheme 17).[39]

SCHEME 17



X = Camphor-10-sulphonate

Presumably, the inductions are not very high in such reactions as the chiral Lewis base would get detached to some extent in the transition state even in the case of the S_N2 like mechanism. Another complicating effect is the formation of R_2BH species resulting from the hydroboration by the RBH_2 species, the mechanism of which may take a different course. Also, simultaneous operations of more than one mechanism (Scheme 12) cannot be ruled out.

CONCLUSIONS

Chiral amines were synthesized from chiral α-methylbenzylamine. The amine-borane complexes were prepared and these complexes along with BF_3:OEt_2 were utilized for asymmetric reduction of prochiral ketones to obtain the corresponding alcohols in 5-56% e.e. These amines were also utilized in the hydroboration of prochiral olefins. After oxidation of the resulting organoboranes, the corresponding alcohols were obtained in 4.0-20% e.e. The results were considered in the context of mechanisms proposed by various workers for the hydroboration reaction. The results indicate that the Lewis base does play a role in the transition state of the hydroboration reaction.

EXPERIMENTAL SECTION

General Information:

Several of the general experimental details outlined in Chapter 1 and 2 are also applicable here. S-(-)-α-Methylbenzylamine $[\alpha]_D^{20}$ = -30^{o} (neat), benzylamine, acetophenone, propiophenone, butyrophenone, α-methylstyrene and 2,3-dihydrofuran supplied by Fluka, Switzerland were utilized. Optical rotations were measured on a Autopol II automatic polarimeter ($\pm 0.01^{o}$). The condition of the polarimeter was checked by measuring a standard solution of camphene, $[\alpha]_D = +17\pm1^{o}$ (C 4, ether) or α-methyl benzylamine, $[\alpha]_D^{20} = 30\pm2^{o}$ (C 10, EtOH) supplied by Fluka. The polarimeter was set to zero reading using the solvent used. Measurements for reacemic compounds were also run in all cases.

Synthesis of S-(-)-N,N-dibenzyl-α-methylbenzylamine:

A mixture of S-(-)-α-methylbenzylamine (1.21 g, 100 mM), KOH powder (32.0 g, 500 mM), benzyl bromide (25 ml, 250 mM) and NaI (3.0 g, 20 mM) was refluxed for 20h. The contents were brought to room temperature and extracted with ether (3 x 50 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 washed with ether (30 ml) and the amine was regenerated with 5N KOH (phenolphthalein indicator). The amine was extracted into ether (3 x 25 ml) dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was recrystallized from benzene-hexane mixture to yield white crystalline S-(-)-N,N-dibenzyl-α-methylbenzyl- amine.

Yield	: 80% (24 g)
M.P.	: $72^{o}C$
$[\alpha]_D^{25}$	: 100.5^{o} (C 2.54, $CHCl_3$)
IR (KBr) ν_{max}	: 1610, 1400, 1220, 1025 cm^{-1}
^{13}C NMR (25.0 MHz, $CDCl_3$)	: δ ppm 13.9, 53.7, 56.3, 127.0, 128.3, 128.4, 129.3, 140.4, 143.0.
Analysis	: C% ; H% ; N%
Calculated	: 87.7; 7.6; 4.7
Found	: 88.0; 7.7; 5.0

Synthesis of (S,S)-α,α'-dimethyldibenzylamine:

A procedure slightly modified from a reported procedure was followed.[40] A solution of acetophenone (0.2 mole, 24.0 g), S-(-)-α-methylbeznylamine (0.2 mole, 24.2 g) and a catalytic amount of p-toluenesulfonic acid (~ 40 mg) in 200 ml of benzene was refluxed under nitrogen atmosphere with continuous removal of water by means of a Dean-Stark trap during 36h. The reaction mixture was coold in an ice bath and subsequently washed with sodium bicarbonate solution, brine and dried over anhydrous $MgSO_4$. Solvent was evaporated, the corresponding imine was obtained in (40.3 g) 90% yield.

The imine (50 mM, 11.2 g) was dissolved in 40 ml ethyl acetate and 0.1 g of 5% Pd/C was added. This mixture was shaken in a parr apparatus during 16h under 3 atmosphere of hydrogen pressure. After removal of the catalyst by filtration, and evaporation of the solvent, the product was treated with 3N HCl (50 ml). The resulting white crystalline hydrochloride salt exhibited a rotation $[\alpha]_D^{25}$ = -84.1 (C3, EtOH) (yield 70% M.P. >300^{o}C).

The amine hydrochloride was washed with ether (30 ml) and the amine was regenerated with 5N KOH (phenolphthalein indicator). It was extracted into ether (3 x 25 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was purified by distillation (b.p. 150°C at 0.4 mm) to obtain S,S'-α,α'-dimethyldibenzylamine.

Yield : 65% (14.6 g)

$[\alpha]_D^{25}$: -157° (C 2.4, EtOH)

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

^1H (100 MHz, $CDCl_3$) :δ ppm 1.24 (d, 6H), 1.58 (br s, 1H), 3.47 (q, 2H), 7.17 (m, 10H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.8, 54.8, 126.3, 126.5, 128.1, 145.6.

The data are identical with the data of this product reported in the literature.[40]

Benzylation of (S,S)-α,α'-dimethyldibenzylamine:

A mixture of (S,S)-α,α'-dimethyldibenzylamine (22.5 g, 100 mM), NaI (3 g, 20 mM), powdered KOH (40 g, 625 mM) and benzyl bromide (21.3 g, 125 mM) was refluxed for 14h at 100°C. The mixture was cooled and extracted with ether (3 x 50 ml) and the combined ether extracts were treated with 5N HCl (3 x 10 ml). The amine hydrochloride was washed with ether (30 ml) and the amine was regenerated with 5N KOH (phenolphthalein indicator). The amine was extracted into ether (3 x 30 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The amine thus obtained was purified by column chromatography on a silica gel column (hexane), and distilled under reduced pressure to

isolate S,S-(-)-N-benzyl-α-α'-dimethyldibenzylamine.

Yield : 80% (25.2 g)

$[\alpha]_D^{25}$: -63.7^{o} (C 1.0, $CHCl_3$)

IR (neat) ν_{max} : 3050, 2950, 1600, 1375, 680 cm^{-1}

^1H (100 MHz, $CDCl_3$) :δ ppm 1.36-1.40 (d, 6H), 3.44 (s, 2H), 3.88-4.12 (m, 2H), 7.12-7.48 (m, 15H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 18.7, 49.9, 57.6, 126.3, 126.7, 127.9, 143.1, 144.5. (Spectrum Number 19)

Synthesis of N-benzyl-2,5-diphenylpyrrolidine:

a) Hydrogenation of *trans,trans*-1,4-Diphenyl-1,3-butadiene:

The *trans,trans*-1,4-diphenyl-1,3-butadiene (10.3 g, 50 mM) was dissolved in ethyl acetate (40 ml) and 5% Pd/C (50 mg) was added. This mixture was shaken in a parr appratus during 1h under 3 atmosphere of hydrogen pressure. After removal of the catalyst by filtration, the filtrate over was dried anhydrous $MgSO_4$. On evaporation of the solvent and purification by chromatography on silica gel column (hexane), 1,4-diphenylbutane was isolated.

Yield : 90% (9.6 g)

M.P. : $50^{o}C$, Lit.[41] $52^{o}C$

IR (KBr) ν_{max} : 3050, 2950, 1600 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 31.1, 35.8, 125.8, 128.4, 128.5, 142.7.

This compound has been reported in the literature.[41]

b) Bromination of 1,4-diphenylbutane using N-bromosuccinamide

In a 250 ml round-bottomed flask, N-bromosuccinamide (10 g, 100 mM) and 1,4-diphenylbutane (10.7 g, 50 mM) in carbon tetrachloride (100 ml) were placed and benzoyl peroxide (50 mg) was added. The reaction mixture was refluxed for 12h. The succinimide was filtered off and washed with dry carbon tetrachloride. After evaporation of solvent under reduced pressure and the residue was recrystallized from hexane, to obtain 1,4-dibromo-1,4-diphenylbutane.

Yield : 80% (15 g)

M.P. : 124°C, Lit.[42] 124.5 °

IR (KBr) ν_{max} : 3050, 2950, 1600, 780 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 38.6, 54.3, 127.3, 128.7, 128.9, 147.7.

Spectral data of this product showed 1:1 correspondence to the data reported in the literature.[42]

c) Reaction of 1,4-dibromo-1,4-diphenylbutane with benzylamine:

In a 250 ml round-bottomed flask, 1,4-dibromo-1,4-diphenylbutane (18.4 g, 50 mM), benzylamine (5.35 g, 50 mM), and dry benzene (100 ml) were placed. Anhydrous potassium carbonate (27.6 g, 200 mM) was added. The mixture was stirred for 12h at room temperature. The reaction mixture was quenched with water and extracted with ether. The combined organic extract was treated with 5N HCl (3 x 10 ml). The amine hydrochloride was washed with ether (30 ml) and the amine was regenerated using 5N KOH (phenolphthalein indicator). It was

extracted into ether (3 x 50 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The amine thus obtained was purified by column chromatography on a silica gel column (hexane), to obtain N-benzyl-2,5-diphenylpyrrolidine.

Yield : 70% (10.9 g)

M.P. : $94^{o}C$

IR (KBr) ν_{max} : 1600, 1350, 690 cm^{-1}

^{1}H (100 MHz, $CDCl_3$) :δ ppm 1.52-2.08 (m, 4H), 3.40-3.52 (s, 2H), 3.76-3.8 (t, 2H), 6.76-7.52 (m, 15H). (Spectrum Number 21)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 34.3, 52.2, 65.6, 126.7, 127.0, 127.7, 128.5, 130.4, 135.7, 144.7. (Spectrum Number 20)

The ^{1}H-NMR data showed 1:1 correspondence to the data reported for the meso-N-benzyl-2,5-diphenylpyrrolidine.[8]

Synthesis of N-α-methylbenzyl-2-phenylpyrrolidine:

a) Preparation of β-benzoylpropionic acid:

Dry benzene (100 ml) and succinic anhydride (17 g, 170 mM) were placed in a 1-liter three necked flask equipped with a sealed stirrer unit and two efficient reflux condensers, the tops of which are connected through a Y-junction to a gas absorption device. The mixture was stirred and powdered anhydrous aluminium chloride (50 g, 375 mM) was added all at once. The reaction starts immediately, hydrogen chloride is evolved and the mixture becomes hot. The reaction mixture was refluxed for 2h, with continued stirring. It was allowed to cool, and the flask was immersed in a bath of cold water

and water (50 ml) was slowly added from a separatory funnel inserted into the top of one of the condensers. HCl (13N, 25 ml) was added and the organic layer was separated. It was washed with water (25 ml), brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, β-benzylpropanoic acid was isolated.

Yield : 83% (50 g)

M.P. : 113°C, Lit.[43] m.p. 115 C°

IR (KBr) ν_{max} : 1680, 1600, 760, 680 cm^{-1}

^1H (100 MHz, $CDCl_3$) :δ ppm 2.72-2.79 (t, 2H), 3.22-3.29 (t, 2H), 7.40-7.48 (m, 3H), 7.9-7.95 (m, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 28.0, 33.1, 128.1, 128.7, 133.4, 136.5, 179.1, 198.1.

This compound has been reported in the literature.[43]

b) Reduction of β-benzoylpropanoic acid using $NaBH_4$ and I_2:

A solution of iodine (12.7 g, 50 mM) in THF (50 ml) was added slowly to suspension of $NaBH_4$ (4.56 g, 120 mM) in THF (100 ml) at 0°C under nitrogen atmosphere. β-Benzoylpropanoic acid (8.9 g, 50 mM) in THF (50 ml) was added slowly at 0°C under nitrogen atmosphere. The contents were further stirred for 3h at 25°C. 3N HCl (10 ml) was added carefully and the reaction mixture was extracted with ether. The combined ether extract was washed with 3N NaOH (3 x 20 ml), water, brine and dried over $MgSO_4$. After evaporation of solvent and purification by column chromatography on silica gel column (hexane:ethyl acetate/75:25), 1-phenyl-1,4-butane diol was isolated.

Yield : 70% (5.81 g)

IR (neat) ν_{max} : 1300, 2950, 3050, 1600, 1060, 700 cm^{-1}

^{1}H (100 MHz, $CDCl_3$) : δ ppm 1.66-2.08 (m, 6H), 3.66-3.72 (t, 2H), 4.71-4.77 (t, 1H), 7.26-7.37 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 28.8, 36.0, 62.3, 74.0, 125.9, 127.4, 128.4, 144.7.

This compound has been reported in the literature.[44]

c) Bromination of 1-phenyl-1,4-butanediol:

In a 250 ml round-bottomed flask 1-phenyl-1,4-butane diol (16.6 g, 100 mM), hydrobormic acid 48% (42 g, 28.4 ml) and con.sul- phuric acid (12.0 g, 6.6 ml) were placed. The mixture was stirred for 12h at room temperature. The contents were extracted with hexane, aqueous layer was neutralized with sodium hydroxide and extracted with hexane. The combined hexane layer was washed with water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel (hexane), 1-phenyl-1,4-dibromo butane was isolated.

Yield : 50% (14.6 g)

IR (neat) ν_{max} : 3025, 2950, 1600, 740, 680 cm^{-1}

^{1}H (100 MHz, $CDCl_3$) : δ ppm 2.33-2.4 (m, 4H), 3.39-3.46 (t, 2H), 4.92-5.0 (t, 1H), 7.25-7.40 (t, 2H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 31.2, 32.5, 38.4, 54.2, 127.3, 128.7, 128.9, 141.8.

This compound has been reported in the literature.[45]

d) Reaction of 1-phenyl-1,4-dibromobutane with S-(-)-α-methyl benzylamine:

In a 250 ml round bottomed flask, 1-phenyl-1,4-dibromobutane (14.6 g, 50 mM), α-methylbenzylamine (6.0 g, 50 mM), dry DMF (20 ml) and sodium hydride (1.2 g, 20 mM) were placed. The mixture was stirred for 12h at room temperature. The reaction mixture was quenched with ethyl acetate and extracted with ether (3 x 30 ml). The combined organic extract was washed with 5N HCl (2 x 20 ml) to precipitate the amine as hydrochloride salt which was found to be insoluble in water. The amine hydrochloride was washed with ether (30 ml) and the amine was regenerated with 5N KOH (phenolphthalein indicator). The amine was extracted into ether (3 x 25 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated, to isolate the mixture of diastereoisomers (10 g, 80%). The isomers were separated by column chromatography (neutral alumina:hexane).

Fraction 1:

Yield	:40% (5.12 g)
$[\alpha]_D^{25}$	: $-120.^o$ (C 1.5, $CHCl_3$)
IR (neat) ν_{max}	: 3050, 2950, 1600, 1350, 690 cm^{-1}
^1H (100 MHz, $CDCl_3$)	: δ ppm 1.12-1.32 (d, 3H), 1.40-2.40 (m, 6H), 2.88-3.80 (m, 2H),7.00-7.48 (m, 10H)
^{13}C NMR (25.0 MHz, $CDCl_3$)	: δ ppm 21.8, 22.6, 35.8, 48.8, 59.7, 65.2, 126.6, 126.7, 127.2, 127.9, 128.1, 128.4, 141.2, 146.4. (Spectrum Number 22)
Mass (m/e)	: 236
Analysis	: C% ; H% ; N%
Calculated	: 86.01 8.42 5.57
Found	: 86.04 8.61 5.54

Fraction 2:

Yield : 38% (4.86 g)

$[\alpha]_D^{25}$: $+37^o$ (C 0.5, $CHCl_3$)

IR (neat) ν_{max} : 3050, 2950, 1600, 1350, 690 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 1.12–1.32 (d, 3H), 1.48–2.92 (m, 6H), 3.60–3.88 (m, 2H), 7.00–7.40 (m, 10H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 12.1, 22.9, 35.7, 46.6, 56.2, 65.3, 126.4, 126.7, 127.6, 127.9, 128.3, 144.5, 145.4. Spectrum Number 23

Mass (m/e) : 236 Spectrum Number 24

Analysis : C% ; H% ; N%

Calculated : 86.01 8.42 5.57

Found : 86.05 8.50 5.55

Preparation of methyl β-benzoylpropionate:

In a 250 ml round bottomed flask β-benzoyl propinoic acid (8.9 g, 50 mM) and methanol (50 ml) were placed. Thionyl chloride (5.9 g, 50 mM) was added slowly at 0^oC. The reaction mixture was brought to room temperature and stirred for 12h. It was flushed with dry nitrogen to remove traces of thionyl chloride. Methanol was evaporated under reduced pressure and the residue was purified by chromatography on silica gel column (hexane:ethyl acetate/90:10), to obtain methyl β-benzoylpropionate.

Yield : 85% (16.3 g)

IR (neat) ν_{max} : 3050, 2950, 1720, 1680, 1600 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 2.73-2.79 (t, 2H), 3.28-3.35 (t, 2H), 3.70 (s, 3H), 7.41-7.57 (m, 3H), 7.9-8.0 (m, 2H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 27.0, 33.0, 51.4, 127.8, 128.5, 133.0, 136.4, 173.2, 197.9.

This compound has been reported in the literature.[46]

Preparation N-α-methylbenzyl-2-phenylpyrrolidine:

In a 250 ml R.B. flask, methyl β-benzyl propionate (9.6 g, 50 mM), S-(-)-α-methylbenzylamine (6.0 g, 50 mM) and 100 ml of benzene were placed. The mixture was refluxed under nitrogen atmosphere with continuous removal of water by means of a Dean-Stark trap during 12h. The reaction mixture was cooled and the solvent was evaporated. The residue was purified by distillation (134°C/4 mm), which was further purified by column chromatography on basic alumina (hexane:ethyl acetate/95:5), to obtain the imine of α-methylbenzylamine (9.58 g, 65%).

A solution of iodine (12.7 g, 50 mM) in THF (50 ml) was added slowly to a suspension of $NaBH_4$ (4.56 g, 120 mM) in THF (100 ml) at 0°C under nitrogen atmosphere. The imine mixture (14.7 g, 50 mM) was added slowly at 0°C under nitrogen atmosphere. The contents were stirred for 2h at 25°C, and refluxed for 6h. The reaction mixture was cooled to 0°C, quenched with water (10 ml) and extracted with ether (3 x 50 ml). The organic extract was stirred with 6N HCl (30 ml) for 2h at 25°C. Aqueous layer was separated, organic layer was treated with 3N HCl (2 x 20 ml). The combined aqueous layer was neutralized with 5N KOH (phenolphthalein indicator). The amine was extracted into

ether (3 x 30 ml), dried over anhydrous $MgSO_4$ and solvent was evaporated. A mixture of diastereomers (10.6 g, 85%) was isolated. The isomers were separated by column chromatography (neutral alumnia, hexane).

Fraction 1:

$[\alpha]_D^{25}$ = -118.57°C (C 1.2, $CHCl_3$), Yield: 45%

Spectral data of this product showed 1:1 correspondence to the data of the product obtained in the earlier experiment.

Fraction 2:

$[\alpha]_D^{25}$ = +37.8°C (C 0.475 $CHCl_3$), Yield: 40%

Spectral data of this product showed 1:1 correspondence to the data of the product obtained in the earlier experiment.

Asymmetric reduction of acetophenone with S-(-)-N,N'dibenzyl-α-methylbenzylamine-borane in the presence of BF_3:OEt_2:

S-(-)-N,N-dibenzyl-α-methylbenzylamine-borane (10 mM) complex was prepared *in situ* by bubbling diborane, generated by dropwise addition of I_2 (2.54 g, 10 mM) in diglyme (15 ml) to $NaBH_4$ (0.8 g, 20 mM) in diglyme (5 ml) at 25°C, into a solution of S-(-)-N,N-dibenzyl-α-methylbenzylamine (3.0 g, 10 mM) in dry benzene (50 ml) for 1h. Acetophenone (1.2 g, 10 mM) and BF_3:OEt_2 (1.41 g, 10 mM) were added to this reaction mixture at 10°C, stirred for 6h at room temperature. The reaction was quenched with water (5 ml), and organic layer was separated. The combined organic extract was washed with 3N HCl (2 x 20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation

of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 1-phenylethanol was isolated which was further purified by distillation under reduced pressure and the optical rotation was measured.

Yield : 80% (0.97 g)

B.P. : 95°C (10 mm), Lit.[3] 203°C (760 mm)

$[\alpha]_D^{25}$ = +11° (C 2, CH_3OH), Lit.[3] $[\alpha]_D^{15}$ = -45.5° (C3, CH_3OH)

IR (neat) ν_{max} : 3350, 3050, 1600 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 1.40 (d, 3H), 2.9 (b s, 1H), 4.80 (q, 1H, 7.3 (m 5H).

Asymmetric reductions of propiophenone (10 mM), butyrophenone (10 mM) and methyl-1-naphthylketone (10 mM) were also carried out following the procedure outlined above.

Yield : 78% (1.06 g)

B.P. : 87°C (10 mm Hg), Lit.[12] 214°C (760 mm)

$[\alpha]_D^{25}$ = +10° (C 1.5, $CHCl_3$), Lit.[12] $[\alpha]_D^{20}$ = -45.45° (C5.15, $CHCl)_3$

IR (neat) ν_{max} : 3300, 3050, 2950, 1600 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 0.90–0.99 (t, 3H), 1.70–1.80 (m, 3H), 4.58–4.67 (t, 1H), 7.26–7.37 (m 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 10.2, 31.9, 75.8, 126.4, 127.5, 128.5, 145.1.

Yield : 80% (1.2 g)

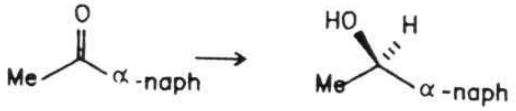
B.P. : 100°C (6 mm Hg), Lit.[13] 232 C°(760 mm)

$[\alpha]_D^{25}$ = +2.5° (C 4, benzene), Lit.[13] $[\alpha]_D^{25}$ = +45.2° (C3, benzene)

IR (neat) ν_{max} : 3300, 3050, 2950, 1600 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 0.86–0.98 (t, 3H), 1.20–2.96 (m, 5h), 4.65–4.75 (t, 1H), 7.28–7.36 (m, 5H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.6, 19.6, 40.9, 73.8, 125.8, 126.9, 128.0, 145.0.



Yield : 75% (1.29 g)

M.P. : 46°C, Lit.[47] 47°C

$[\alpha]_D^{25}$ = +31.4° (C 1.75, CH_3OH), Lit.[12] $[\alpha]_D^{25}$ = -78.9° (C3, CH_3OH)

IR (neat) ν_{max} : 3300, 3050, 2950, 1600 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 1.60–1.70 (d, 3H), 1.95 (s, 1H), 5.65–5.73 (q, 1H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.1, 66.4, 121.9, 123.0, 125.2, 125.4, 125.7, 128.6, 130.1, 133.6, 141.4.

Asymmetric reduction of acetophenone with S,S -(-)-N-benzyl-α,α'-dimethyldibenylamine-borane without BF_3:OEt_2:

S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine-borane (10 mM) complex was prepared *in situ* by bubbling diborane generated by

dropwise addition of I_2 (2.54 g, 10 mM) in diglyme (15 ml) to $NaBH_4$ (0.8 g, 20 mM) in diglyme (5 ml) at 25°C, into a solution of S,S-(-)-N-benzyl-α,α'dimethyldibenzylamine (3.15 g, 10 mM) in dry benzene (50 ml) for 1h. Acetophenone (1.2 g, 10 mM) was added to this reaction mixture at 10°C, stirred for 12h at room temperature. The reaction was quenched with water (5 ml), and organic layer was separated. The combined organic extract was washed with 3N HCl (2 x 20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 1-phenylethanol was isolated, which was further purified by distillation under reduced pressure and the optical rotation was measured.

Yield : 65% (0.77 g)

B.P. : 80°C (6 mm Hg), Lit.[3] 203°C (760 mm)

$[\alpha]_D^{25}$ = +7° (C 2, CH_3OH), Lit.[3] $[\alpha]_D^{25}$ = -45.5° (C3, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in the earlier experiment.

Asymmetric reduction of acetophenone with S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine-borane in the presence of BF_3:OEt_2:

S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine:borane (10 mM) complex was prepared *in situ* as above. Acetophenone (1.2 g, 10 mM) and BF_3:OEt_2 (1.41 g, 10 mM) were added at 10°C and the mixture was stirred for 6h at room temperature. The reaction was quenched with water (5 ml) and the organic layer was separated. The combined organic extract was washed with 5N HCl (2 x 20 ml), water, brine and

dried over anhydrous $MgSO_4$. Upon evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate.95:5), 1-phenylethanol was isolated. It was further purified by distillation under reduced pressure for measurement of optical rotation.

Yield : 82% (1.0 g)

B.P. : 80^{o}C (6 mm Hg), Lit.[3] 203^{o}C (760 mm)

$[\alpha]_D^{25} = +22^{o}$ (C 1.5, CH_3OH), Lit.[3] $[\alpha]_D^{25} = -45.5^{o}$ (C3, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

The reactions using propiophenone (10 mM), butyrophenone (10 mm) and methyl-1-naphthylketone (10 mM) were also carried out following the procedure outlined above.

Yield : 78% (1.06 g)

B.P. : 87^{o}C (10 mm Hg), Lit.[12] 213^{o}C (760 mm)

$[\alpha]_D^{25} = +16.8^{o}$ (C 2.25, $CHCl_3$), Lit.[12] $[\alpha]_D^{25} = -45.5^{o}$ (C 5.15, $CHCl_3$)

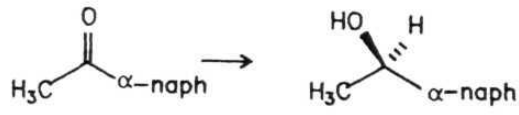
The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

Yield : 75% (1.12 g)

B.P. : 100°C (6 mm Hg), Lit.[13] 232°C (760 mm)

$[\alpha]_D^{25}$ = +4.6° (C 3.25, benzene), Lit.[13] $[\alpha]_D^{25}$ = +45.2° (C3, benzene)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.



Yield : 70% (1.20 g)

M.P. : 46°C, Lit.[47] 47°C

$[\alpha]_D^{25}$ = +41° (C 1, CH_3OH), Lit.[12] $[\alpha]_D^{25}$ = -78.9° (C3 CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

Reduction of acetophenone with (-)-N-α-methylbenzyl-2-phenyl pyrrolidine without BF_3:OEt_2:

(-)-N-α-methylbenzyl-2-phenylpyrrolidine:borane (10 mM) complex was prepared *in situ* by bubbling diborane, generated by dropwise addition of I_2 (2.54 g, 10 mM) in diglyme (15 ml) to $NaBH_4$ (0.8 g, 20 mM) in diglyme (5 ml) at 25°C, into a solution of (-)-N-α-methylbenzyl-2-phenylpyrrolidine (2.51 g, 10 mM) in dry benzene (50 ml) for 1h. Acetophenone (1.2 g, 10 mM) was added at 10°C and the mixture was stirred for 12h at room temperature. The reaction was quenched with water (5 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2x30 ml). The combined

organic extract was washed with 3N HCl (2 x 20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate.95:5), 1-phenylethanol was isolated, which was further purified by distillation under reduced pressure for measurement of optical rotation.

Yield : 72% (0.875 g)

B.P. : 80^oC (6 mm Hg), Lit.[3] 203^oC (760 mm)

$[\alpha]_D^{25} = +7.6^o$ (C 2, CH_3OH), Lit.[3] $[\alpha]_D^{25} = -45.5^o$ (C5.15, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

Reduction of acetophenone with (-)-N-α-methylbenzyl-2-phenyl pyrrolidine in the presence of BF_3:OEt_2:

(-)-N-α-methylbenzyl-2-phenylpyrrolidine-borane complex (10 mM) was prepared *in situ* as above. Acetophenone (1.2 g, 10 mM) and BF_3OEt_2 (1.41 g, 10 mM) were added to this reaction mixture at 10^oC, stirred for 6h at room temperature. The reaction was quenched with water (5 ml) and organic layer was separated. The aqueous layer was extracted with ether (2x20 ml). The combined organic extract was washed with 3N HCl (32 x 20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane, ethyl acetate/95:5), 1-phenyl ethanol was isolated, which was further purified by distillation under reduced pressure for optical rotation measurement.

Yield : 73% (0.88 g)

B.P. : 80°C (6 mm Hg), Lit.[3] 213°C (760 mm)

$[\alpha]_D^{25}$ = +24.3° (C 3, CH_3OH), Lit.[3] $[\alpha]_D^{25}$ = -45.5° (C3, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

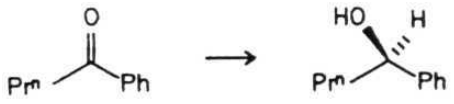
The reactions with propiophenone (10 mM), butyrophenone (10 mM) and methyl-1-naphthylketone (10 mM) were also carried out following the procedure outlined above.

Yield : 70% (0.952 g)

B.P. : 87°C (10 mm Hg), Lit.[12] 213°C (760 mm)

$[\alpha]_D^{25}$ = +18.7° (C 2.4, $CHCl_3$), Lit.[12] $[\alpha]_D^{25}$ = +45.45° (C5.15, $CHCl_3$)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

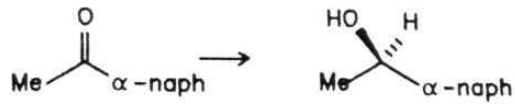


Yield : 65% (0.98 g)

B.P. : 100°C (6 mm Hg), Lit.[13] 232°C (760 mm)

$[\alpha]_D^{25}$ = +7° (C 3.4, benzene), Lit.[13] $[\alpha]_D^{25}$ = +45.2° (C3, benzene)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.



Yield : 71% (1.22 g)

M.P. : 46°C, Lit.[47] 47°C

$[\alpha]_D^{25}$ = +44.3° (C 1.2, CH_3OH), Lit.[12] $[\alpha]_D^{25}$ = -78.9° (C3, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in earlier experiments.

Hydroboration of α-methylstyrene with borane-S,S-(-)-N-benzyl-α,α'-dimethyldibenzylamine:

Borane-S,S-(-)-N-benzyl-α,α'-dimethyldibenzylamine (10 mM) was prepared *in situ* by bubbling diborane, generated by dropwise addition of iodine (2.54 g, 10 mM) in diglyme (10 ml) to $NaBH_4$ (0.8 g, 20 mM) in diglyme (5 ml) at 25°C, into a solution of S,S-(-)-N-benzyl-α,α'-dimethyldibenzylamine (3.07 g, 10 mM) in dry benzene (60 ml) for 1h. The reaction mixture was flushed with dry nitrogen to remove traces of diborane gas present above the benzene solution. The α-methylstyrene (1.18 g, 10 mM) was injected and the mixture was stirred at room temperature for 18h. The reaction mixture was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml) and H_2O_2 (16%, 20 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N

HCl (2 x 20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 2-phenyl-1-propanol was isolated which was further purified by distillation under reduced pressure for optical rotation measurement.

Yield : 65% (15.3 g)

$[\alpha]_D^{25}$ = +0.58° (C 3, CH_3OH), Lit.[48] $[\alpha]_D^{25}$ = -14.2° (C3.76 CH_3OH)

IR (neat) ν_{max} : 3350, 3050, 2950, 1600, 1050 cm^{-1}

^1H (100 MHz, $CDCl_3$) : δ ppm 1.12-1.32 (d, 3H), 1.88 (s, 1H), 2.76-3.12 (q, 1H), 3.52-3.72 (d, 2H), 7.20-7.48 (m, 5H)

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 143.9, 128.3, 127.3, 126.3, 68.1, 42.1, 17.4.

Hydroboration of 2,3-dihydrofuran with borane-S,S -(-)-N-benzyl-α,α' -dimethyldibenzylamine:

Borane-S,S -(-)-N-benzyl-α,α'-dimethyldibenzylamine (10 mM) was prepared *in situ* as above. 2,3-Dihydrofuran (0.7 g, 10 mM) was added at room temperature stirred for 12h. The reaction mixture was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml) and H_2O_2 (16% 20 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (2 x 20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 3-hydroxy tetrahydrofuran was isolated which was further purified by distillation under reduced pressure for optical rotation measurement.

Yield : 72% (6.3 g)

B.P. : 67°C (10 mm Hg), Lit.[49] 80°C (15 mm)

$[\alpha]_D^{25}$ = +2.4° (C1.88, CH_3OH), Lit.[49] $[\alpha]_D^{25}$ = −17.3° (C2.4, CH_3OH)

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

^1H (100 MHz, $CDCl_3$) : δ ppm 1.92 (m, 2H), 3.75 (d, 2H), 4.00 (m, 2H), 4.3 (m, 1H).

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

Hydroboration of α-methylstyrene with borane (-)-N-α-methylbenzyl-2-phenylpyrrolidine complex:

(-)-N-α-methylbenzyl-2-phenylpyrrolidine:borane complex (20 mM) was prepared *in situ* as described above. α-Methylstyrene (1.18 g, 10 mM) was added at room temperature, stirred for 12h. The reaction mixture was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml) and H_2O_2 (16%, 20 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate(95:5), 2-phenyl-1-propanol was isolated which was further purified by distillation under reduced pressure for optical rotation measurement.

Yield : 72% (16.9 g)

$[\alpha]_D^{25}$ = +1.4° (C2.3, CH_3OH), Lit.[48] $[\alpha]_D^{25}$ = −14.2° (C3.76, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in the earlier experiment.

Hydroboration of 2,3-dihydrofuran with borane (-)-N-α-methylbenzyl-2-phenylpyrrolidine complex:

(-)-N-α-methylbenzyl-2-phenylpyrrolidine:borane complex (20 mM) was prepared *in situ* as described above. 2,3-Dihydrofuran (0.7 g, 10 mM) was added at room temperature, stirred for 12h. The reaction mixture was quenched with water (5 ml) and oxidized using NaOH (3N, 10 ml) and H_2O_2 (16%, 20 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate(95:5), 3-hydroxy trtrahydrofuran was isolated which was further purified by distillation under reduced pressure for optical rotation measurement.

Yield : 75% (6.6 g)

$[\alpha]_D^{25} = -17.3^o$ (C2.4, CH_3OH), Lit.[49] $[\alpha]_D^{25} = +3.4^o$ (C2.0, CH_3OH)

The spectral data of this compound showed 1:1 correspondence to the data of the product obtained in the earlier experiment.

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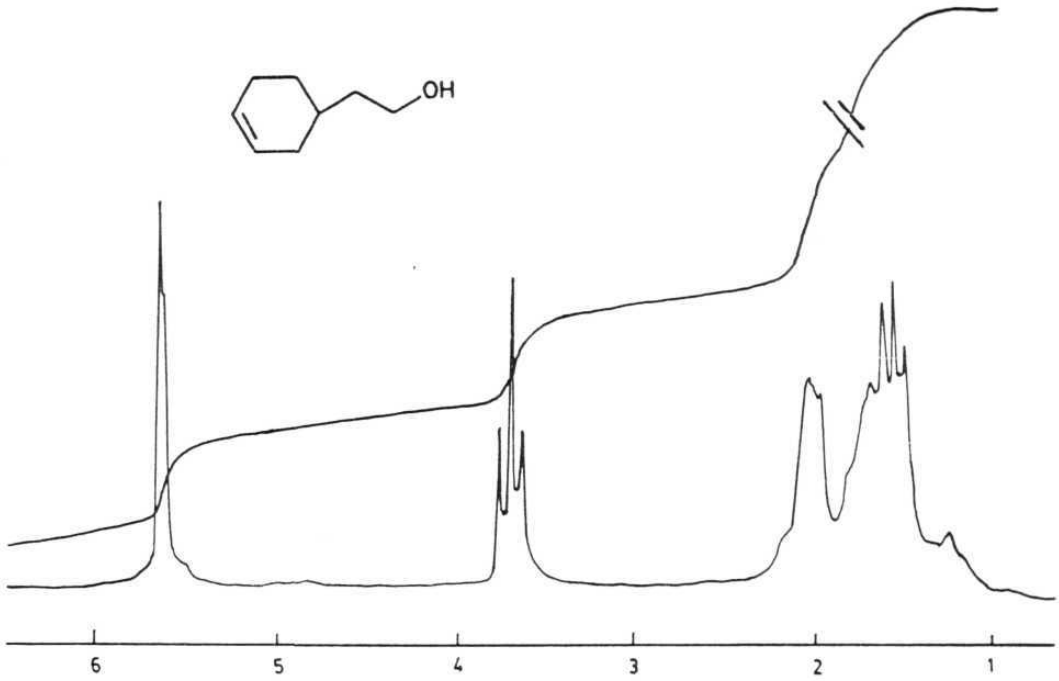
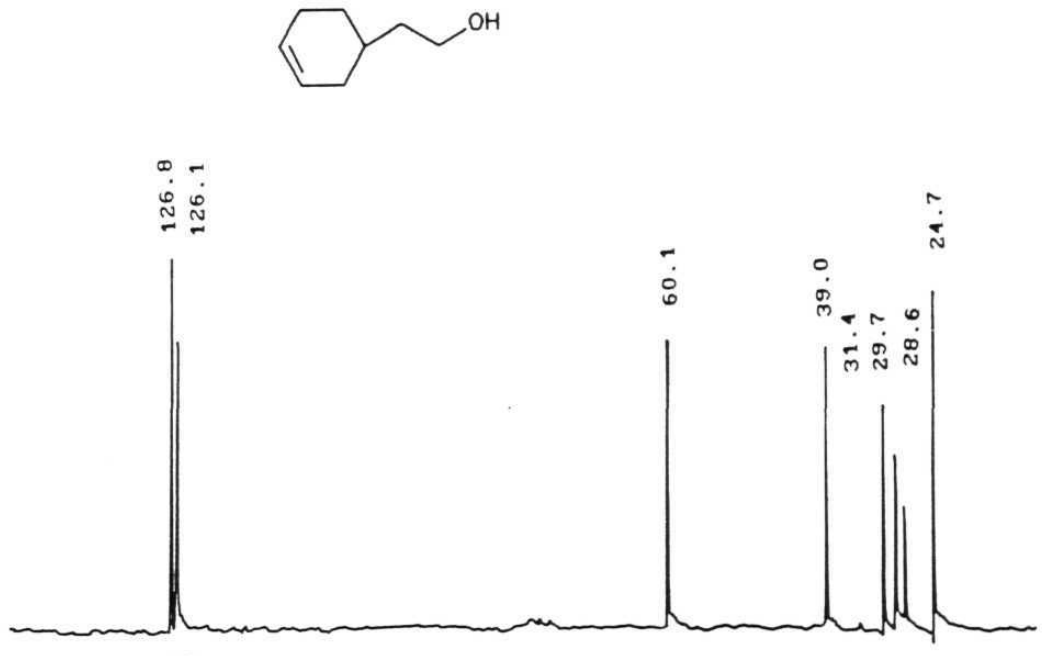
Spectrum Number 1



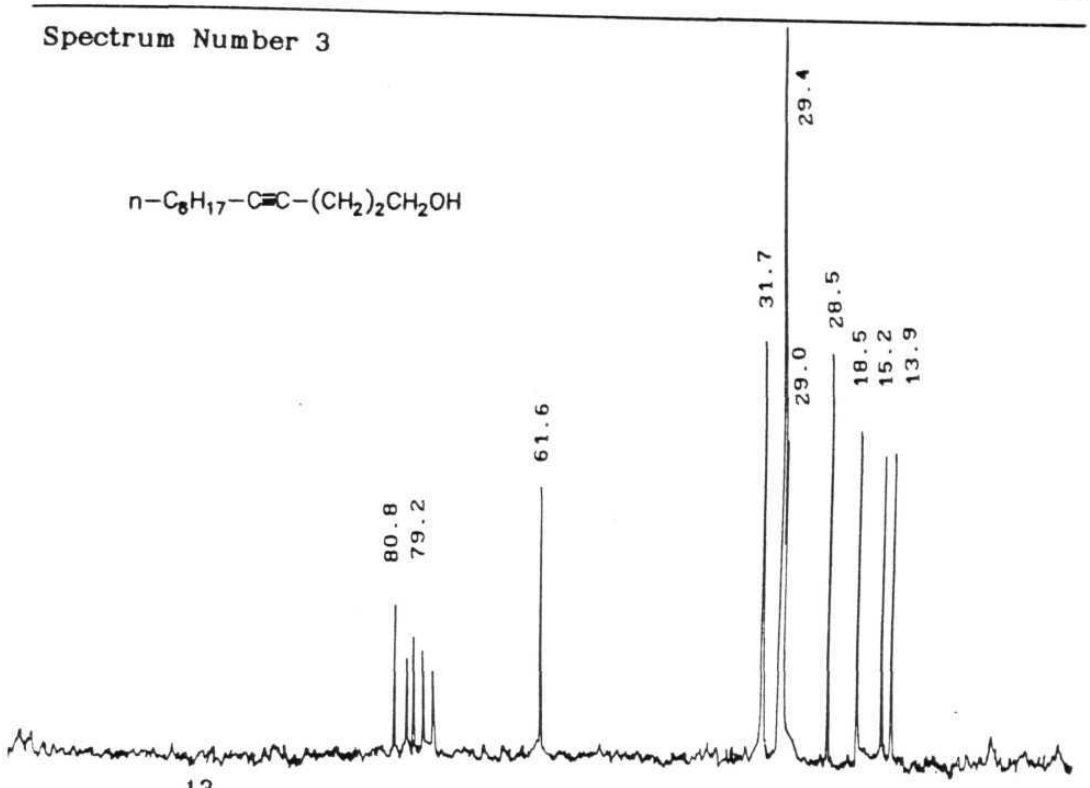
^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 2



^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 3



^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 4

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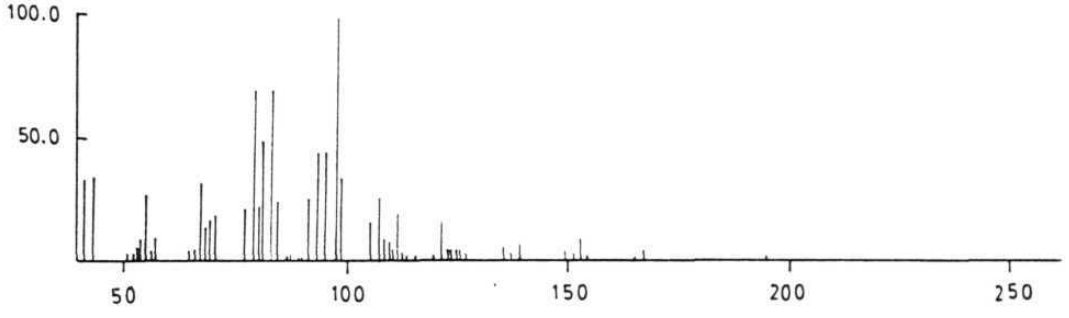
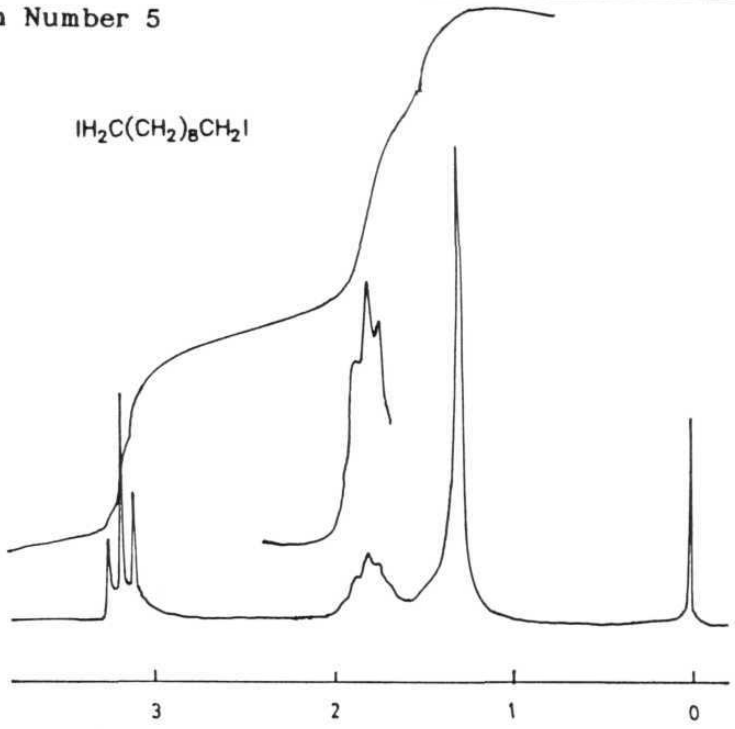


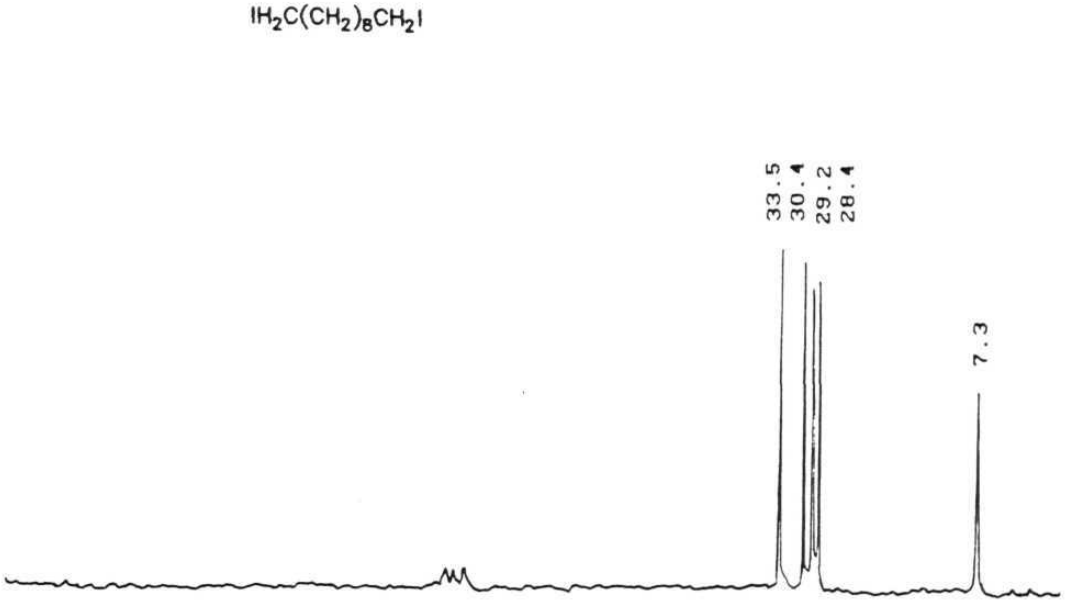
Mass Spectrum (M/e)

Spectrum Number 5



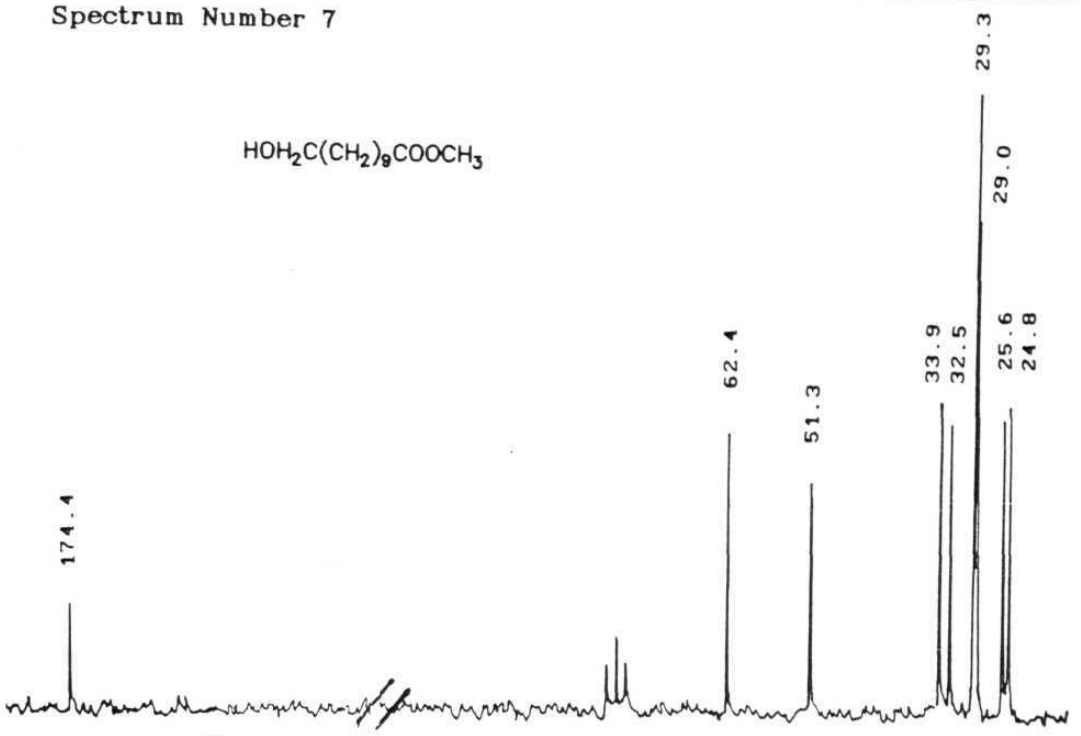
^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 6



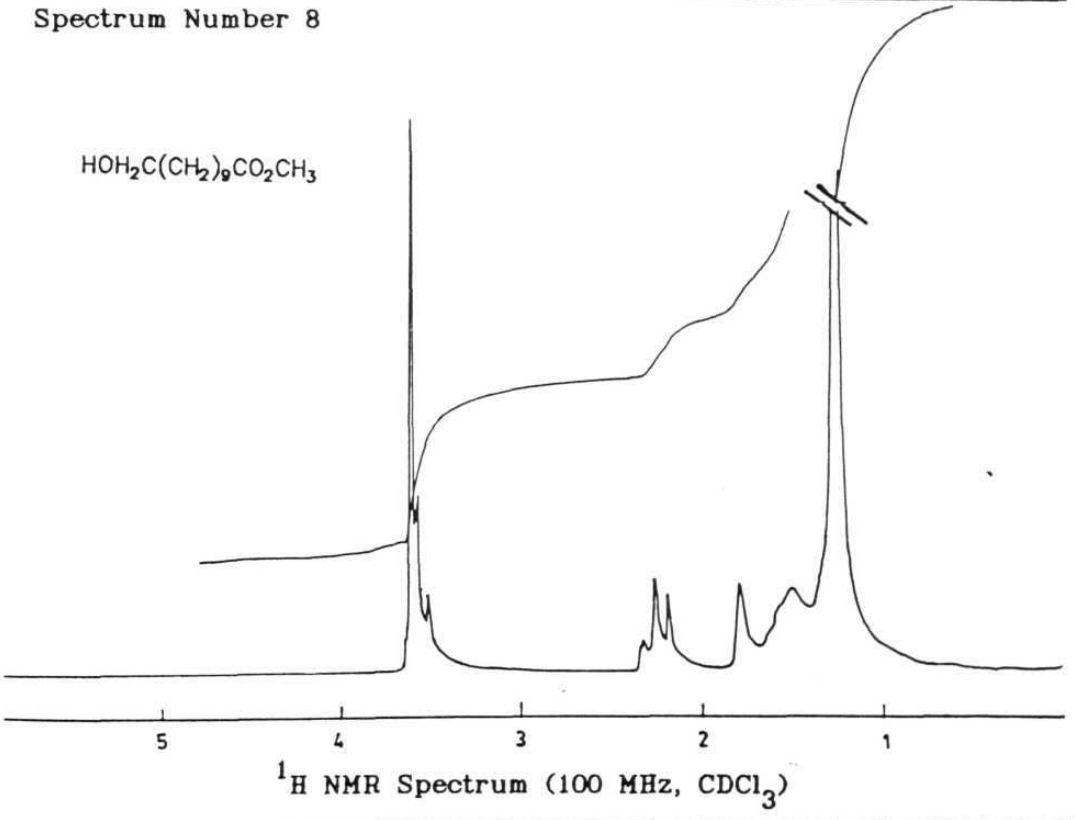
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 7



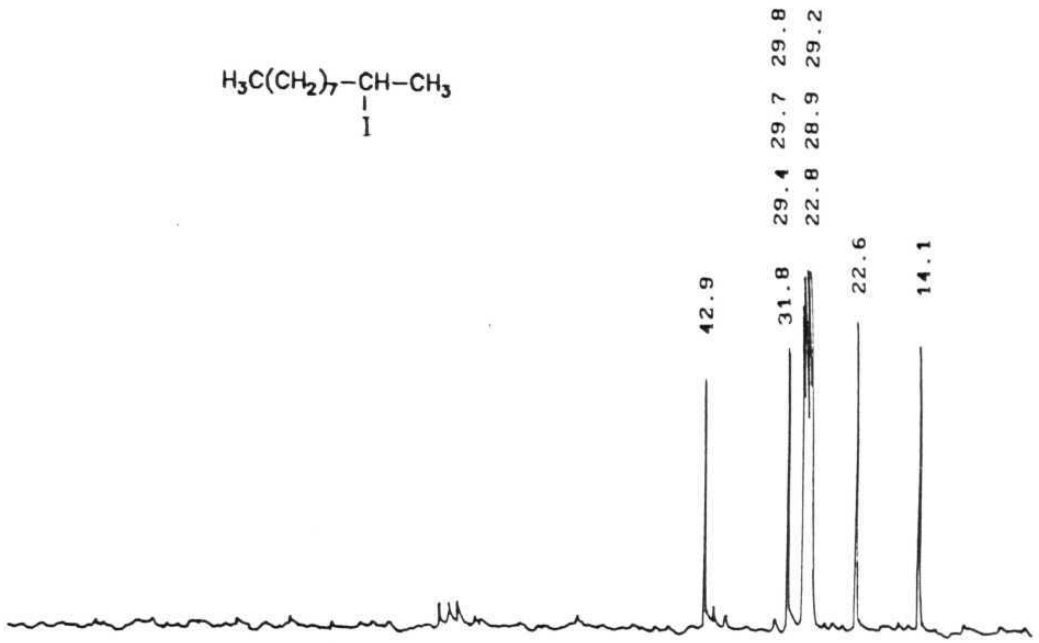
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 8



^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 9



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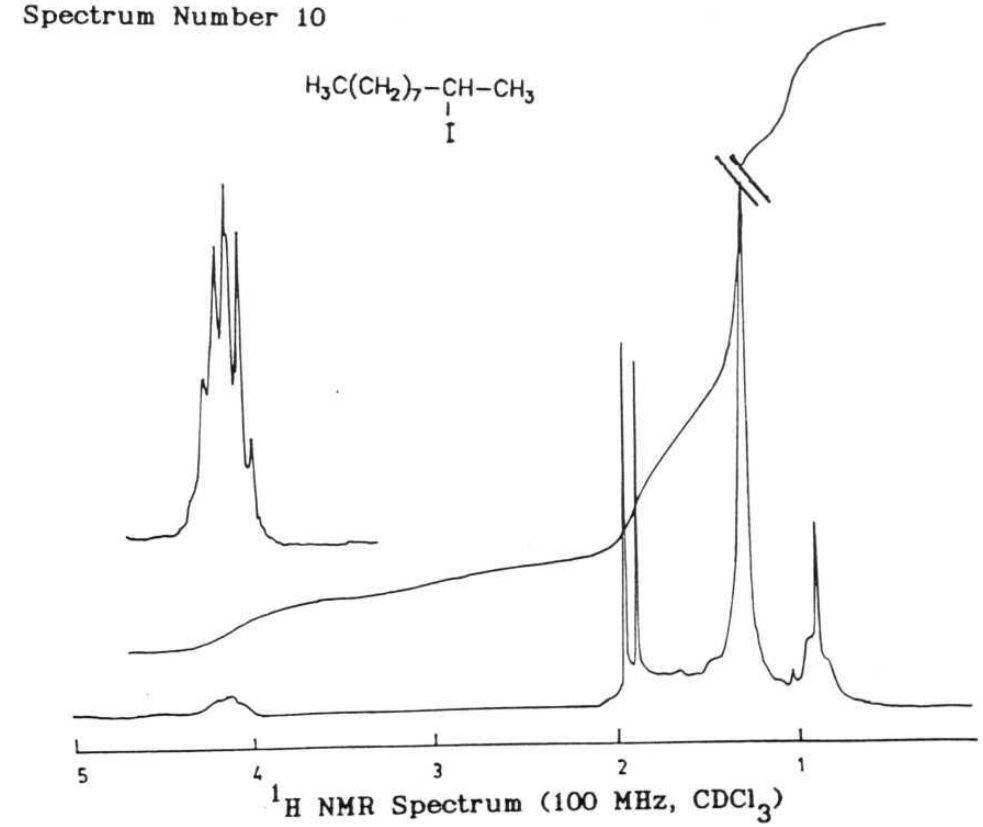
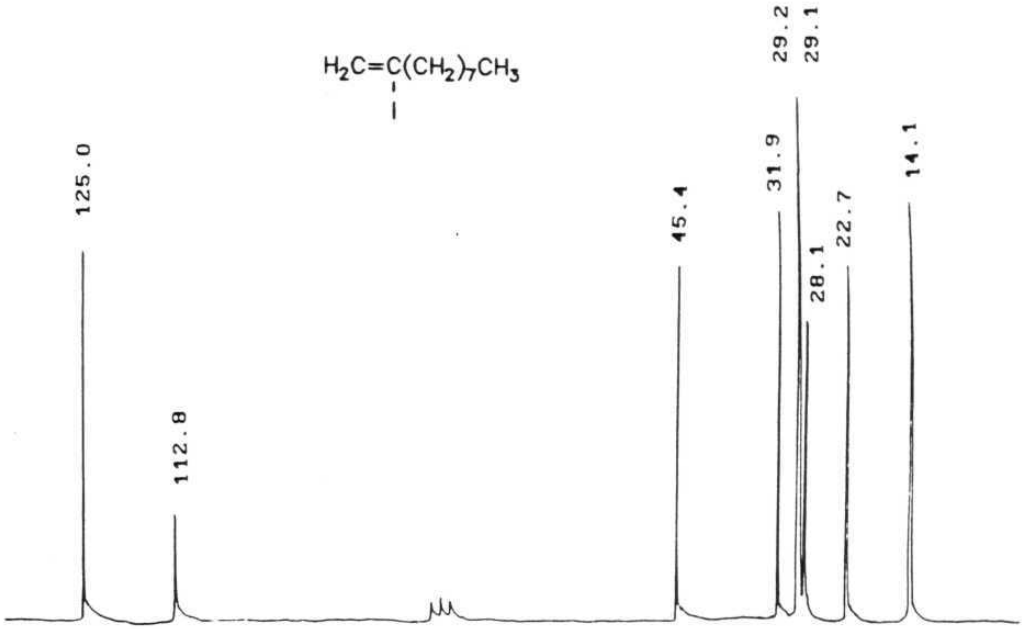


^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 11



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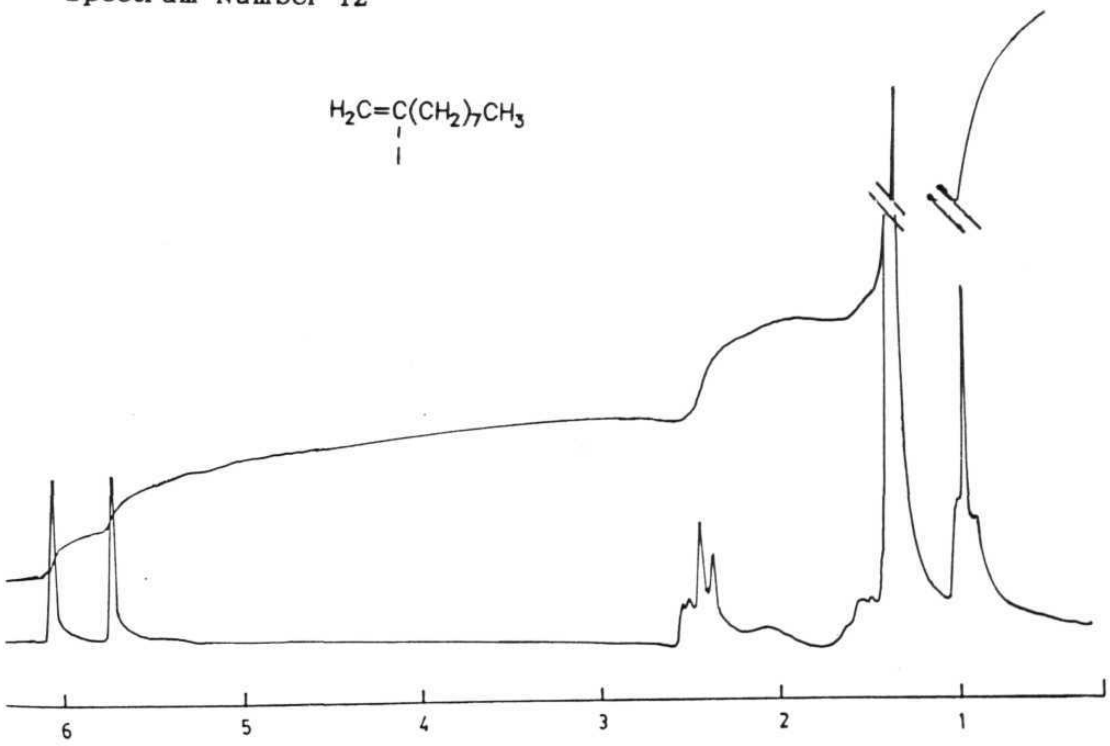

^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

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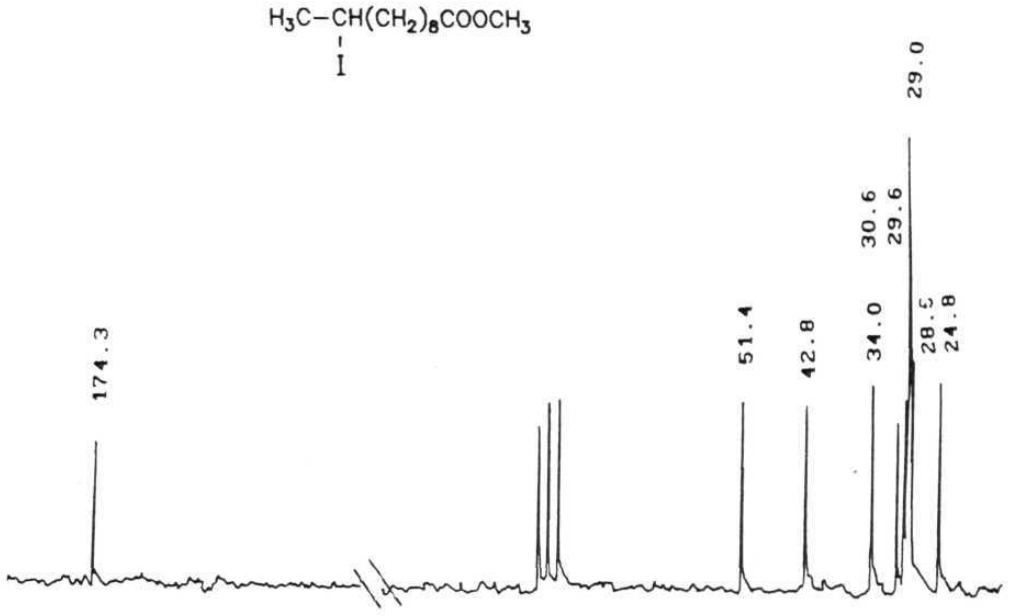

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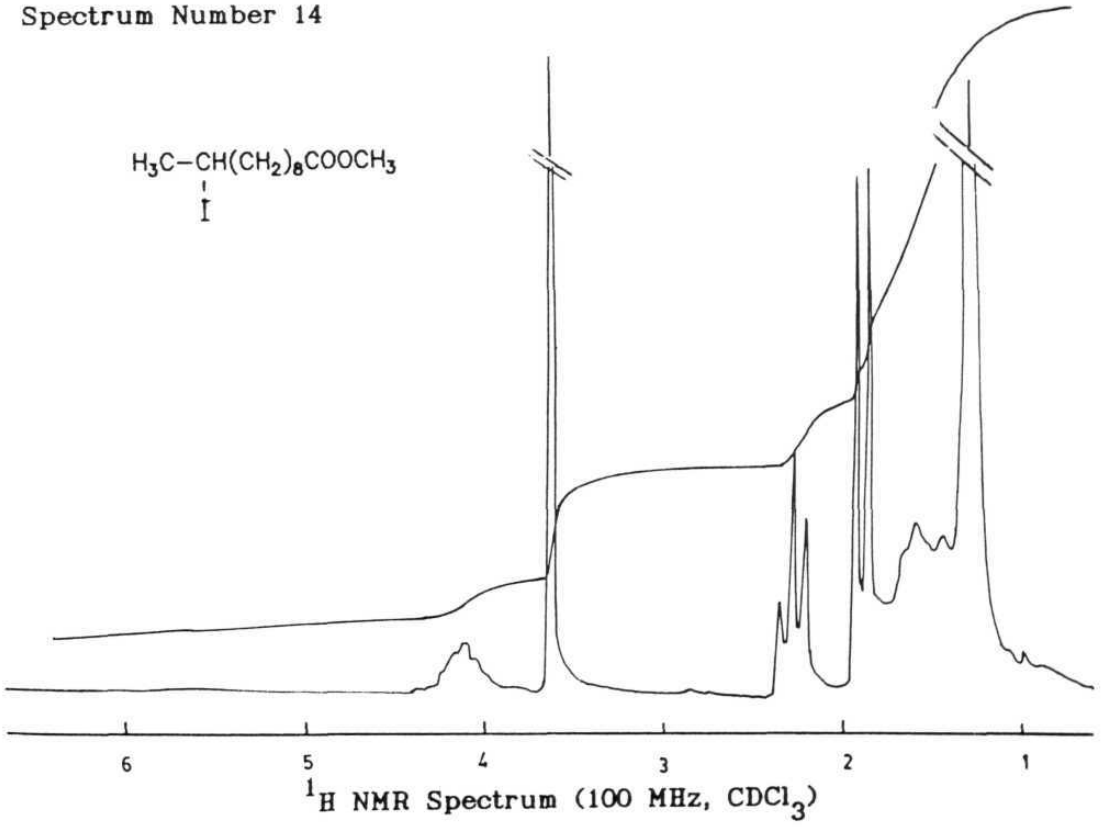

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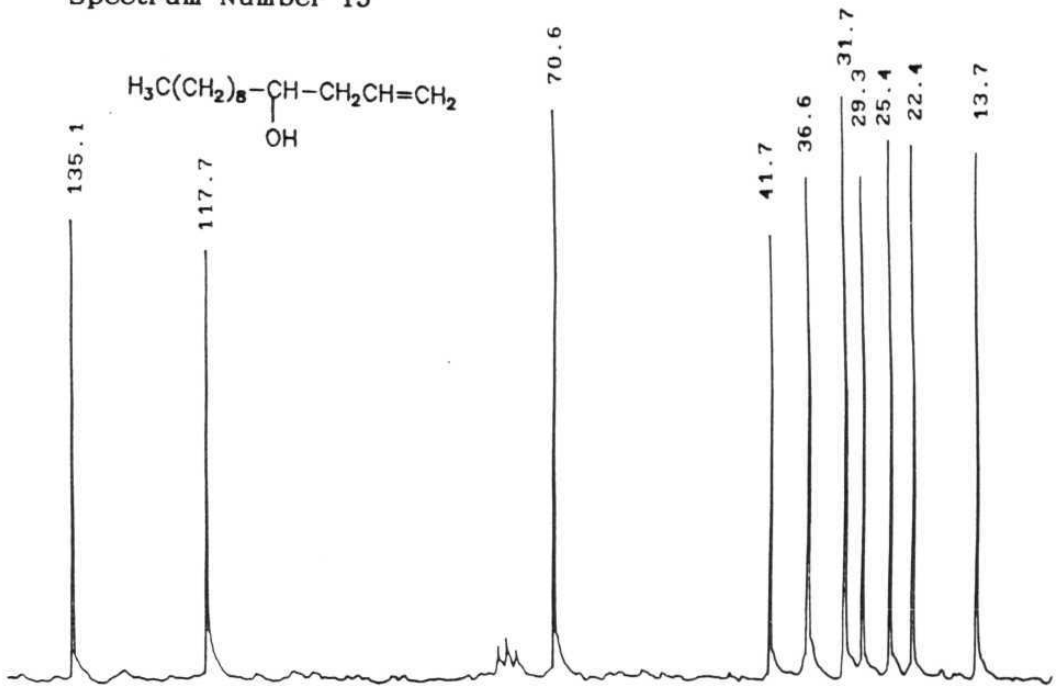

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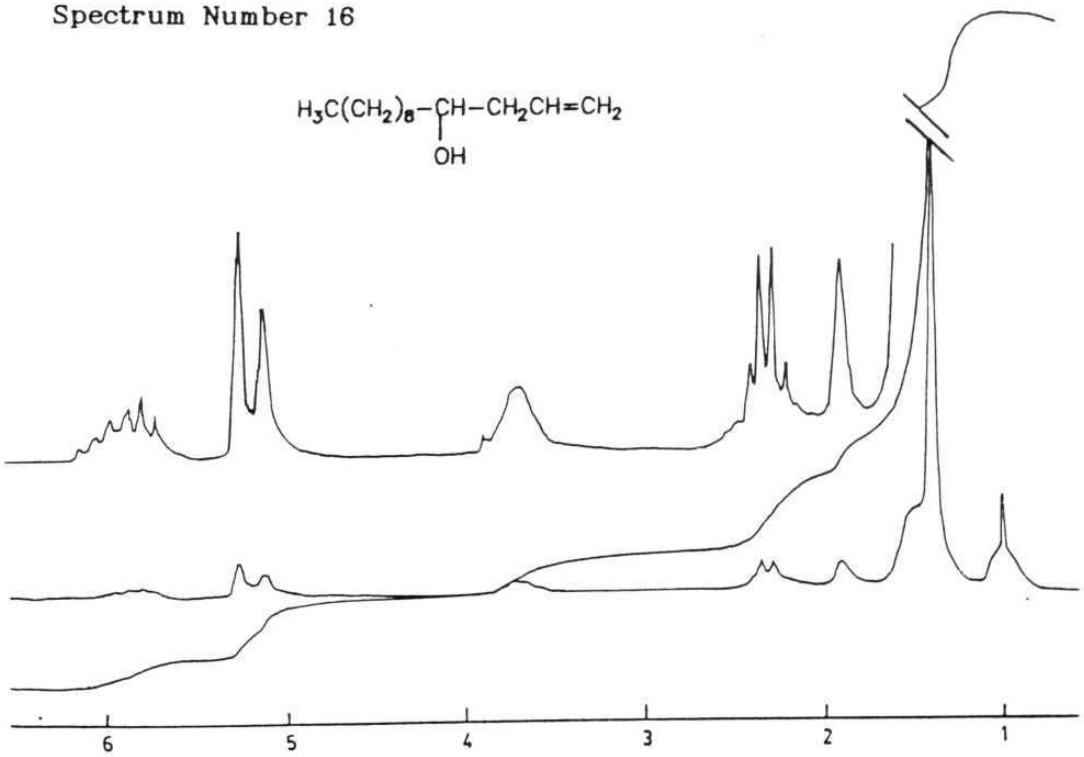

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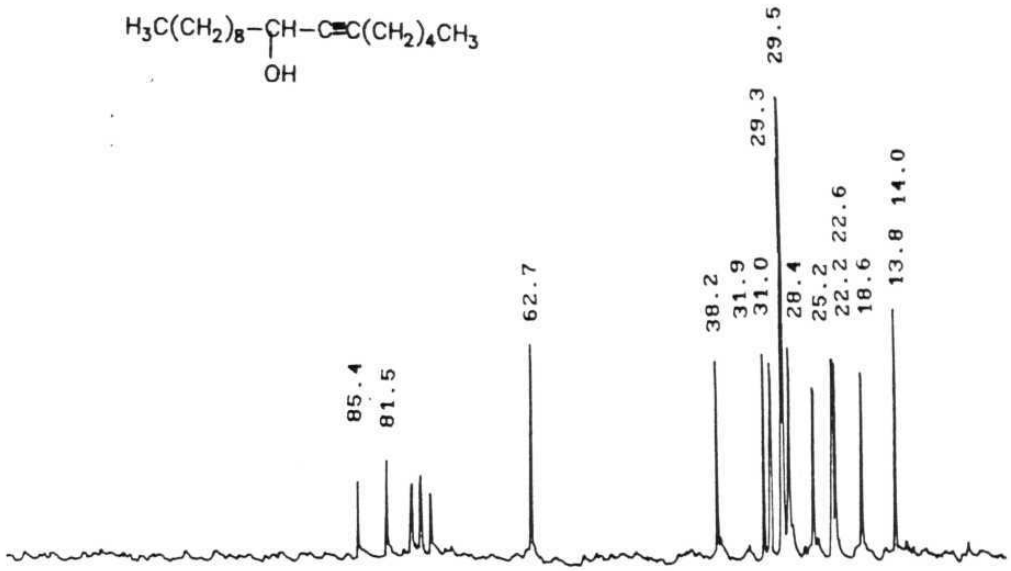

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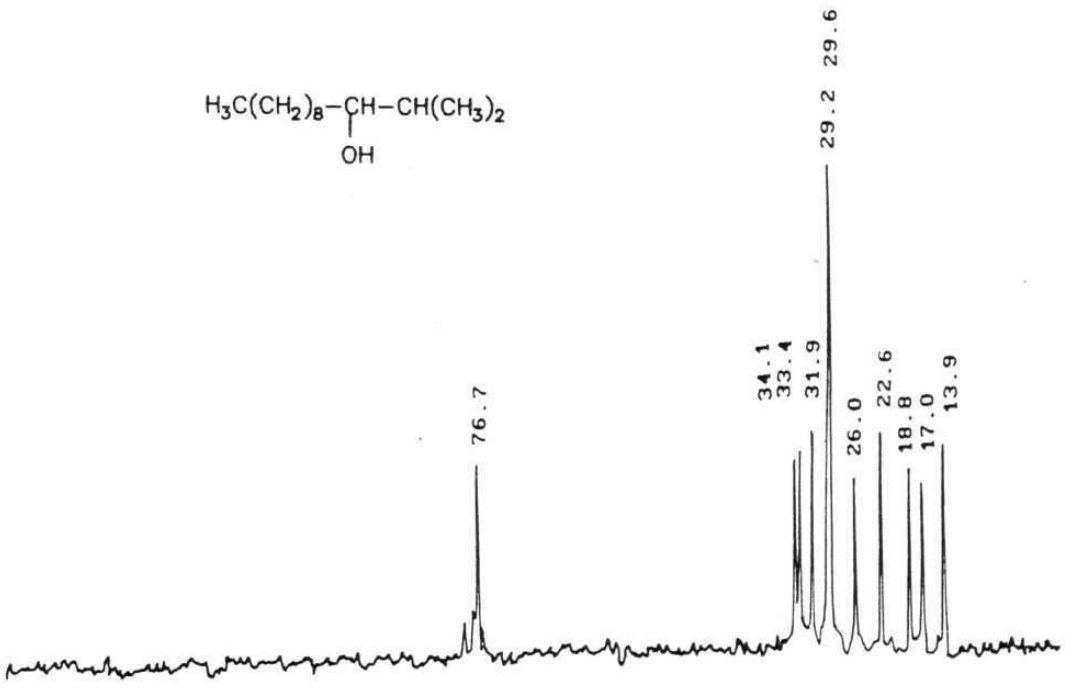

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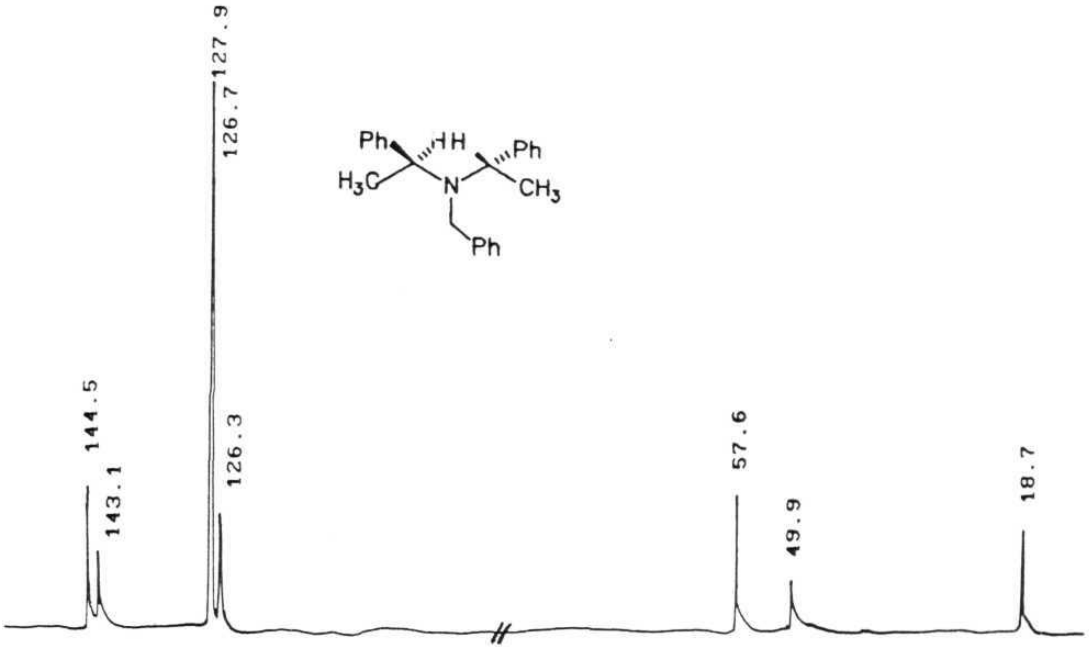

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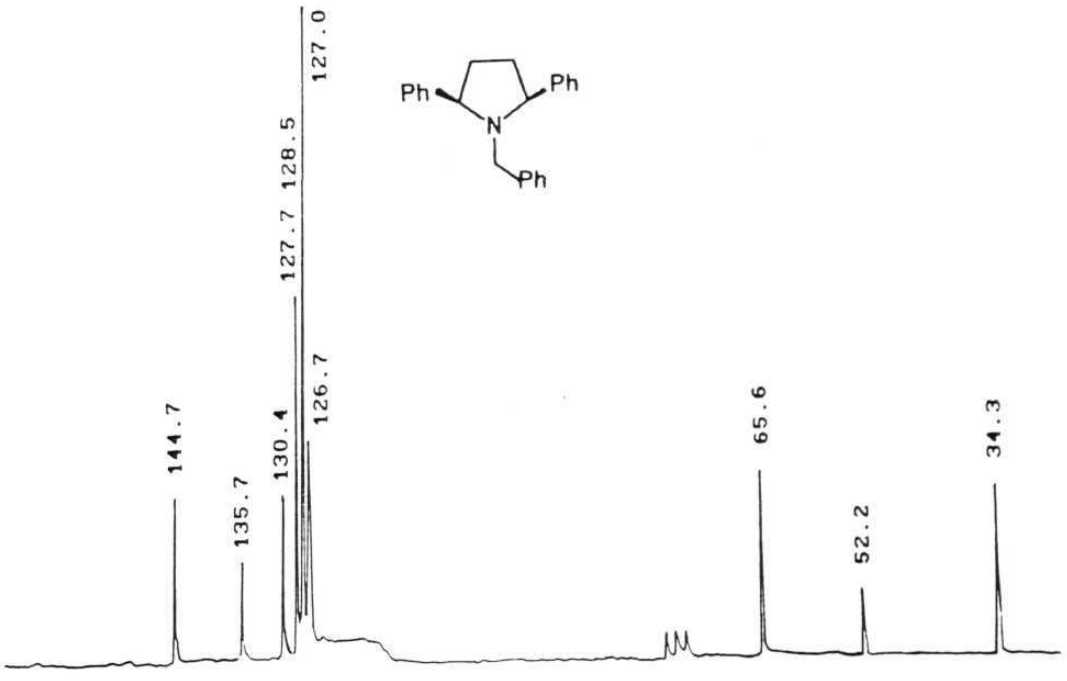

^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

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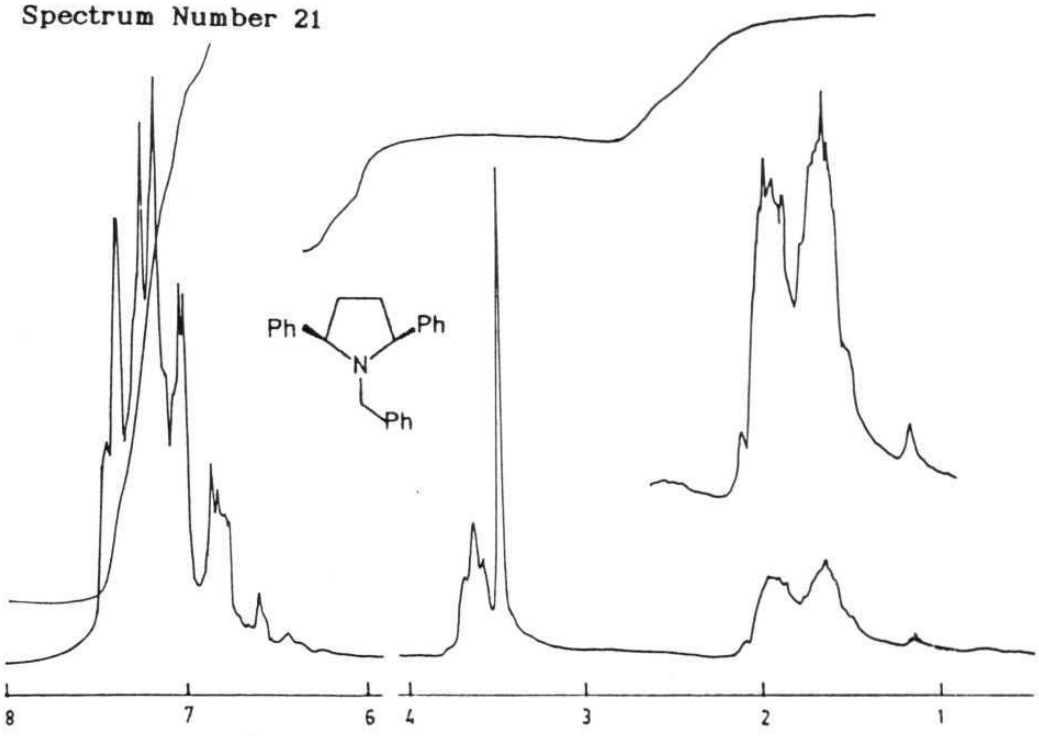

^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

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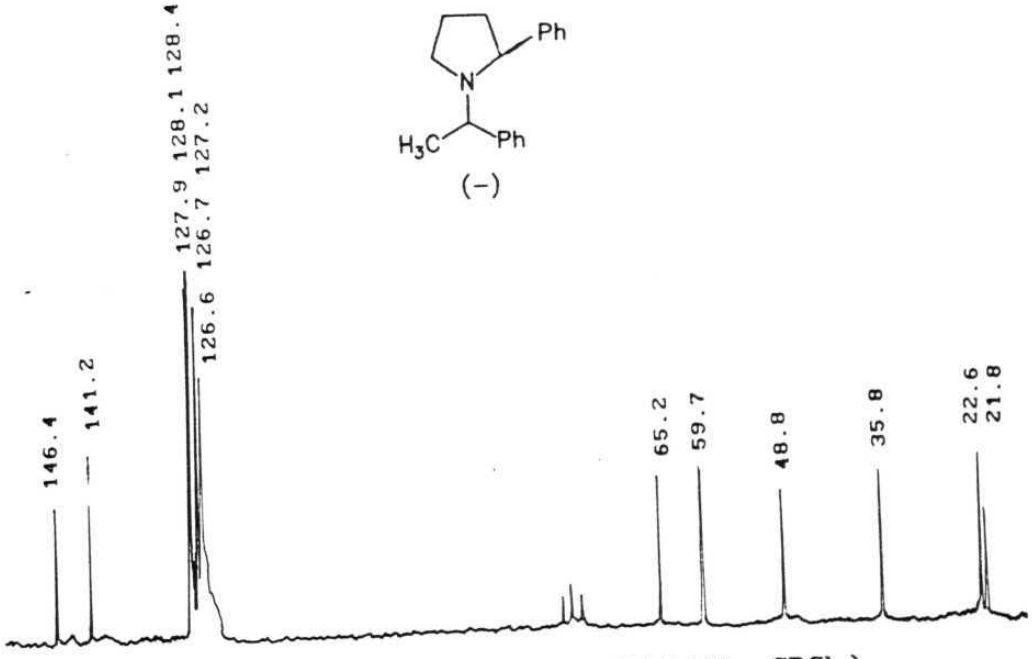

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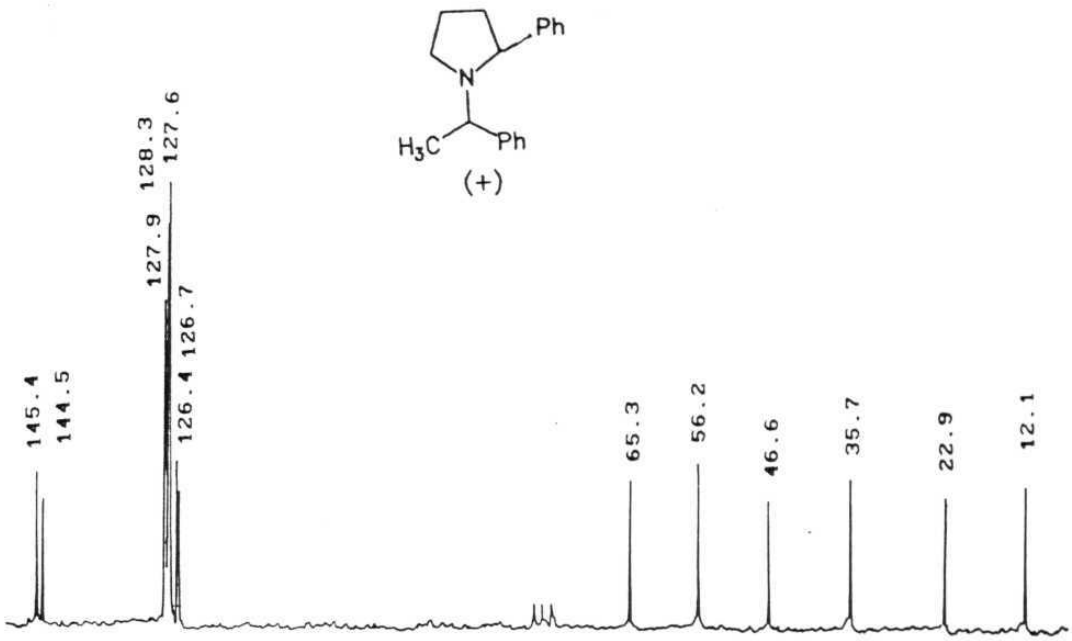

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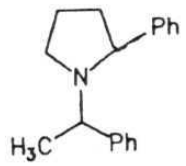

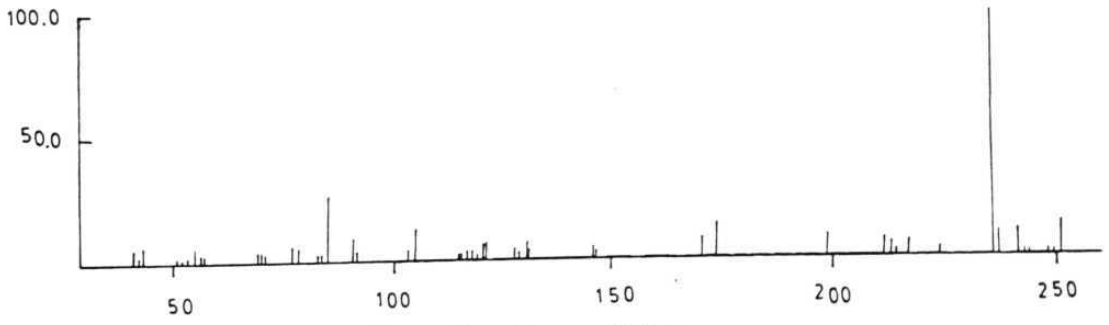

Mass Spectrum (M/e)

VITAE

Ch.Kishan Reddy was born on 24th August 1964 at Chelpur near Warangal, Andhra Pradesh. Following his early education at the Markazi High School, Warangal, he joined the Arts & Science College, Warangal and obtained a B.Sc. degree from Kakatiya University in 1984. He received his M.Sc. degree from Kakatiya University in 1987. Later he joined Ph.D. programme in the School of Chemistry, University of Hyderabad in 1988. He was awarded the Junior and Senior Research Fellowships by the UGC on the basis of CSIR-UGC National level test.

List of Publications:

1. A simple and convenient procedure for iodination of alcohols and reductive iodination of carbonyl compounds using N,N-diethyl aniline–borane–I_2 system.
   Ch. Kishan Reddy and M. Periasamy.
   Tetrahedron Lett.,1989, 5663.

2. A new, simple procedure for the generation and addition of HI to alkenes and alkynes using BI_3:N,N-diethylaniline complex and acetic acid.
   Ch. Kishan Reddy and M. Periasamy.
   Tetrahedron Lett.,1990, 1919.

3. Hydroborations, reductions and reductive iodinations using BHI_2:$N(C_2H_5)_2Ph$ complex.
   Ch. Kishan Reddy and M. Periasamy.
   Tetrahedron, 1992, 8329.

4. Reaction of I_2 with α-boraalkylmagnesium bromide a new synthesis of mixed alkyl secondary alcohols.
   Ch. Kishan Reddy and M. Periasamy.
   Tetrahedron, 1993, 0000.

5. Convenient method for N-debenzylation of tertiary amines.
J.V.B. Kanth, Ch. Kishan Reddy and M.Periasamy.
Synth.Commun., 1993, 0000.

6. Convenient synthesis of N-α-methylbenzyl-2-phenylpyrrolidine.
Ch. Kishan Reddy and M. Periasamy.
manuscript under preparation.

7. Asymmetric reduction of prochiral ketones using Chiral Amine Boranes.
Ch. Kishan Reddy and M. Periasamy.
To be submitted for publication.

8. Hydroboration of prochiral alkenes using Chiral Amine Boranes.
Ch. Kishan Reddy and M. Periasamy.
To be submitted for publication.