INVESTIGATIONS ON THE DEVELOPMENT OF ORGANIC SYNTHETIC METHODS FROM CATECHOLBORANE AND ARYLOXYBORANE DERIVATIVES

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By

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To

my husband

parents

teachers

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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 School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of Dr. M. Periasamy.

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

Y. Suseela

Y. SUSEELA

CERTIFICATE

Certified that the work contained in this thesis entitled 'Investigations on the Development of Organic Synthetic Methods from Catecholborane and Aryloxyborane Derivatives' has been carried out by Mrs. Y. Suseela, under my supervision and the same has not been submitted elsewhere for a Degree.

M. Periasamy 15.3.93

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(Thesis Supervisor)

Dean
School of Chemistry

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Finally, I wish to extend my sincere thanks to authorities of the University of Hyderabad for providing me with all the necessary facilities.

Yuseela

(Y. SUSEELA)

ABBREVIATIONS

AcOH	acetic acid
Ac_2O	acetic anhydride
9-BBN	9-borabicyclo[3.3.1]nonane
BMS	borane-dimethyl sulfide complex
n-BuLi	n-butyllithium
Bu	butyl
Cy_2BH	dicyclohexylborane
DCM	dichloromethane
DCME	α,α-dichloromethylmethylether
DG	diglyme
DME	dimethoxyethane
DMF	dimethylformamide
DMS	dimethyl sulfide
ee	enantiomeric excess
EE	diethyl ether (Et_2O)
Et	ethyl
IPC_2BH	isopinocampheylborane
LAH	lithium aluminium hydride
Ph	phenyl
Pr	propyl
Sia_2BH	disiamylborane
TFAA	trifluoroacetic acid
THF	tetrahydrofuran
Thexyl	2,3-dimethyl-2-butyl
TMS	tetramethylsilane
Ts	tosyl

ABSTRACT

This thesis deals with the investigations on the development of organic synthetic methods from catecholborane and aryloxyborane derivatives. It comprises of four chapters. The first chapter constitutes a review on the synthesis and salient features of various monofunctional hydroborating agents (R_2BH). The other three chapters describe the results of the present studies. They are subdivided into three parts: Introduction, Results and Discussion and Experimental Section. The references are given at the end of each chapter.

The second chapter describes the studies on the syntheses and applications of aryloxyboranes. A new method of preparation of catecholborane in hydrocarbon solvents has been developed by passing B_2H_6, generated using I_2 and $NaBH_4$ in diglyme through a solution of catechol in benzene.

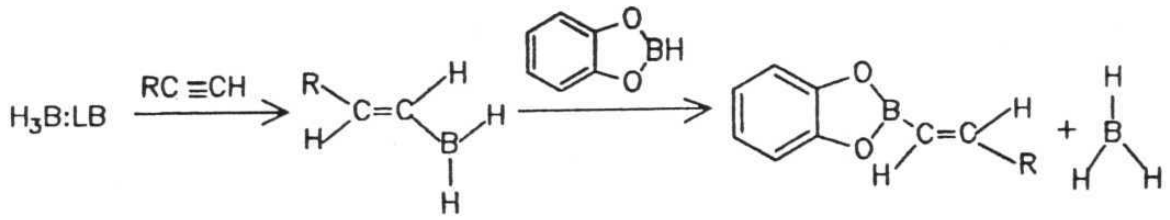
The formation of catecholborane was confirmed by IR studies and hydride analysis. The catecholborane prepared in this way hydroborates alkenes and alkynes in benzene at refluxing conditions. The alkyl and alkenylcatecholboranes formed were oxidized to give the corresponding alcohols and aldehydes in good yields (88-91%). The alkenyl-catecholboranes on treatment with $NaOH/I_2$ gave E-1-iodo-1-alkenes.

The higher temperatures used for hydroboration is not suitable

for hydroboration of alkenes and alkynes in the presence of functional groups such as esters. We have undertaken an investigation to find a means to increase the reactivity of catecholborane, so that hydroboration of 1-alkenes and 1-alkynes can be achieved at lower temperatures.

It has been observed that 1-alkynes are hydroborated by catecholborane at 25°C in the presence of catalytic amount of N,N-diethylaniline-borane complex, prepared from N,N-diethylaniline and B_2H_6, following a procedure reported from this laboratory. The attempts to prepare alkylcatecholborane following this procedure were unsuccessful. Presumably, the hydroboration of alkynes followed by the exchange of the alkenyl group with catecholborane takes place (Scheme 1).

SCHEME 1:



The alkenylcatecholboranes on oxidation and iodination with $NaOH/I_2$ gave aldehydes and E-1-iodo-1-alkenes, respectively in good yields. Selective hydroboration of 1-decyne over 1-decene was examined. Also, selective hydroboration of an alkyne when it is present along with an ester moiety was achieved under these

conditions.

The preparation of other aryloxyboranes such as phenoxy and binaphthol boranes was attempted. It was found that the reaction mixture did not exhibit -OH and >BH absorptions when excess B_2H_6 was passed through a solution of phenol or binaphthol in benzene. Hydroboration of 1-decyne using the phenol/B_2H_6/N,N-diethylaniline system gave similar results although the yield of the aldehyde obtained after NaOAc/H_2O_2 oxidation was somewhat low (55%).

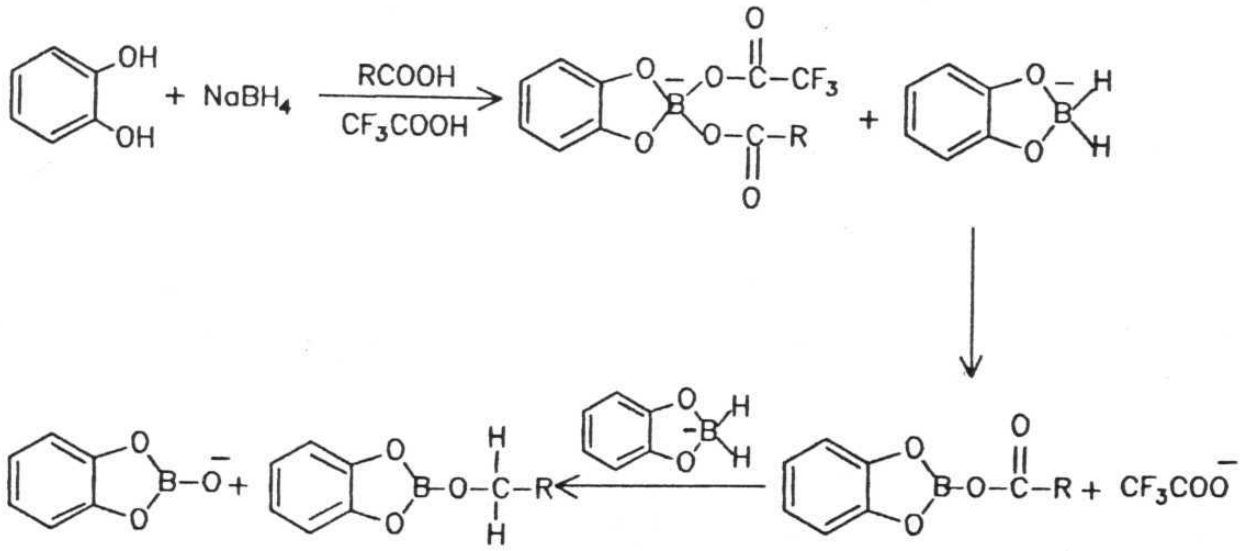
Attempts were also made for the preparation and utilization of iodocatecholborane. It was used as a Lewis acid catalyst in the Diels-Alder reaction of cyclopentadiene with cinnamaldehyde.

In the third chapter, the studies on the reduction and hydroboration with reagents prepared using catechol and $NaBH_4$ are described. Interesting reactivities have been observed for the RCOOH/$NaBH_4$ system. The $NaBH_4$ reduces acids to the corresponding alcohols under THF reflux conditions to an extent of about 50%. We have investigated the effect of catechol in such reductions.

Reduction of capric acid using $NaBH_4$/catechol system under various conditions was carried out. 1-Decanol was obtained in only about 50% yield. Reduction of 10-undecenoic acid with the

$NaBH_4$/catechol system gave the corresponding olefinic alcohol. In all cases, one half equivalent of the acids remained unreacted. It was thought that if a mixture of two carboxylic acids is used and if one of them could readily dissociate to give $RCOO^-$, then the reduction of the other acid can be achieved to more extent. Since CF_3COO^- species is expected to be relatively stable, good leaving and poorly coordinating group, CF_3COOH was chosen for this purpose (Scheme 2). It has been observed that aliphatic acids give the corresponding alcohols in good yields (87-94%).

SCHEME 2:



Aromatic acids were found to be reduced to a lesser extent. This property was made use of in selective reduction of capric acid in the presence of benzoic acid. Selective reduction of an acid in the presence of an ester group was also achieved. An attempt to reduce an acid in the presence of an olefinic moiety (eg. 10-undecenoic acid), gave the competitive hydroborated product. This is surprising, since

catecholborane does not hydroborate olefins at room temperature.

As mentioned previously, acyloxyborohydride in refluxing THF gives reduction to an extent of 50%. It was of interest to examine whether the use of CF_3COOH instead of CH_3COOH would help in carrying out such reductions to more extent at ambient conditions. If this is the case, then the hydride can be utilized in a more efficient manner. It was indeed observed that $NaBH_4/CF_3COOH$ reduces aliphatic acids to the corresponding alcohols in quantitative yields. Again, the yields with aromatic acids are poor. Selectivities similar to that observed using the $NaBH_4$/catechol/CF_3COOH reagent system have been obtained.

As outlined earlier, it was found that the olefinic moiety underwent hydroboration in the reduction of 10-undecenoic acid with $NaBH_4$/catechol/CF_3COOH reagent system. This observation prompted us to further explore the reactivity of this system. It was found that 1-decene is hydroborated by this reagent and the resulting organoborane on oxidation gives 1-decanol in good yield. The generality of the reaction was examined with several other olefins. It was found that whereas the yields of the hydroboration-oxidation products obtained in the case of terminal olefins are good, with the internal olefins the yields are low. The selective hydroboration of 1-decene over α-pinene with this reagent system was examined.

Surprisingly, the hydroboration of 1-decyne using $NaBH_4$/catechol/CF_3COOH reagent system was somewhat slow compared to 1-decene. Hydroboration of enynes were carried out in order to examine the possibility of achieving hydroboration of a terminal alkene over alkyne. Although, the yield of the product was lower in these cases, the results indicate that there is some preference for the hydroboration of alkene over alkyne.

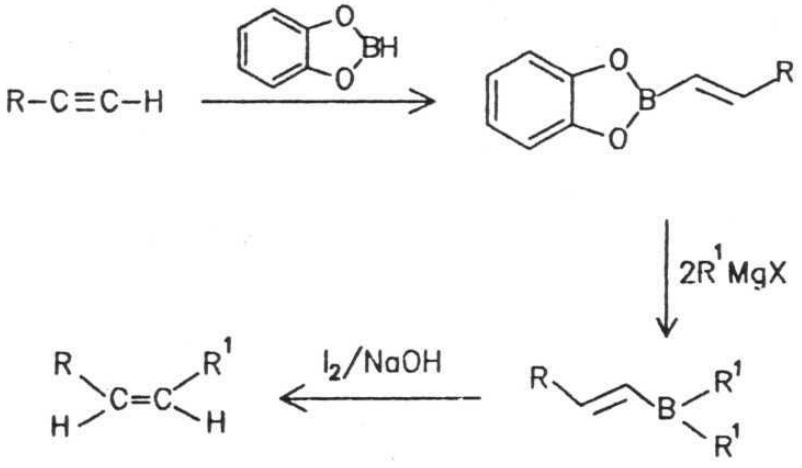
Hydroboration using the $NaBH_4/CF_3COOH$ system, has also been examined. The reaction with this reagent system was found to be faster compared to the $NaBH_4$/catechol/CF_3COOH system. Hydroboration of 1-decyne with this reagent gave 1-decanol, after $NaOAc/H_2O$ oxidation through the gem-diboron intermediate. Although the nature of the intermediate species involved in these reagent systems is not clearly understood, the synthetic methods developed utilizing these readily accessible reagents should be useful.

The fourth chapter deals with the studies on the development of C-C bond formation reactions using alkyl and alkenylcatecholboranes. Attempts have been made to transfer alkyl and alkenyl groups to copper and carry out C-C bond formations. It has been observed that the alkyl and alkenylcatecholboranes fail to undergo intermolecular transfer reaction through the reaction with the $NaOCH_3$/CuX reagent. Utilization of alkyl free radicals, generated from organoboranes using Ag^+/KOH in

the addition reaction with α,β-unsaturated compounds has been attempted.

Alkenylcatecholboranes have been successfully applied in the Grignard addition-intramolecular rearrangement using I_2/NaOH to obtain Z-olefins in good yields. The generality of the transformation was examined with various alkynes. The transformation may be visualized through the sequence of reactions outlined in Scheme 3.

SCHEME 3:



This method is a good alternative to Zwiefel's cis-olefin systhesis, since alkyl and aryl groups not available through hydroboration reaction (eg. B-phenyl, B-isopropyl) can also be utilized here. The Z-1-phenyl-1-decene was isomerized to the E-1-phenyl-1-decene using the $CoCl_2/NaBH_4/Ph_3P$ reagent following a procedure reported from this laboratory.

CHAPTER - 1

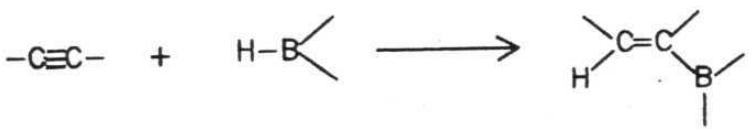
Syntheses and applications of monofunctional hydroborating agents (R_2BH) - A review.

CHAPTER - 1

Syntheses and Applications of Monofunctional Hydroborating Agents (R_2BH) - A Review:

Organoboranes (R_3B) were originally synthesized by the reaction of an organometallic derivative (eg. RLi or RMgX) with a boron ester or halide.[1] These alkylboranes (R_3B) are relatively less reactive compared to RLi or RMgX and hence the chemistry of these compounds received little attention.[2] The discovery of hydroboration of alkenes and alkynes (eq. 1 and 2)[3] in ether solvents using BH_3-Lewis base complexes made a number of organoboranes available which resulted in the development of the organoborane chemistry during the last 35 years.

— (1)

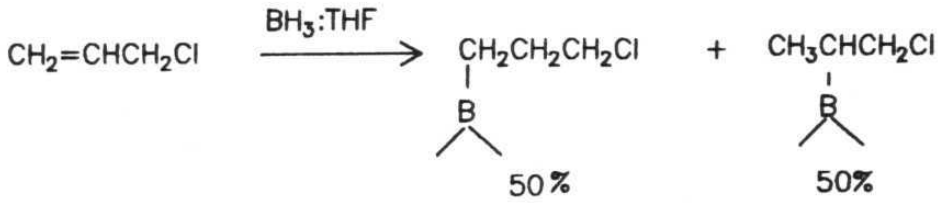


— (2)

In the hydroboration reactions, the boron-hydrogen bond adds to alkenes and alkynes fast in a quantitative manner. Many new reactions of major significance in synthetic organic chemistry have been discovered using these organoboranes. The chemistry of these reactions has been extensively reviewed.[4-6]

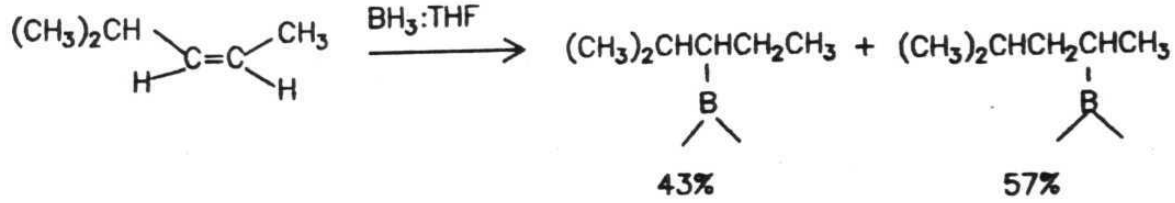
The pioneering efforts of Brown and co-workers made available a number of borane reagents such as BH_3:THF, BH_3:DMS, BH_3:NR_3[4-7] etc., for the preparation of trialkylboranes. The polyfunctional nature of borane (BH_3), the relatively low selectivity, and its low steric requirements often lead to complications. For example, the powerful directive influence of chlorine in alkyl chloride leads to approximately 50:50 distribution of the boron at the terminal positions when BH_3:THF is used as the hydroborating agent (Scheme 1).

SCHEME 1:



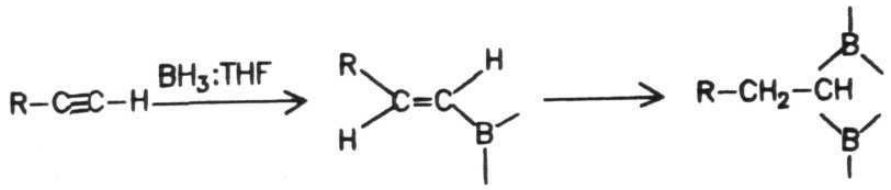
The hydroboration of cis-4-methyl-2-pentene results in little selectivity between the two positions (Scheme 2).

SCHEME 2:

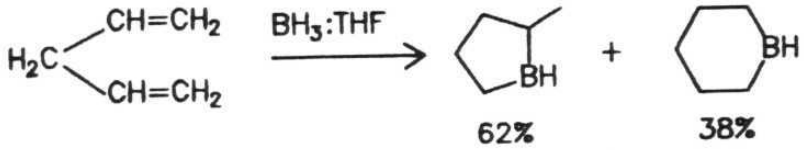


The hydroboration of terminal alkynes using BH_3-Lewis base complexes proceeds past the vinylborane stage (Scheme 3) and the hydroboration of dienes is complicated by the formation of cyclic intermediates (Scheme 4).

SCHEME 3:



SCHEME 4:



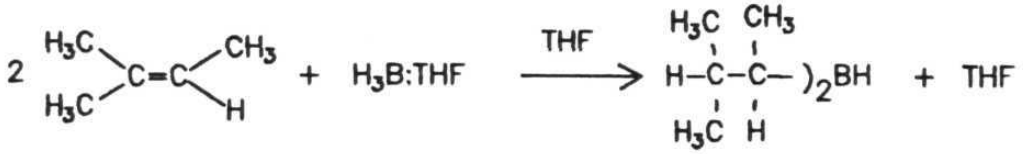
Some of these complications can be alleviated using partially substituted boranes for the hydroboration reaction. We have decided to investigate the development of new routes for the synthesis and utilization of aryloxyboranes, catecholborane in particular. It will be helpful here to briefly review the synthesis and applications of some disubstituted monofunctional hydroborating agents such as disiamylborane, diisopinocampheylborane, 9-BBN, dicyclohexylborane, dibromoborane, thexylchloroborane and catecholborane which have some unique applications.

Disiamylborane:

Disiamylborane can be prepared by the reaction of 2-methyl-2-butene with borane which proceeds rapidly to the dialkylborane stage,

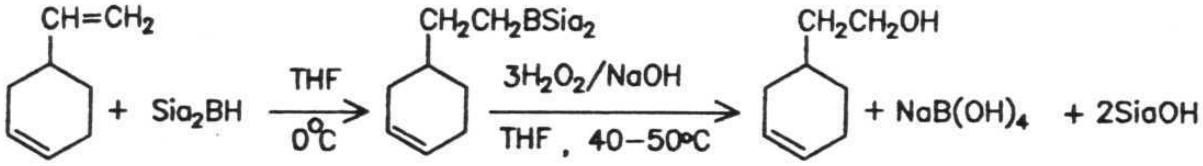
but only slowly beyond (Scheme 5).[8]

SCHEME 5:



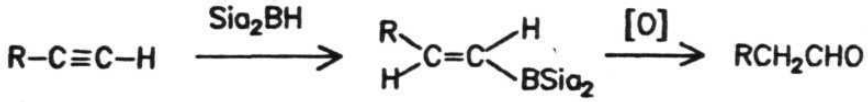
Disiamylborane is highly sensitive to the structure of olefin.[9,10] It hydroborates terminal olefins much faster than internal olefins (Scheme 6). Also, cis-alkenes react faster than trans-alkenes. These characteristics make certain selective hydroborations possible.[10]

SCHEME 6:



1-Alkynes react with disiamylborane to give the corresponding vinylboron derivatives which upon alkaline peroxide oxidation give the corresponding aldehyde (Scheme 7).[11]

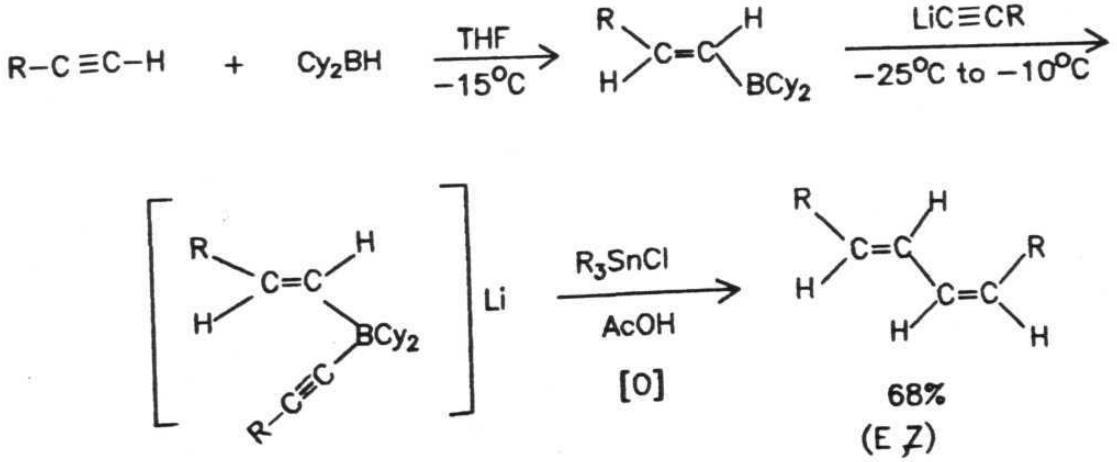
SCHEME 7:



Dicyclohexylborane:

In many cases, disiamylborane can be replaced by dicyclohexylborane which can be readily prepared by the reaction of BH_3:THF with 2 equivalents of cyclohexene. Due to powerful directive effects of these reagents, it is possible to achieve interesting syntheses.[12] Dicyclohexylborane offers advantages in some transformations of dialkylalkenylboranes as exemplified in the synthesis of 1,4-disubstituted-(E,Z)-1,3-dienes from lithium dicyclohexyl-trans-1-alkenyl-1-alkynylborates (Scheme 8).[13]

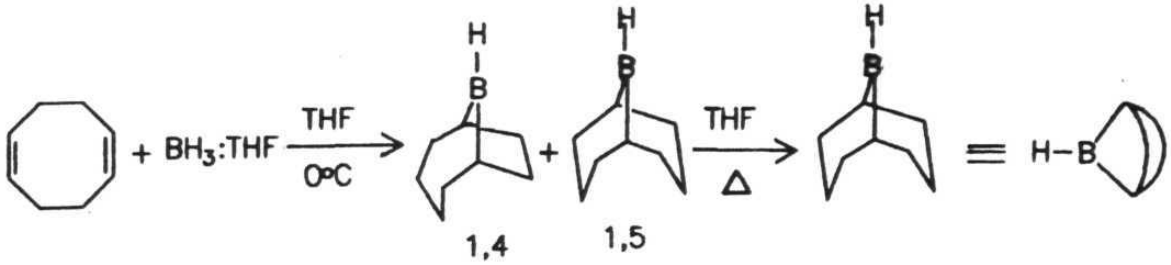
SCHEME 8:



9-Borabicyclo[3.3.1]nonane:

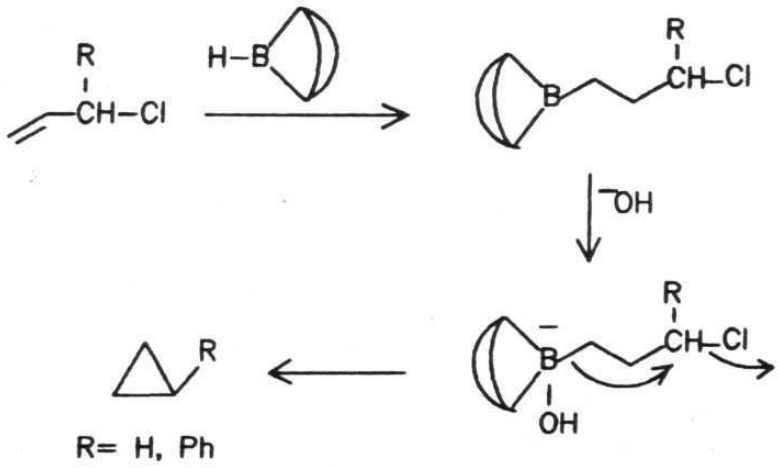
The reaction of 1,5-cyclooctadiene with borane in THF can be controlled to provide the bicyclic borane, 9-borabicyclo[3.3.1]nonane[14] (Scheme 9) which shows remarkable thermal and air stability.

SCHEME 9:



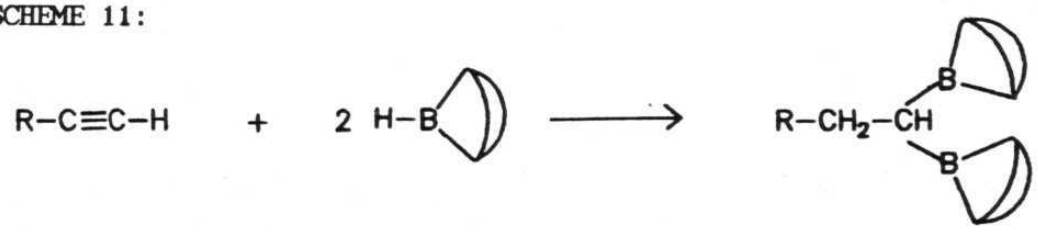
9-BBN hydroborates olefins slower than disiamylborane. Because of its thermal stability, reactions can be carried out in refluxing THF. At this condition, all olefins including 2,3-dimethyl-2-butene, which fails to react with disiamylborane can be hydroborated. Several useful reactions have been reported with B-alkyl-9-BBN derivatives (Scheme 10).[7]

SCHEME 10:



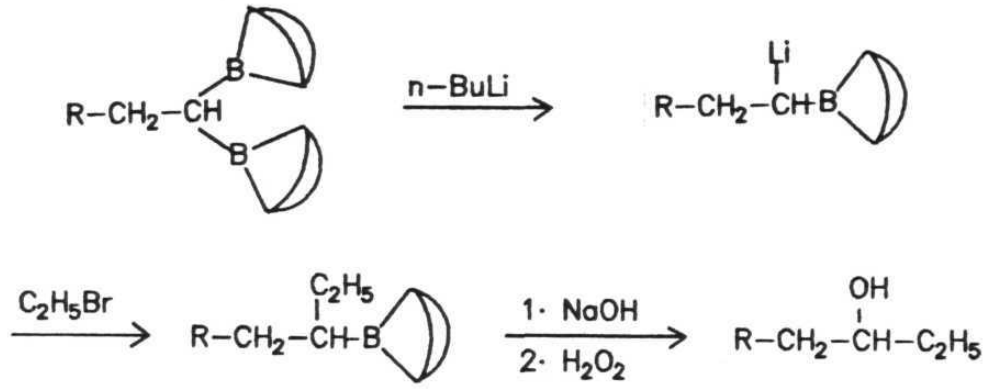
Alkynes are converted to the corresponding 1,1-dibora derivatives (Scheme 11).[7]

SCHEME 11:



Such gem-dibora compounds react with n-BuLi to give the corresponding 1-bora-1-lithio derivatives which are useful synthetic intermediates (Scheme 12).[15]

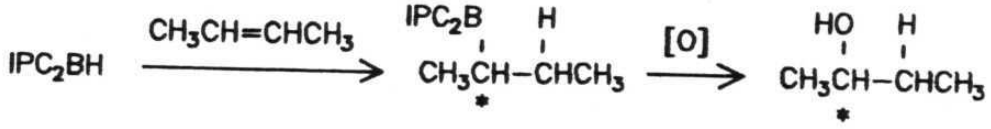
SCHEME 12:



Diisopinocampheylborane:

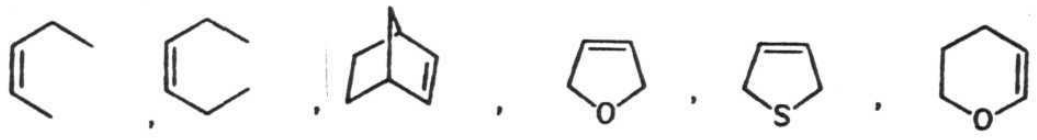
Diisopinocampheylborane (IPC_2BH) can be prepared by the hydroboration of α-pinene. Since α-pinene is available from natural sources in both optically active forms (+) and (-), the optically active diisopinocampheylborane can be used for asymmetric synthesis. For example, cis-2-butene on hydroboration using (+)-IPC_2BH followed by oxidation gives (-)-2-butanol in 87% ee (Scheme 13).[16]

SCHEME 13:



The IPC_2BH gives good optical inductions in the hydroborations of cis-olefins[17,18,19] (Figure 1), but gives poor inductions in the case of more hindered olefins.

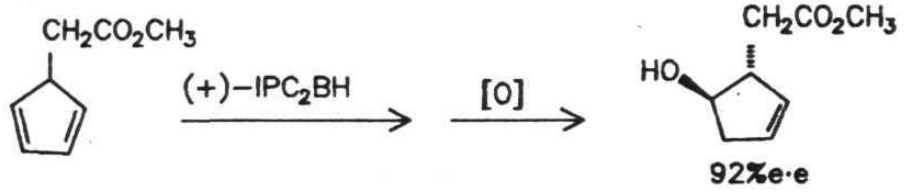
FIGURE 1:



e·e 92·3 % 93% 83% 99% 99% 99%

IPC_2BH has been successfully utilized to achieve asymmetric synthesis of a prostaglandin intermediate.[20] This reagent is also useful for asymmetric reductions (Scheme 14).[4]

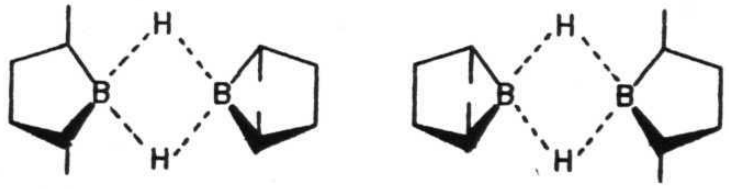
SCHEME 14:



92%e·e

Masamune *et al*[21] have developed an enantiomeric pair of borane reagents 1 and 2 which have C_2 symmetry. This reagent hydroborates prochiral olefins with upto 98% ee in most cases.

FIGURE 2:



1 2

These boranes (1 and 2) were found to be superior over existing chiral boranes such as IPC_2BH in terms of chiral inductions and also provide information about the transition state geometry of the reaction. However, preparation of these reagents involve several steps.

Dihaloborane:

Dichloroborane, Cl_2BH is unstable and disproportionates spontaneously into diborane and boron trichloride. However in ether solvents, dichloroborane ethyl etherates are formed by the reaction of boron trichloride with lithium borohydride which appear more favourable (eq. 3).[22,23]

$$LiBH_4 + 3BCl_3 + 4Et_2O \xrightarrow{EE} LiCl \downarrow + 4Cl_2BH{:}OEt_2 \quad \text{---} \quad (3)$$

The dichloroborane-ethyl etherate fails to react spontaneously with olefins or acetylenes at any convenient rate.[24]

The dihaloborane-dimethyl sulfide reagents are readily prepared in high yield and purity by the exchange reaction between the commercially available borane-dimethyl sulfide ($H_3B{:}SMe_2$, BMS) and the respective boron trihalide-dimethyl sulfide (X = Cl or Br) (eq. 4).[25]

$$H_3B{:}SMe_2 + 2BX_3{:}SMe_2 \longrightarrow 3HBX_2{:}SMe_2 \quad \text{---- (4)}$$

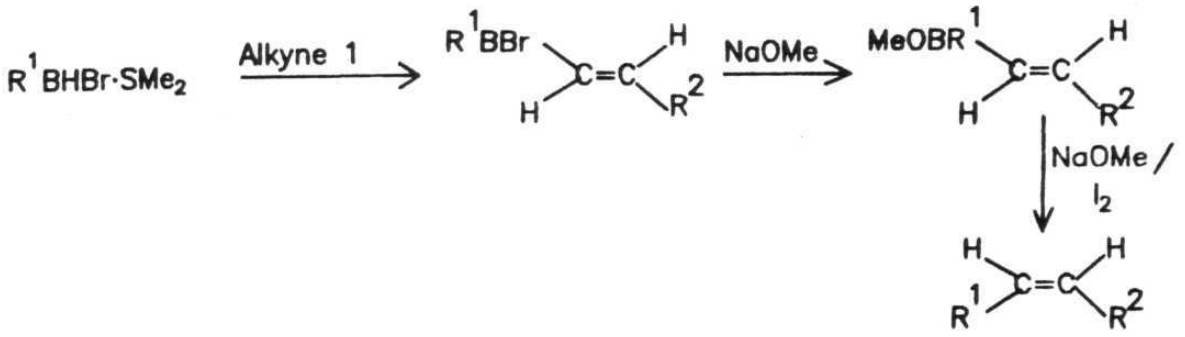
Dichloroborane-dimethyl sulfide ($HBCl_2{:}SMe_2$) hydroborates representative olefins relatively slow and require the presence of a strong Lewis acid such as boron trichloride, to complete the hydroboration reaction rapidly. Unexpectedly, diboromoborane-dimethyl sulfide ($HBBr_2{:}SMe_2$) and diiodoborane-dimethyl sulfide ($HBI_2{:}SMe_2$) react rapidly with olefins, even in the absence of such Lewis acids.[26]

The syntheses of mixed dialkylhaloboranes (R^1R^2BBr) and trialkylboranes ($R^1R^2R^3B$) expand the applications of the versatile organoboranes to a large extent. Such mixed organoborane derivatives are prepared via the controlled hydridation of alkyldihaloboranes ($R^1BBr_2{:}SMe_2$)[27] followed by sequential hydroboration (Scheme 15) by taking required quantity of $LiAlH_4$ in ether.[28]

SCHEME 15:

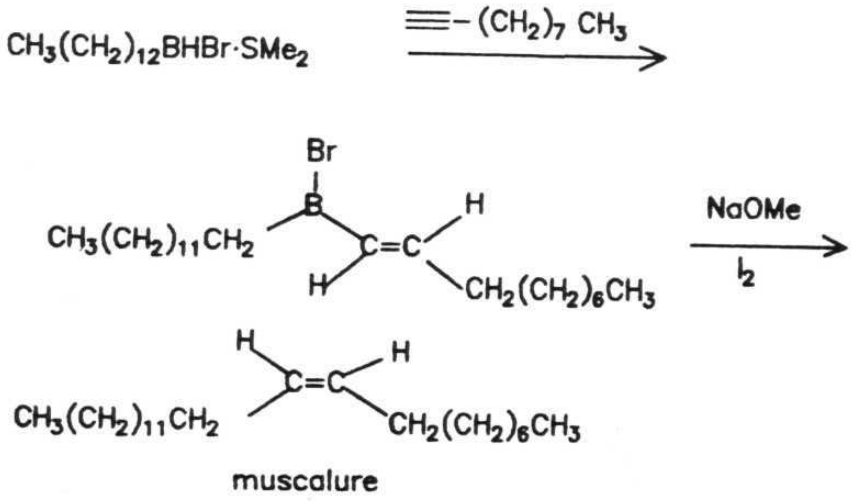
This reaction sequence was used to obtain cis-alkenes (Scheme 16).[29]

SCHEME 16:

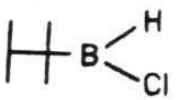


It has been extended successfully to the synthesis of muscalure,[30] a sex pheromone of the housefly (Musca domestica), from 1-tridecene and 1-decyne (Scheme 17).

SCHEME 17:



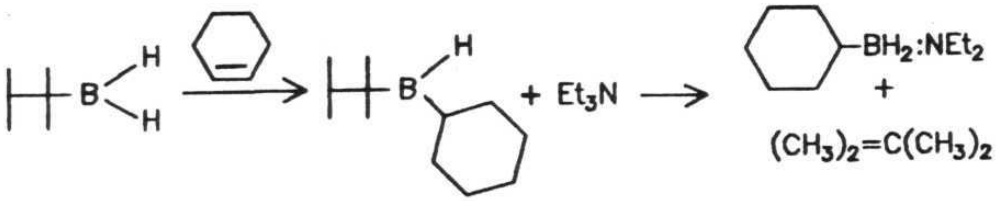
Thexylchloroborane:

Thexylchloroborane,  can be prepared by treating thexylborane with an ethereal solution containing an equimolar amounts of dry hydrogen chloride (eq. 5).[31]

— (5)

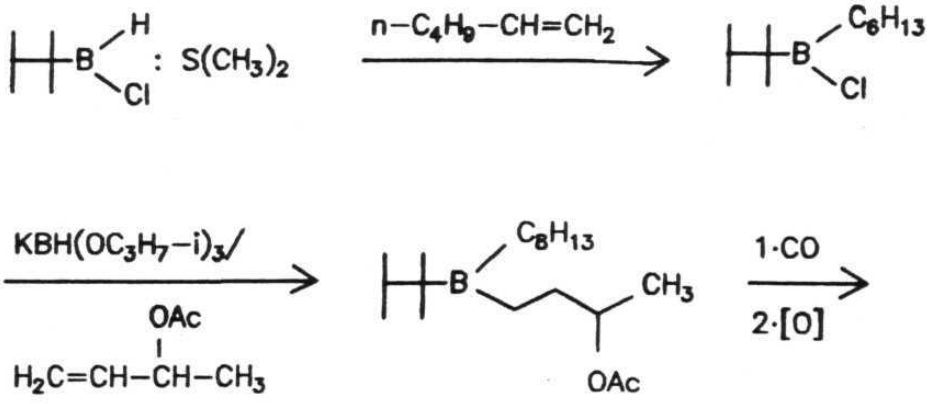
Thexylborane itself can be used for the preparation of monoalkylborane aminates through a hydroboration-elimination sequence (Scheme 18).[32]

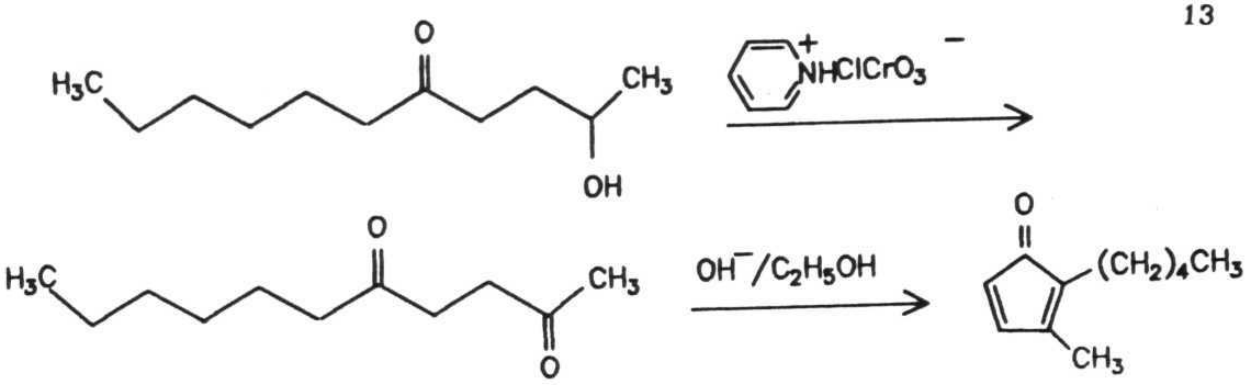
SCHEME 18:



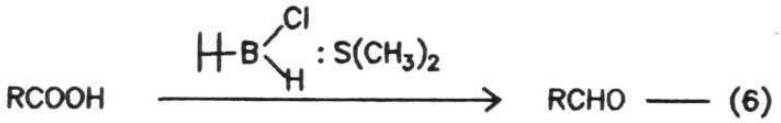
Thexylchloroborane has been used in the synthesis of dihydrojasmone [33] (Scheme 19), which is an important perfume ingredient and is a constituent of bargamot oil.

SCHEME 19:





An useful application of thexylchloroborane (eq. 6) is in the reduction of RCOOH into RCHO. Other borane reagents generally lead to over reduction to the corresponding alcohols.[34]



Catecholborane:

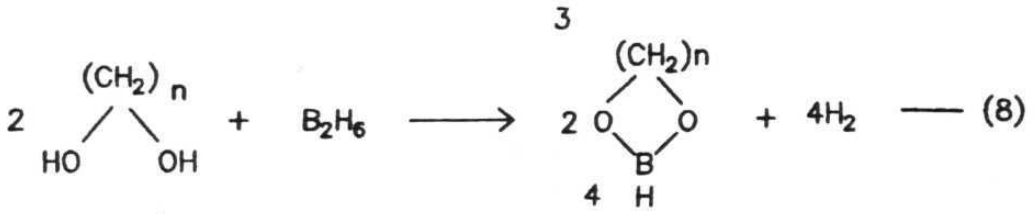
Preparation and applications of catecholborane (1,3,2-benzodioxo-borole) in the hydroboration of alkenes and alkynes:

Although many interesting transformations can be achieved using partially alkylated hydroborating agents, there is always a disadvantage of the need of separation of a side product formed during oxidation. Use of haloboranes X_2BH (X = Cl or Br) has advantages in this aspect. However, preparation and hydroboration using haloboranes

of this type require BCl_3 or BBr_3 reagents which are relatively strong acids and are not readily accessible. Alkoxy and aryloxyboranes of the type $(RO)_2BH$ or $(ArO)_2BH$ should be also useful and catecholborane has been proved to be a very useful reagent.[35] Since the present work has been undertaken for developing synthetic methods based on catecholborane, it will be helpful to review the synthesis and applications of catecholborane in detail.

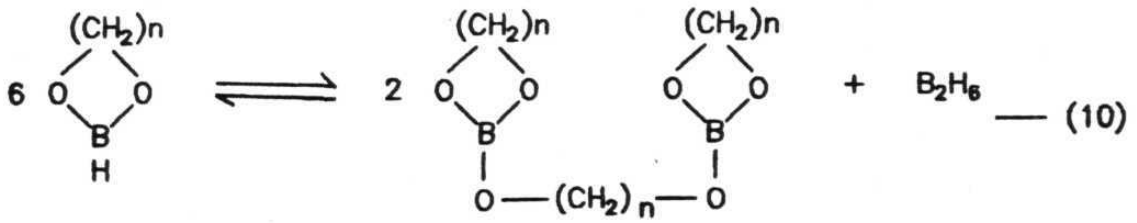
Alcohols such as methanol and glycols readily react with diborane to give dialkoxyboranes 3[36] and 4[37] respectively (eq. 7 and 8).

$$4CH_3OH + B_2H_6 \longrightarrow 2(CH_3O)_2BH + 4H_2 \quad \text{— (7)}$$

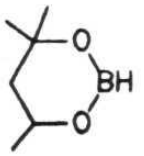


Unfortunately, these alkoxyboranes cannot be used for hydroboration, since they are unstable and rapidly undergo disproportionation (eq. 9 and 10).

$$6(CH_3O)_2BH \rightleftharpoons 4(CH_3O)_3B + B_2H_6 \quad \text{— (9)}$$

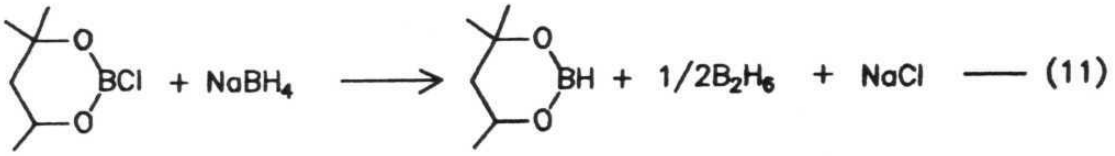


However, more hindered analogue of these dialkoxyboranes such as 4,4,6-trimethyl-1,3,2-dioxaborinane, 5 is reported to be stable towards disproportionation and hence can be used for the hydroboration of alkenes[38] and allenes[39].



5

This reagent was found to be less reactive than borane which can be attributed to the Π-bonding between boron and oxygen.[38] It was prepared from 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane by reduction with sodium borohydride in tetraglyme in 50% yield (eq. 11).

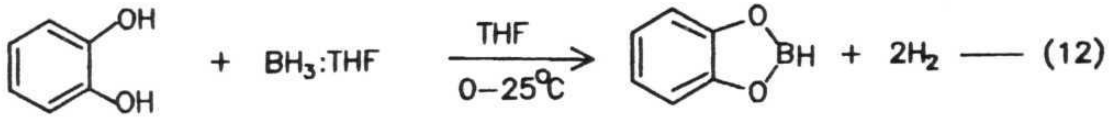


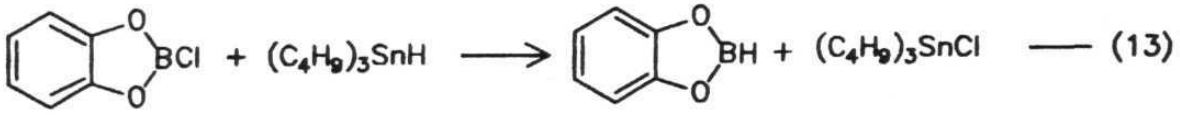
The hydroboration of 1-octene with this reagent takes place at 100° to give the addition of boron at the terminal position as the only observable product, in 20% yield. Hydroboration of alkynes and allenes have also been carried out with this reagent.

The diaryloxy analogue, such as catecholborane has been found to be a more reactive hydroborating agent.[40] In this case, since the oxygen 2p electrons can be delocalized into the benzene ring, the Π-bonding between boron and oxygen gets weakened. This makes

catecholborane a versatile hydroborating and reducing agent. The chemistry of catecholborane was extensively studied by various groups.

Catecholborane can be readily prepared by the reaction of catechol dissolved in THF with borane-THF (eq. 12).[41,42] Catecholborane has been also prepared by the reduction of 2-chloro-1,3,2-benzodioxaborole with tributyltin hydride (eq. 13).[43] Catecholborane formed in these cases was isolated by distillation.

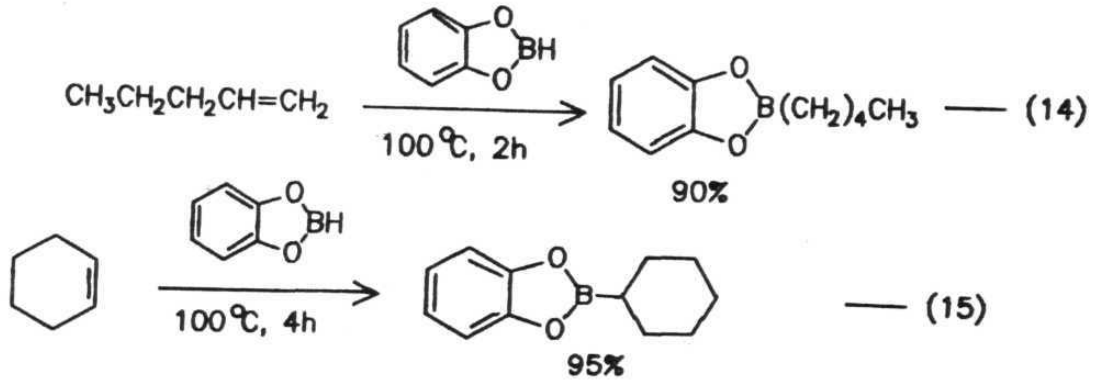




Catecholborane has remarkable stability compared to other dialkoxyboranes such as 3[36] and 4[37], which undergo rapid disproportionation (eq. 9 and 10). It shows no decomposition for 4h in refluxing THF solution or for 2h at 120°C as a neat reagent.[41] Catecholborane can be stored even for 1 yr. at 0-5°C without any detectable loss in hydride activity.

Hydroboration of alkenes with catecholborane is sluggish at 25°C. Since catecholborane is thermally stable, these hydroborations can be

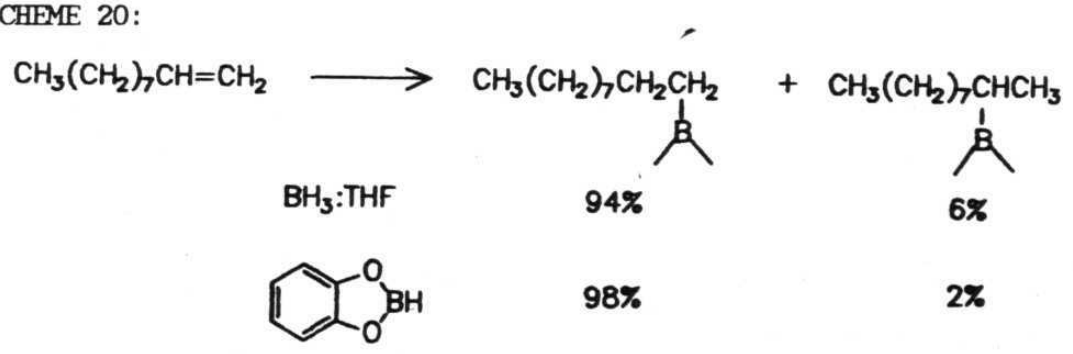
carried out at higher temperatures. For example, 1-pentene and cyclohexene were hydroborated at 100°C (eq. 14 and 15) giving quantitative yields with 10% excess of the reagent.



We have investigated the possibility of performing hydroborations using catecholborane in the presence of BH_3-Lewis base complexes (Chapter-2).

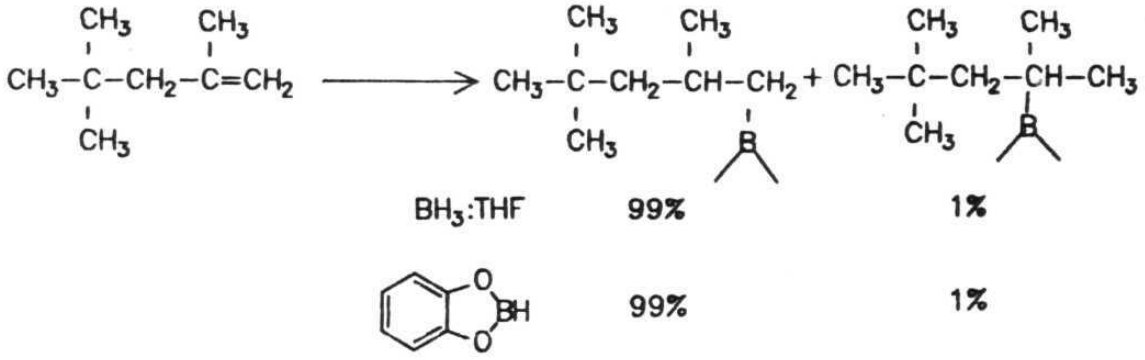
A study of directive effects in the hydroboration of alkenes showed that catecholborane is more sensitive to the structure of the alkene than BH_3:THF (Scheme 20).[35] Boron addition is exclusively observed at the less hindered C-atom of the alkene. With BH_3:THF as a hydroborating agent, monosubstituted terminal alkenes proceed to place the boron atom preferentially at the terminal position.

SCHEME 20:



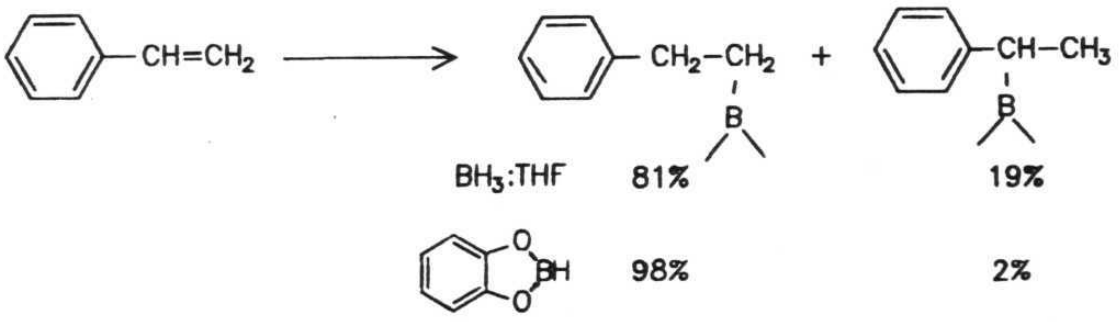
Disubstituted terminal alkene places the boron atom exclusively at the terminal position (Scheme 21).

SCHEME 21:



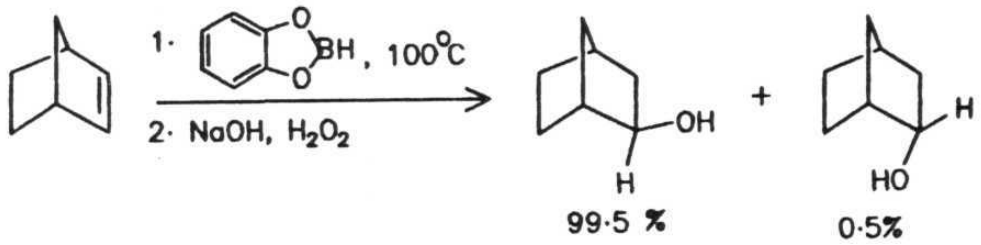
The hydroboration of styrene with BH_3:THF results in only 81% of 2-phenyl-1-ethyl boron compound due to the powerful electronic effect of the phenyl substituent (Scheme 22).

SCHEME 22:

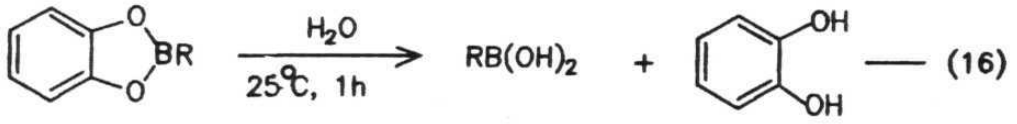


Stereoselectivity observed in the hydroboration of alkenes with catecholborane is comparable to that observed for BH_3:THF. For example, hydroboration-oxidation of norbornene with catecholborane gives predominantly exo-norboneol (Scheme 23).

SCHEME 23:



The B-alkylcatecholboronic esters undergo rapid hydrolysis upon stirring with excess water at 25°C to yield water insoluble crystalline boronic acids (eq. 16) which can be easily separated from highly water soluble catechol. These boronic acids have been found to be useful synthetic intermediates. This is where, catecholborane wins over the partially alkylated boranes.



— (16)

One of the important features of these B-alkylcatecholborane derivatives is their use in the preparation of mixed trialkylboranes (RBR^1_2), which are generally not possible via direct hydroboration with BH_3:THF. These mixed trialkylboranes can be prepared by the direct reaction of B-alkylcatecholborane with alkylmagnesium reagent (eq. 17).[44]

— (17)

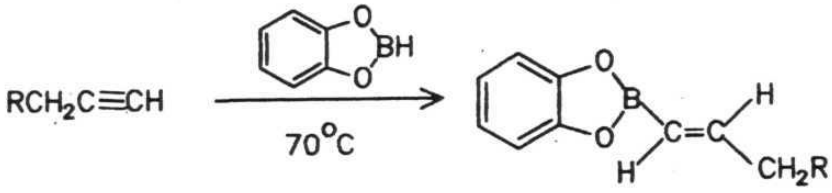
where R= Et, Pr, Bu

R^1=Et, Pr, Bu, Ph, $PhCH_2$

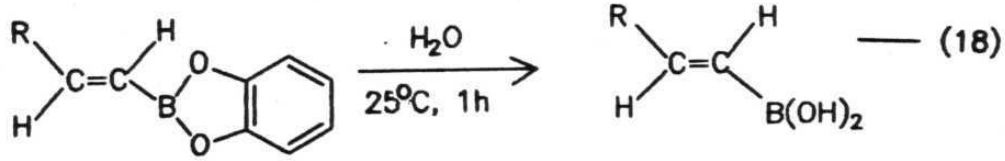
These mixed trialkylboranes can be utilized in the various synthetic transformations that are possible with organoboranes.[4-7] We have utilized this reactivity pattern for the synthesis of alkyl and aryl olefins from alkenylcatecholborane (Chapter-4).

Catecholborane hydroborates alkynes only at elevated temperature. Terminal alkynes are hydroborated at 70°C in 1h (Scheme 24) and internal alkynes get hydroborated in 2-4h at 70°C. Quantitative yields of alkenylcatecholborane are obtained without any dihydroboration.[41]

SCHEME 24:



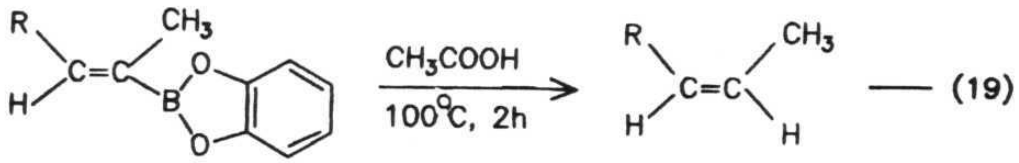
The B-alkenylcatecholboranes undergo rapid hydrolysis upon stirring with excess of water at 25°C (eq. 18),[41] to give crystalline solids of low solubility in water.These can be conveniently isolated and handled in air, without significant deterioration.[45]



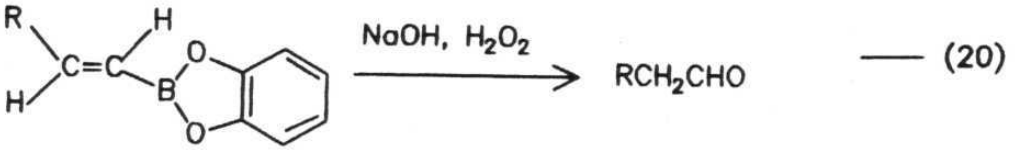
(18)

Protonolysis of these alkenylcatecholboranes give stereo-

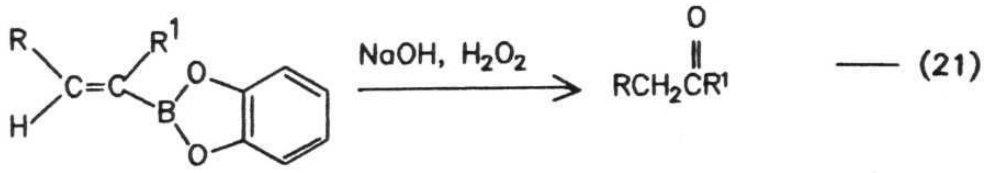
specific alkenes (eq.19).[41] The terminal alkenylcatecholboranes upon oxidation with alkaline peroxide give aldehydes (eq. 20) and the internal alkenylcatecholboranes give the corresponding ketones (eq. 21) in good yields.[41]



— (19)



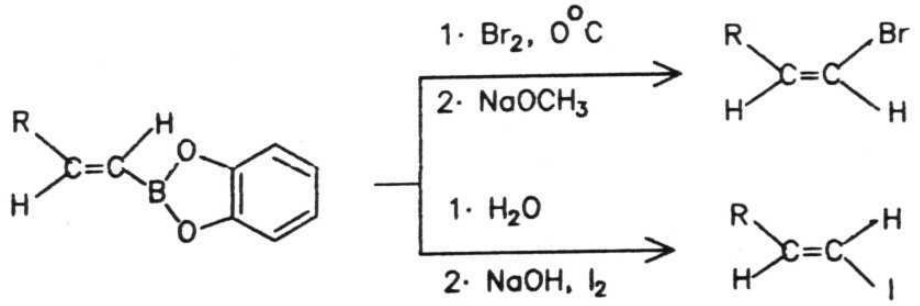
— (20)



— (21)

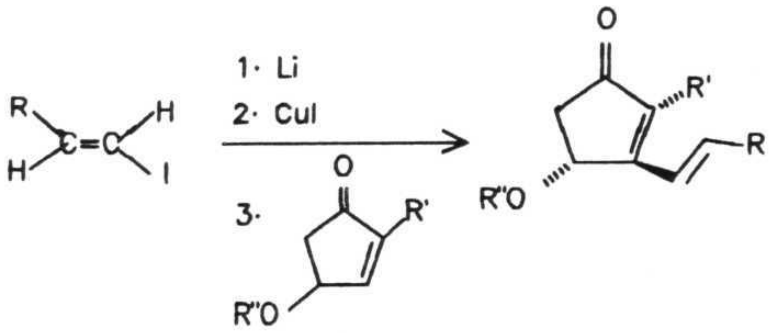
Alkenylcatecholborane reagents can be converted selectively to cis or trans halo-alkenes depending on halogen used (Scheme 25).[46,47]

SCHEME 25:



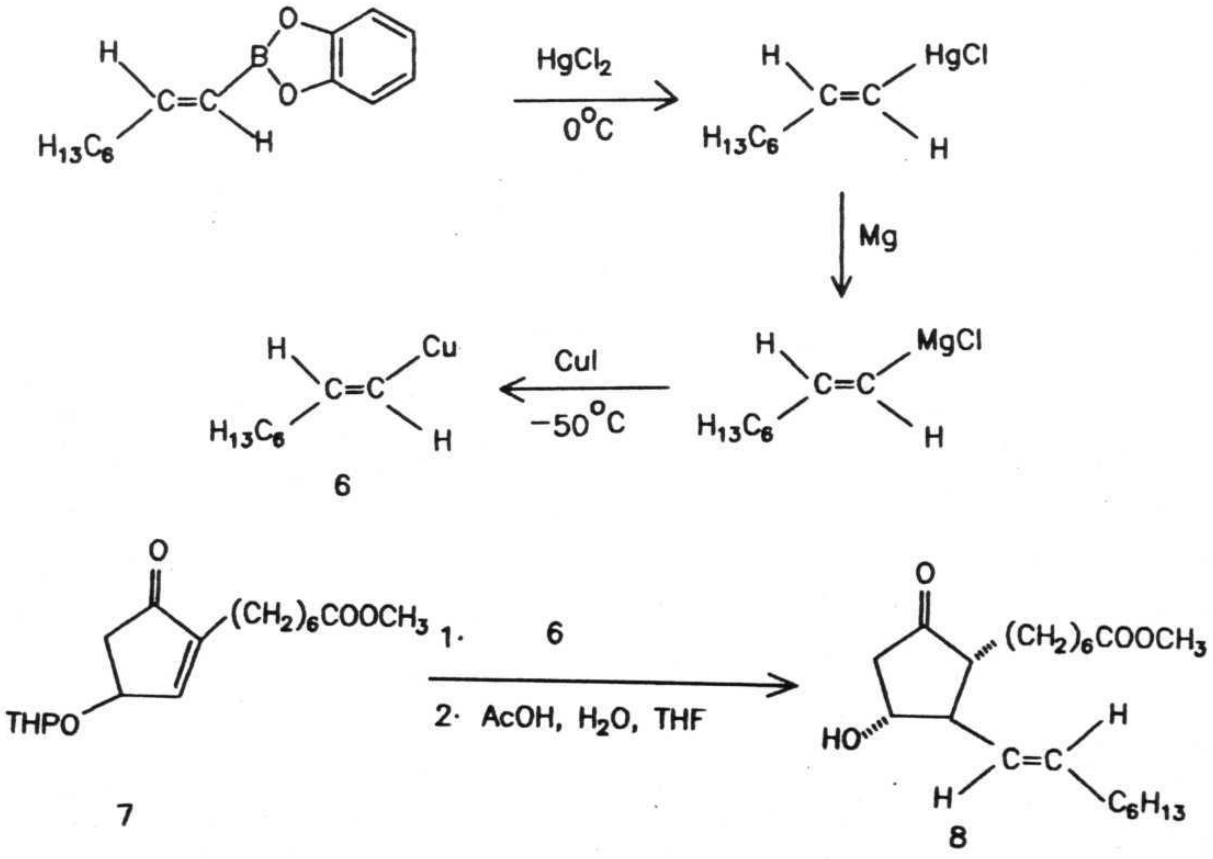
The E-alkenyl-1-iodides thus prepared, were utilized in the syntheses of prostaglandins (Scheme 26).[48-50]

SCHEME 26:



Mercury(II) compounds react with alkenylboronic acids to yield organomercurials (Scheme 27). This provides a convenient route for the preparation of other alkenylmetallics stereospecifically. For example, alkenylcopper reagent can be prepared from alkenylmercurial which are used in the synthesis of a prostaglandin analogue[51] (Scheme 27).

SCHEME 27:

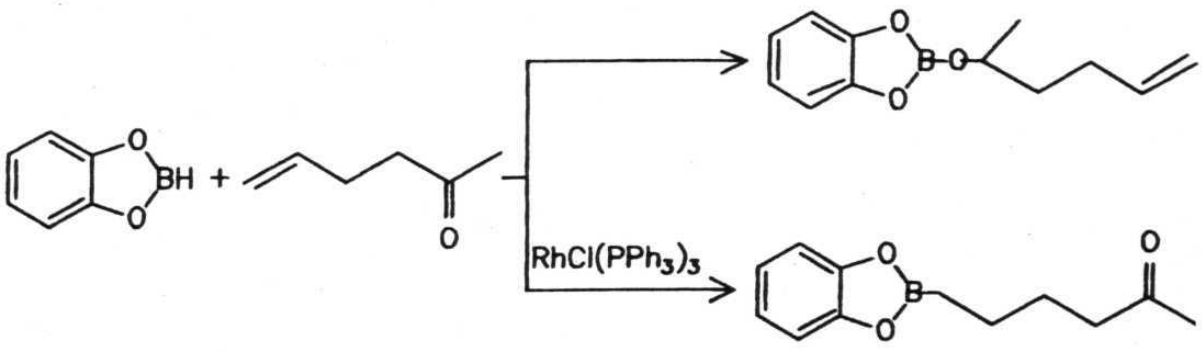


The alkenylcopper reagent 6 can be added stereospecifically to 7 which upon O-deprotection gives (+)-15-deoxy PGE, methyl ester 8.

We have investigated the transfer of alkyl and alkenyl groups from catecholborane to copper (Chapter-4).

As mentioned earlier, catecholborane hydroboration of alkenes and alkynes is sluggish at 25°C. Manning and Noth[52] in 1985 reported that the activity of catecholborane could be increased catalytically using certain metal catalysts such as Wilkinson's complex, $[ClRh(PPh_3)_3]$. Alkynes and alkenes were hydroborated without difficulty at room temperature in the presence of this catalyst. It was found that CC double bonds of olefins were preferentially hyroborated even in the presence of reactive keto group using Wilkinson's complex as a catalyst. In the absence of the catalyst, keto group was attacked preferentially over olefin group (Scheme 28).

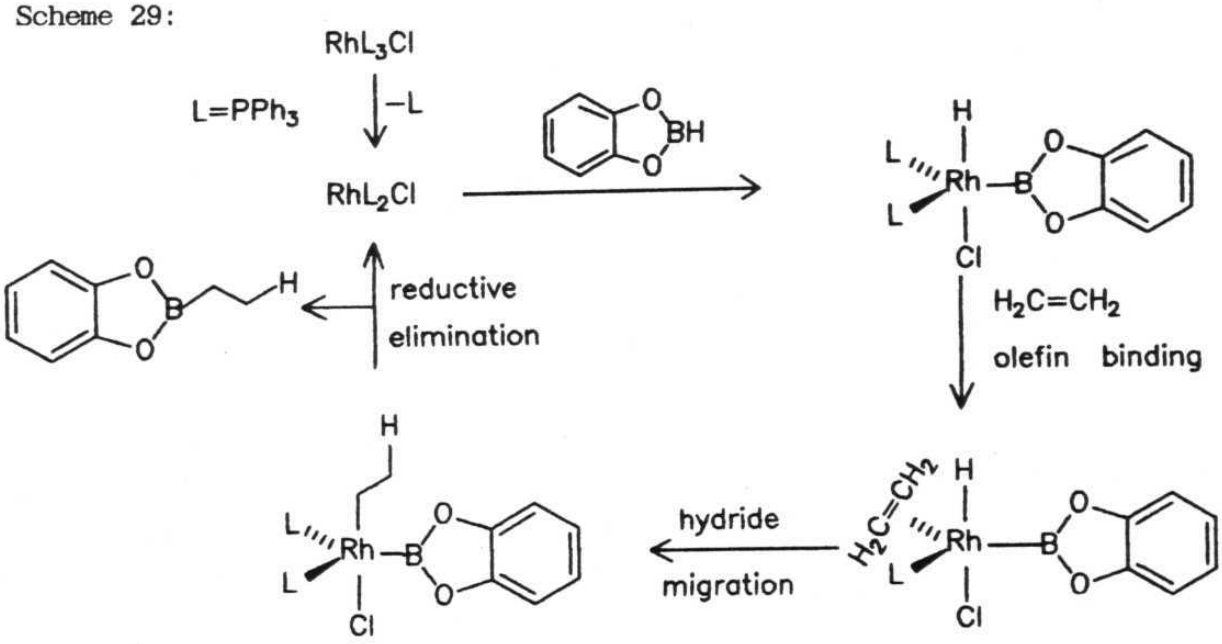
SCHEME 28:



Several other rhodium complexes such as $[RhCl(CO)\{P(C_6H_5)_3\}_2]$, $[RhCl(CO)\{As(C_6H_5)_3\}_2]$, and $[RhCl(cod)_2]$ (cod = 1,5 cyclooctadiene) were also suitable as catalysts for the hydroboration with catecholborane.

Manning and Noth suggested a mechanism for olefin hydroboration (Scheme 29), which is analogous to that proposed for more thoroughly investigated reactions such as hydrogenation (Scheme 29), hydrosilation and hydroformylation.[53]

Scheme 29:

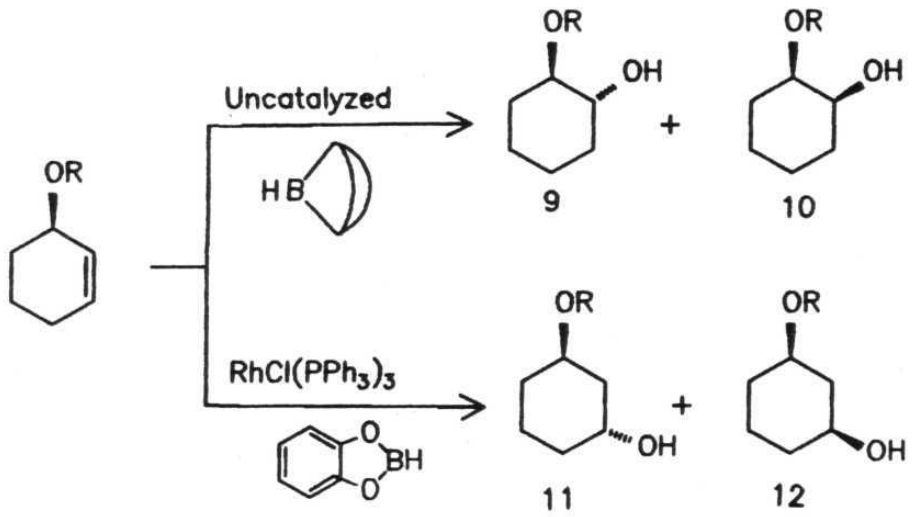


Evans *et al.*[54] were the first to report that the stereochemical consequences of the catalyzed and uncatalyzed processes are different.

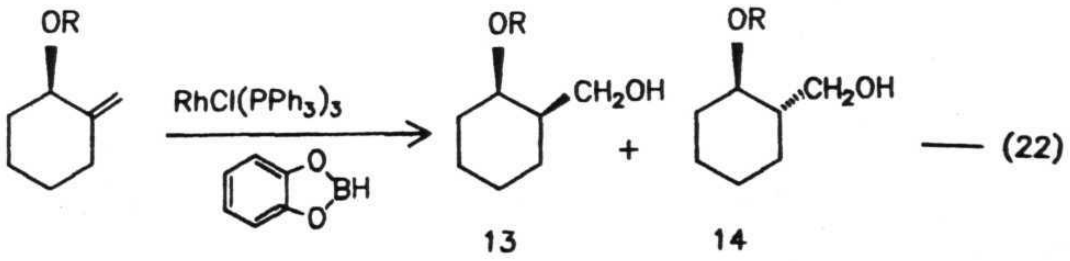
For example, in the hydroboration of cyclic 1,2-disubstituted allylic alcohol derivatives, it was found that the regioselectivity of

the catalyzed reaction is opposite to that of the uncatalyzed reaction (Scheme 30). The hydroboration reaction using 9-BBN, without a catalyst is dominated by electronic effects favouring the anti 1,2-diol 9, while the catalyzed reaction of catecholborane favours the anti 1,3-diol 11.

SCHEME 30:



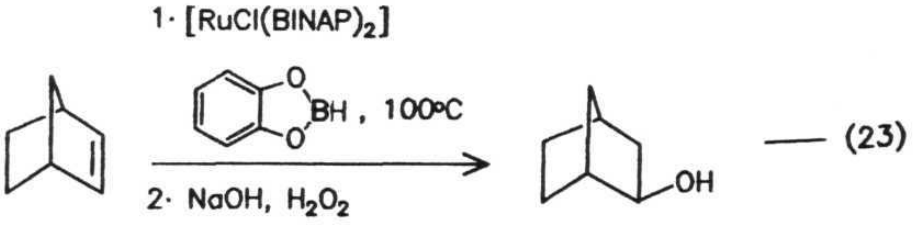
The uncatalyzed reactions with 9-BBN show only marginal levels of stereo control in the hydroboration of exocyclic cycloalkenes whereas the catalyzed hydroboration provides the Z-isomer 13, with excellent diastereoselectivity (eq. 22).



(22)

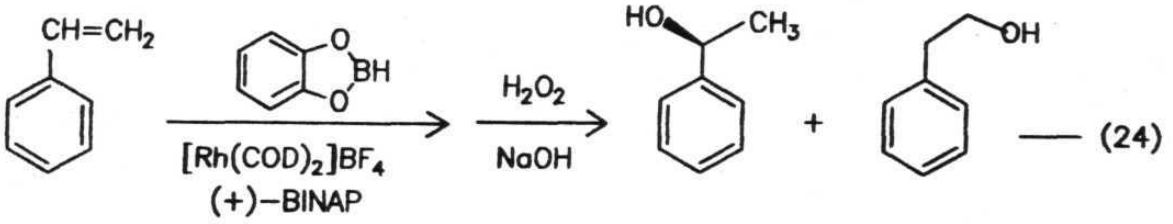
Burgess *et al.*[55] found that the enantioselective hydroboration of

alkenes by catecholborane is facilitated by using homochiral Rh-phosphine complexes and the oxidation of these products were found to afford optically active alcohols. For example, treatment of norbornene with catecholborane in the presence of rhodium-DIOP or rodium-BINAP catalysts gave after oxidation, exo-norbornol (eq. 23) in near quantitative yield. The optical purity of the norborneol produced was found to be inversely proportional to the reaction temperature. The Rh-BINAP catalyst gives slightly more enantioselective product than the Rh-DIOP catalyst.



— (23)

The hydroboration of several other prochiral olefins were studied (eq. 24 and 25).[56]



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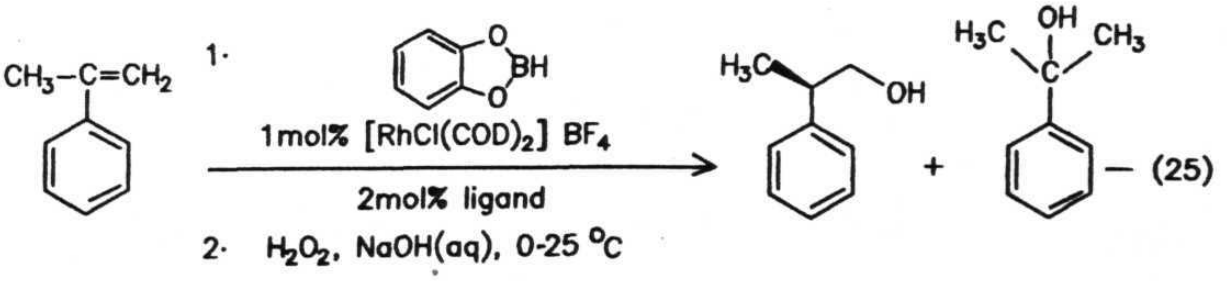
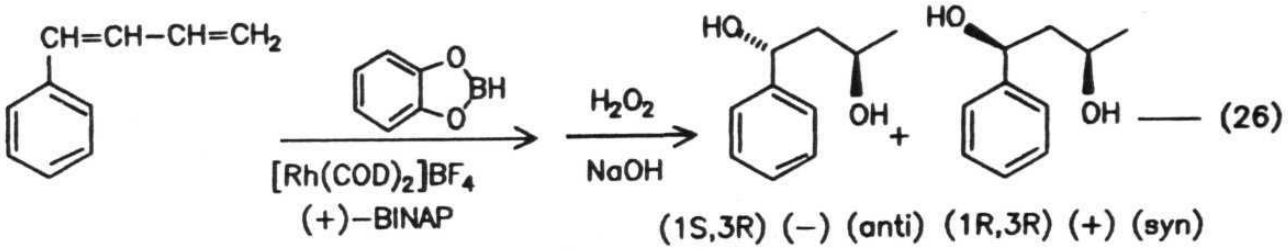


— (25)

1-Phenyl-1,3-butadiene gives optically active (1S, 3R)-1-phenyl-

1,3-butanediol upto 67% ee (eq. 26).[57]



(26)

Catecholborane as a reducing agent:

Catecholborane is also an useful reducing agent (Table 1). In addition to being used in the reduction of common functional groups such as aldehydes and ketones, it is advantageous in the reduction of certain functional groups and also in selective reductions.

Catecholborane in conjunction with Corey's oxazaborolidine[58-63] has been used for the reduction of α-chloro substituted ketones (Scheme 31)[64] which are used for the enantioselective synthesis of aminoacids .

SCHEME 31:

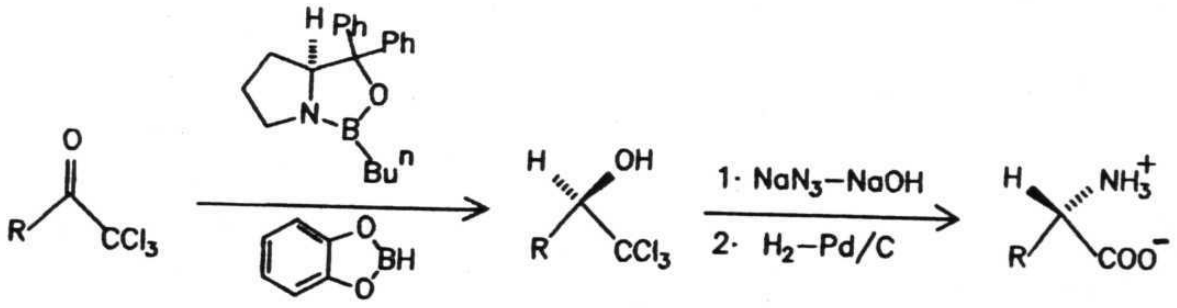
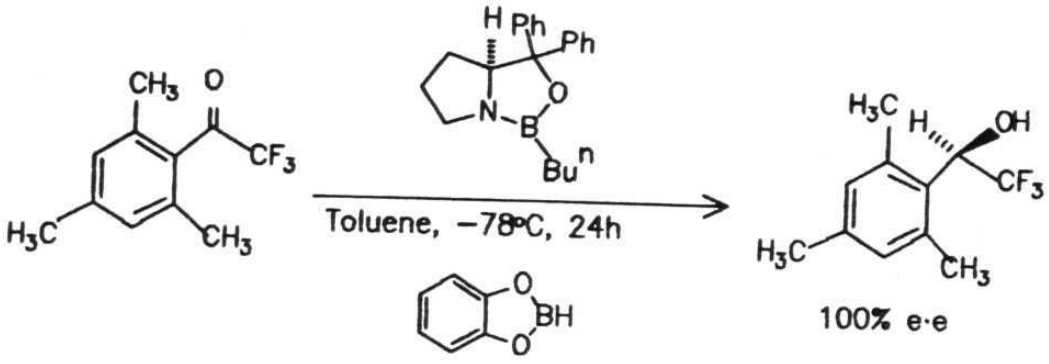


Table 1.1: Relative reactivity of catecholborane towards various functional groups.

S.No.	Functional Groups	Product	Rate
1.	>C = NNHTS	>CH_2	Fast
2.	$-\overset{H}{\underset{\vert}{C}} = O$	$-CH_2OH$	Fast
3.	>S = O	-S-	Fast
4.	>C = O	>CHOH	Moderate
5.	$-\overset{OH}{\underset{\vert}{C}} = O$	$-CH_2OH$	Moderate
6.	$-\overset{NR_2}{\underset{\vert}{C}} = O$	$-CH_2NR_2$	Moderate
7.	$-\overset{O}{\overset{\diagup\diagdown}{\underset{O}{\underset{\vert\vert}{C}}}}-\underset{O}{\underset{\vert\vert}{C}}-$	$-\overset{\vert}{\underset{\vert}{CH}}-\overset{\vert}{\underset{\vert}{COH}}$	Moderate
8.	$-\overset{O}{\underset{\vert\vert}{C}}-O-\overset{O}{\underset{\vert\vert}{C}}-$	2-CH_2OH	Moderate
9.	-C≡C-	Alkenyl-B<	Moderate
10.	$-\overset{OR}{\underset{\vert}{C}}=O$	$-CH_2OH$	Slow
11.	$-\overset{Cl}{\underset{\vert}{C}}=O$	$-CH_2OH$	Slow
12.	-C≡N	$-CH_2NH_2$	Slow
13.	>C=C<	Alkyl-B<	Slow

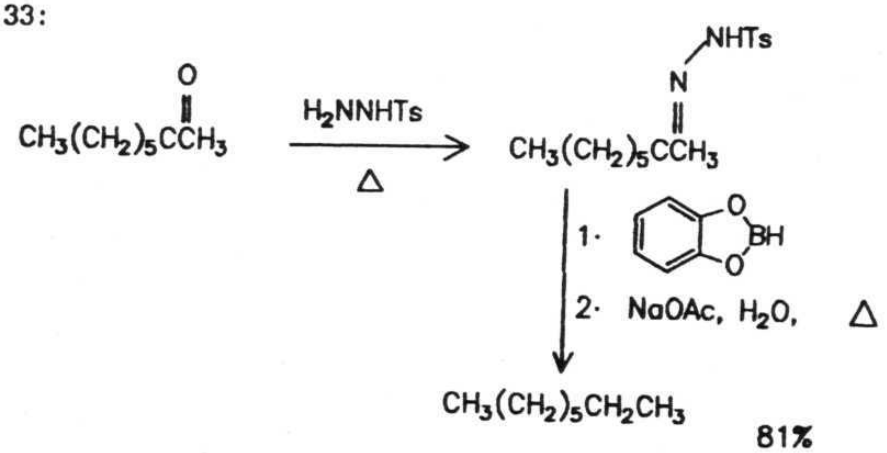
Reduction of trifluoroacetylmesitylene with catecholborane produces mesityl-2,2,2-trifluoroethanol as a single pure enantiomer in 100% yield (Scheme 32).[65]

SCHEME 32:



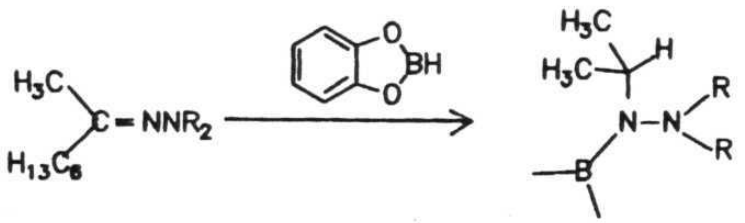
Catecholborane can be used as a mild alternative to the Wolff-Kishner process. For example, tosylhydrazones are readily reduced with catecholborane (Scheme 33).[66,67]

SCHEME 33:



Similarly 2-octanone N,N-dimethylhydrazone is also very reactive with catecholborane and produces the corresponding hydrazinoborane derivative, in nearly quantitative yields (Scheme 34).

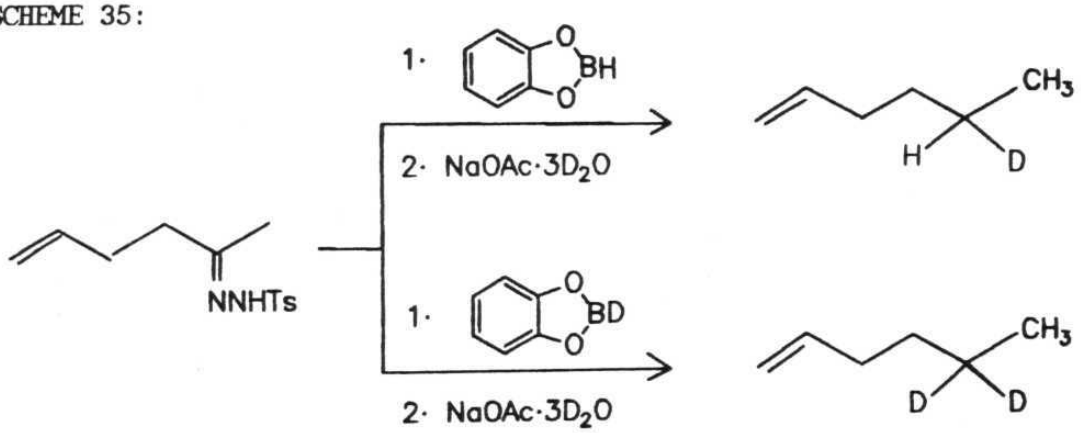
SCHEME 34:



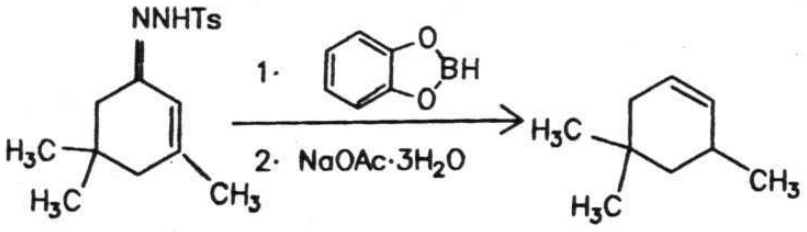
R=CH_3, CH_3; H, Ts

Hydrazones derived from olefinic aldehydes and ketones also yield hydrocarbon products (Scheme 35). Hydrazones derived from α, β-unsaturated derivatives lead to double bond migration (Scheme 36).[66,68,69]

SCHEME 35:



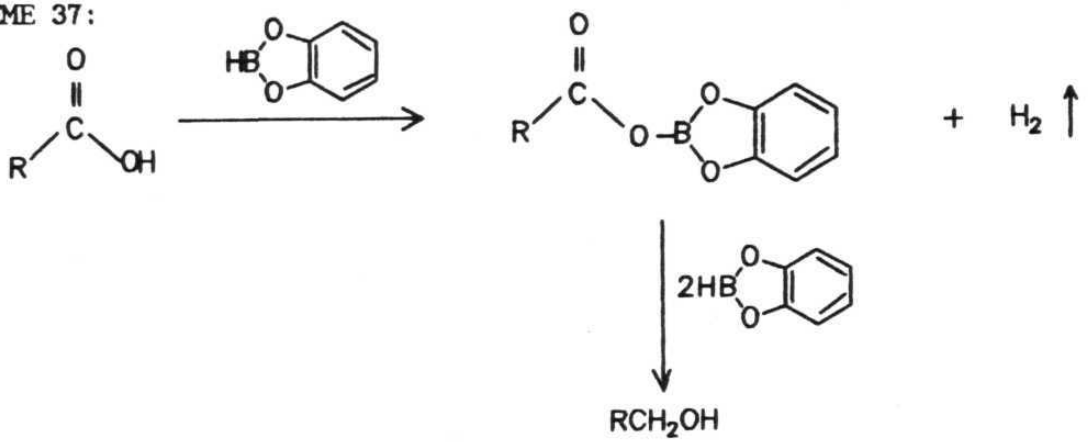
SCHEME 36:



Aliphatic and aromatic acids react rapidly with 1 equivalent of catecholborane liberating H_2 gas to form the corresponding

acyloxyborane in quantitative yield[70,71] (Scheme 37), which on reaction with two mole eq. of catecholborane yields the corresponding alcohol after hydrolysis.

SCHEME 37:



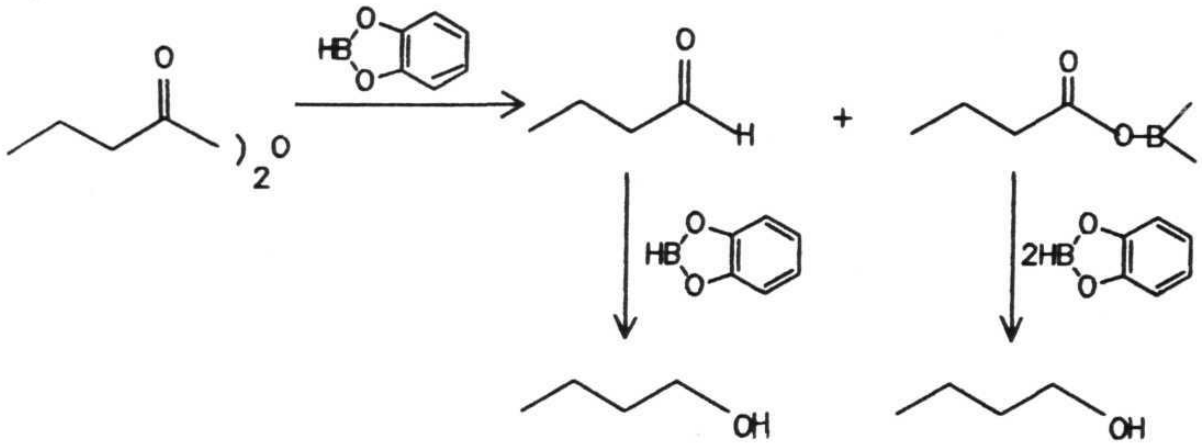
Catecholborane reacts at different rates with aliphatic and aromatic carboxylic acids. For example, propionic acid reacts at a moderate rate, but benzoic acid gets reduced slowly. Presumably, this difference is due to the weaker Lewis basicity of the carbonyl group in the latter compound.

The most interesting feature about the reduction of catecholborane, is the reduction of sodium salt of stearic acid.[67] It is interesting to note that $RCOO^-$ just complexes with BH_3 to give $RCOOBH_3^-$, without undergoing reduction at room temperature.[72] We investigated this aspect to understand this difference in reactivity (Chapter-3).

Anhydrides require 4 equivalents of catecholborane for complete

reduction. Presumably, the first equivalent of hydride produces the corresponding aldehyde and an acyloxyborane (Scheme 38).[67]

SCHEME 38:



Trace amounts of aldehyde have been isolated in this reaction. This indicates that the reduction of anhydride by catecholborane is slow compared to the reduction of the aldehyde, produced from the initial addition of catecholborane to the anhydride.

Functional groups such as nitriles, esters and acid chlorides react slowly with catecholborane. Rate of reduction is comparable to the hydroboration of alkenes and alkynes. Hence, when these functional groups are present along with alkenes and alkynes, a modest amount of concurrent reduction occurs.

Functional groups such as aldehydes, imines and sulfoxides are readily reduced by catecholborane[35,66] and would not be expected to survive a hydroboration reaction. Thus, citronellal is reduced to the

unsaturated alcohol with catecholborane in 87% yield (eq.27).[85]

$$(CH_3)_2C{=}CH(CH_2)_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow[25^{\circ}C]{CHCl_3} \xrightarrow{H_3O^+} (CH_3)_2C{=}CH(CH_2)_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2-CH_2OH \qquad \text{—— (27)}$$

Although various methods are available for the preparation of catecholborane, it was of interest to us to develop simple and convenient method for the preparation of aryloxyboranes, in general and catecholborane, in particular. In this laboratory, simple method of preparation of diborane using $I_2/NaBH_4$ was developed through modification of a method reported in 1965.[73] The B_2H_6 generated in this way has been used for the preparation of BH_3-Lewis base complexes for synthetic applications (Scheme 39).[74-77]

SCHEME 39:

$$2NaBH_4 + I_2 \xrightarrow[25^{\circ}C]{\text{diglyme}} 2NaI + B_2H_6 + 1/2H_2$$

$$B_2H_6 \xrightarrow{2LB} 2LB{:}BH_3$$

We have decided to investigate the preparation of aryloxyboranes by the reaction of B_2H_6 with appropriate phenolic derivatives and examine their reactivities. The results obtained in these investigations are discussed in Chapters 2, 3 and 4.

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CHAPTER - 2

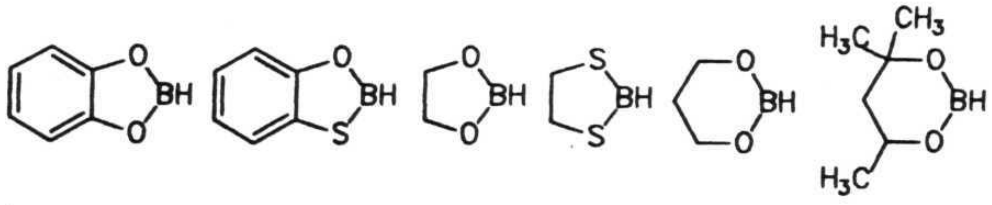
Studies on the syntheses and applications of aryloxyboranes.

INTRODUCTION

Selective hydroboration is achieved with a number of partially alkylated borane (R_2BH, RBH_2 *etc.*) complexes.[1] Some disubstituted monofunctional reagents such as isopinocampheylborane, 9-borabicyclo-nonane, dicyclohexylborane have been extensively used as mono-hydroborating agents. This property has been used for carrying out various useful transformations as discussed in Chapter-1. However, the side products obtained in the oxidation of alkyl boranes may pose problems in the isolation of products. Use of haloboranes is advantageous in this respect.[2-4]

Unfortunately, these haloboranes are strong Lewis acids and are not very stable and are not readily accessible. There are a number of stable heterosubstituted borolanes and borinanes available (Figure 1). All these reagents show reduced reactivity compared to BH_3 or dialkylboranes due to additional Π-bonding between oxygen and boron.[5-8]

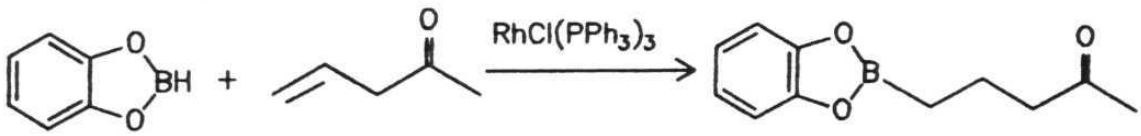
FIGURE 1:



As outlined in Chapter-1, catecholborane hydroborates alkenes at 100°C and alkynes at 70°C.[9,10,11] The chemoselectivity of catecholborane in the reaction of functionalized alkenes is not well established, but moderately reactive functional groups like esters, might be reduced competitively at higher temperatures used for hydroboration. Hence, there is a need for finding means to increase the reactivity, so that hydroboration of alkenes and alkynes can be achieved at lower temperature.

Manning and Nöth[12] in 1985 successfully hydroborated olefins, in the presence of ketone functionality at room temperature using a transition metal complex as catalyst (Scheme 1).

SCHEME 1:



Later, many groups were successful in their attempts of hydroborating olefins using various transition metal complexes as catalysts.[13,14,15] We have undertaken this investigation in order to develop new routes of syntheses and utilization of catecholborane and other aryloxyboranes.

RESULTS AND DISCUSSION

Synthesis and Utilization of catecholborane:

Recently, a convenient method has been developed in this laboratory for the generation of diborane through a slight modification of a reported procedure, using $NaBH_4$ and I_2. The diborane generated in this way can be complexed with Lewis bases in a solvent of interest (eq. 2).[16]

$$\underset{\text{in DG}}{2NaBH_4} + \underset{\text{in DG}}{I_2} \longrightarrow B_2H_6 + 2NaI + H_2 \quad \text{—— (1)}$$

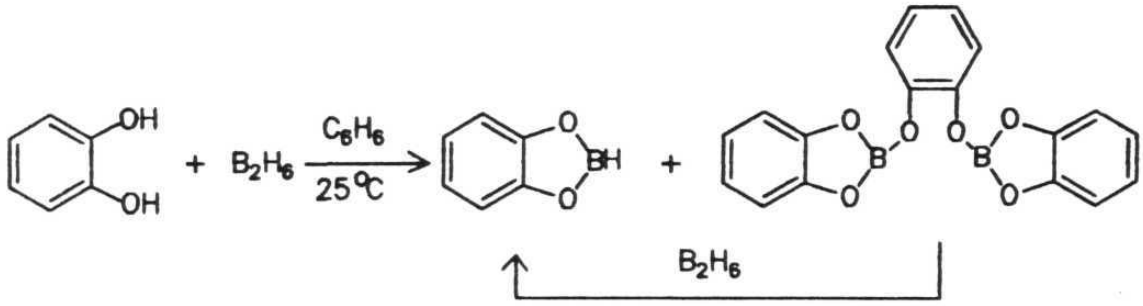
$$B_2H_6 + LB \longrightarrow H_3B{:}LB \quad \text{—— (2)}$$

Generally, catecholborane (1,3,2-benzodioxaborole) is prepared in THF solvent by the reaction of catechol with BH_3:THF.[9,17] The catecholborane is isolated by prior distillation of THF solvent, followed by distillation of the residue under vacuum. Since excess BH_3 is generally used for preparation in THF, the distillation is necessary. It was thought that catecholborane could be prepared in non-polar solvents such as benzene and toluene by passing B_2H_6 through a suspension of catechol. Since B_2H_6 is not soluble in these solvents, there will not be any other borane species present. Indeed, this was

observed. The catecholborane prepared in this way showed a sharp >BH absorption at 2680 cm^{-1}, similar to that reported for catecholborane.[18] Hydride analysis data were in accordance with the presence of a single hydride.

Since some polymeric aryloxyboranes could also be formed along with catecholborane, excess diborane was utilized (Scheme 2).

SCHEME 2:



The catecholborane thus prepared was used for the hydroboration of alkenes and 1-alkynes (Scheme 3).

SCHEME 3:

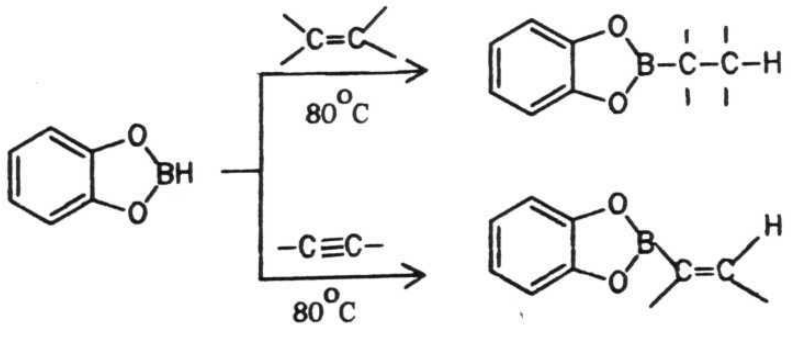
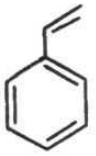
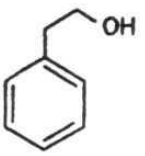
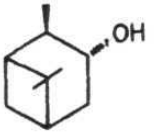


Table 2.1: Hydroboration of representative alkenes using catecholborane prepared in benzene.[a]

Entry No.	Substrate	Product[b]	Yield(%)[d]
1.	$n\text{-}C_8H_{17}CH{=}CH_2$	$n\text{-}C_8H_{17}CH_2CH_2OH$	88
2.			80[c]
3.			85

a) Reactions were carried out under N_2 atmosphere using catecholborane (10.5 mmol) and substrate (10 mmol) in benzene (40 mL) at 80°C for 12h (see experimental section).

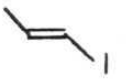
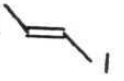
b) Oxidation was carried out using 1N $NaOH/H_2O_2$.

c) ^1H NMR spectrum indicated the presence of isomeric 1-phenylethanol upto 8%.

d) Yields are of products isolated by distillation under reduced pressure and/or by column chromatography on silica gel. The products were identified by spectral data (IR, ^1H and ^{13}C NMR) and comparison with the data of authentic samples.

Alkenes such as 1-decene, styrene and α-pinene were hydroborated by refluxing in benzene solvent in 12h in individual runs. The regio and stereoselectivites obtained in the hydroboration of representative alkenes are same as those observed in the hydroboration of catecholborane, prepared using BH_3:THF.[19]

Table 2.2: Hydroboration of alkynes using catecholborane prepared in benzene.[a]

Entry No.	Substrate	Product	Yield(%)[d]
1.	$n\text{-}C_8H_{17}\text{-}C\equiv CH$	$n\text{-}C_8H_{17}\text{-}CH_2\text{-}CHO$	90[b]
2.	$n\text{-}C_{10}H_{21}\text{-}C\equiv CH$	$n\text{-}C_{10}H_{21}\text{-}CH_2\text{-}CHO$	91[b]
3.	$n\text{-}C_8H_{17}\text{-}C\equiv CH$		70[c]
4.	$n\text{-}C_{10}\text{-}H_{21}\text{-}C\equiv CH$		72[c]

a) Reactions were carried out under N_2 atmosphere using catecholborane (10.5 mmol) and substrate (10 mmol) in benzene (40 mL) at 80°C for 12h (see experimental section).

b) Oxidation was carried out using 3N NaOAc/H_2O_2.

c) Iodination was carried out using 3N NaOH and I_2.

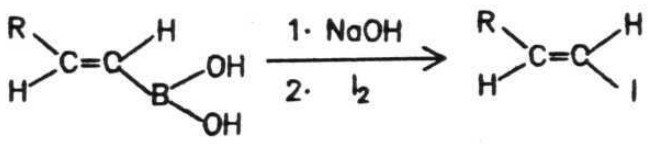
.....contd.

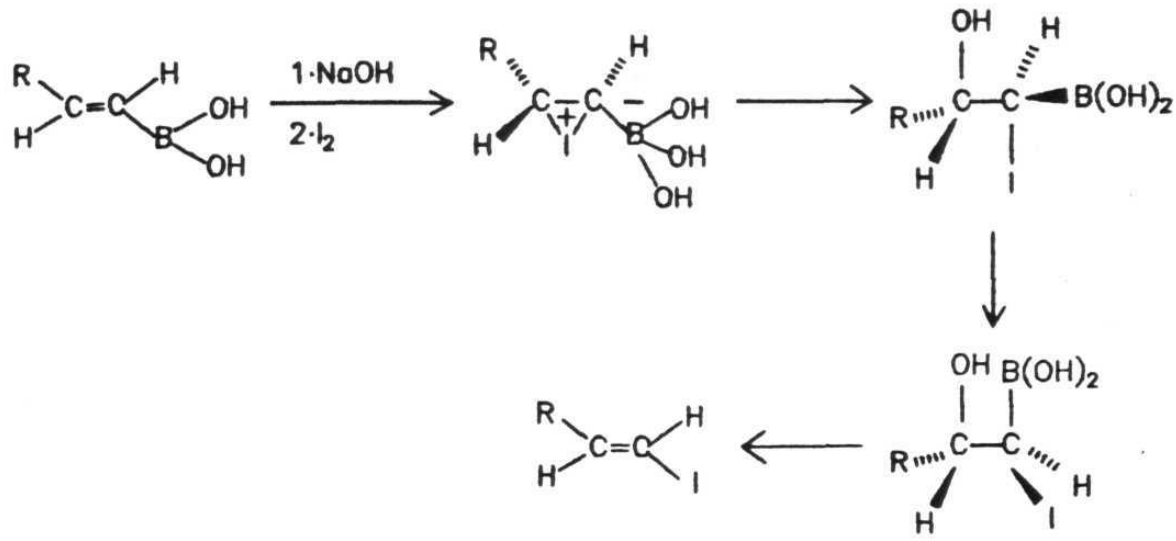
d) Yields are of products isolated by column chromatography on silica gel. The products were identified by spectral data (IR, ^{1}H and ^{13}C NMR) and comparison with the data of authentic samples.

In a similar manner, 1-decyne and 1-dodecyne were hydroborated to give alkenylboron derivatives, which on oxidation with $NaOAc/H_2O_2$ gave the corresponding aldehydes in 90-91% yields (Table 2.2). The alkenylboronic acids obtained through the addition of water to alkenylcatecholborane intermediates are readily converted to the corresponding E-1-iodo-1-alkenes on reaction with excess of NaOH and I_2 (entry nos. 3 and 4, Table 2.2) in 70-72% yield following the reported procedure.[20]

E-1-iodo-1-alkenes are useful compounds as discussed in Chapter-1 and the present synthesis from alkynes using the readily accessible starting materials should make this synthetic method attractive. The mechanism of the formation of the iodoalkene can be visualized as shown in Scheme 4.

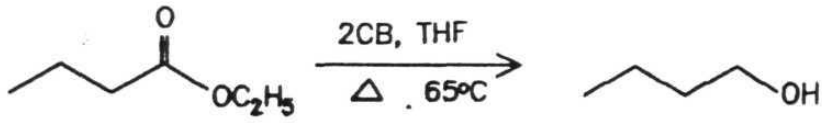
SCHEME 4:





The hydroborations using catecholborane can be carried out only at elevated temperatures.[19] At these temperatures other functional groups such as ketones, acids, esters, amides, nitriles, *etc.*, will be reduced competitively.[20,21] For example, the ester group is reduced by catecholborane at 65°C (Scheme 5).[21]

SCHEME 5:



Since competitive reduction is possible at higher temperatures along with hydroboration, it is of interest to examine the possibility of performing the hydroboration at room temperature so as to keep the other functional groups intact.

As described in Chapter-1, Manning and Nöth successfully hydroborated olefins with catecholborane at room temperature using

transition metal complexes such as Wilkinson's catalyst.[12] Later, several other groups[13,14,15] employed various transition metal complexes as catalysts. Enantioselective hydroborations were also carried out using homochiral transition metal complexes. (For details, see Chapter-1). Unfortunately most of these complexes used are expensive. In continuation of our studies on the development of new hydroborating agents,[23,24] we were looking for a convenient means for the catalysis of catecholborane hydroboration. In 1971, Brown and coworkers reported that triaryloxyboranes exchange with trialkylboranes in the presence of catalytic amount of BH_3:THF at 100°C to give the corresponding alkyl aryloxyborane derivatives (eq. 3).[25]

$$2R_3B + (ArO)_3B \xrightarrow[100\,^{\circ}C]{\text{cat } H_3B:THF} 3R_2BOAr \quad \text{—— (3)}$$

It was anticipated that such disproportionation reactions would most probably go through intermediates such as $(ArO)_2BH$ and/or R_2BH species (eq. 4-6).

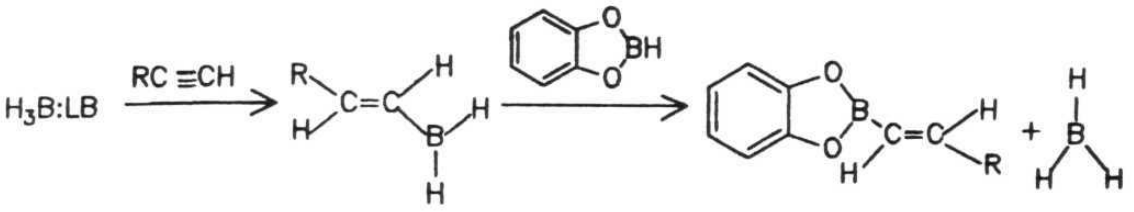
$$R_3B \xrightarrow{\text{cat } H_3B:THF} R_2BH + RBH_2 \quad \text{—— (4)}$$

$$(ArO)_3B \xrightarrow{\text{cat } H_3B:THF} (ArO)_2BH + ArOBH_2 \quad \text{—— (5)}$$

$$R_2BH + (ArO)_2BH \longrightarrow R_2BOAr + ArOBH_2 \quad \text{—— (6)}$$

This suggested the possibility of achieving hydroboration and exchanging alkenyl/alkyl group with diaryloxyborane such as catecholborane as envisaged in Scheme 6.

SCHEME 6:

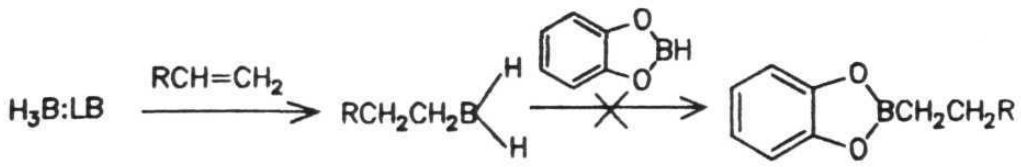


Since catecholborane does not react with alkynes at room temperature, the H_3B:LB catalyst is expected to hydroborate the alkyne first followed by the exchange with catecholborane, giving alkenylcatecholborane, there by regenerating the catalyst.

As outlined previously, we have convenient methods for the generation of borane-Lewis base complexes such as N,N-diethylaniline $-BH_3$. We decided to study the exchange phenomenon using N,N-diethylaniline-BH_3. Catecholborane (10 mmol) was prepared and the reaction with 1-decene (16 mmol) was performed at 25°C for 24h in the presence of N,N-diethylaniline-borane complex (1 mmol). Only 7.5% of 1-decanol was isolated after oxidation of the resulting organoborane. This could have resulted from the hydroboration of 1-decene with the N,N-diethylaniline-BH_3 complex. This shows that the alkyl group does not transfer

from alkylborane to catecholborane as envisaged in Scheme 7.

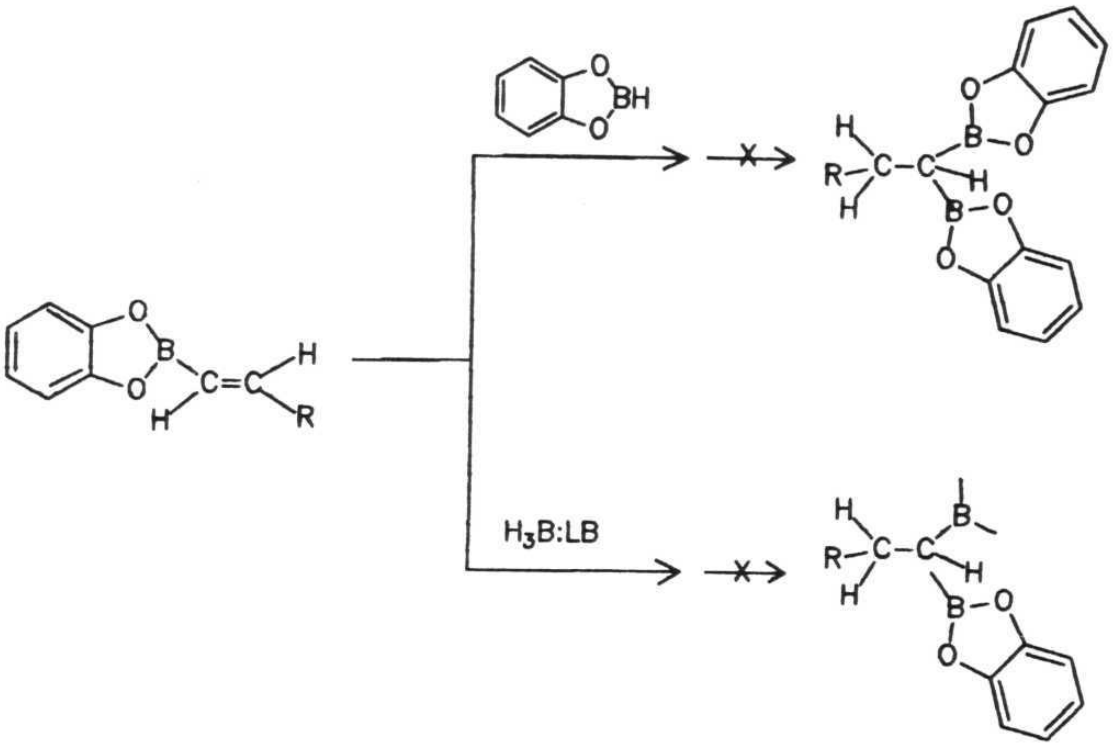
SCHEME 7:



However, when 1-alkene in the above experiment was replaced by 1-alkynes (16 mmol), 1-alkanals were obtained in 65-81% yields after the oxidation with $NaOAc/H_2O_2$. (Table 2.3).[26] The formation of alkenylborane derivatives under the present conditions was further confirmed by carrying out the iodination reaction with $NaOH/I_2$. The benzene solvent was distilled out after hydrolysis and the alkenylboronic acid was isolated free of catechol. The crude alkenylboronic acid was iodinated with $NaOH/I_2$, following the reported procedure.[20] The corresponding isomerically pure E-1-iodo-1-alkenes were obtained in 65-67% yield (entry nos 5 and 6, Table 2.3).

These results indicate that the exchange process envisaged above (Scheme 6) takes place in the reaction with 1-alkynes. The absence of 1-decanol in this reaction rules out the formation of gem-dibora derivative, *i.e.*, further hydroboration of alkenylcatecholborane does not take place with either BH_3:LB or catecholborane present (Scheme 8).

SCHEME 8:



We have also found that the catecholborane does not hydroborate 1-alkynes at 25°C even after 24h in the absence of the borane catalyst. The reaction of 1-decyne with N,N-diethylaniline-borane complex followed by $NaOAc/H_2O_2$ oxidation gave 1-decanol and not 1-decanal. Presumably, the hydroboration leading to the formation of gem-dibora derivative (Scheme 9) takes place in the absence of catecholborane.

SCHEME 9:

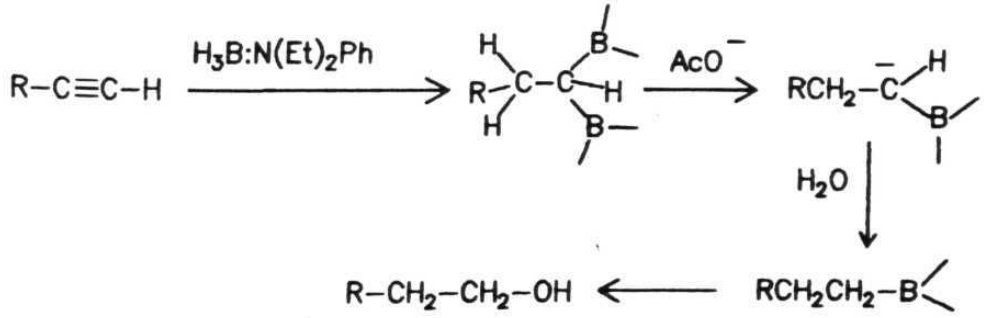
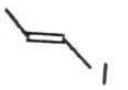
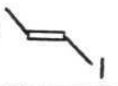


Table 2.3: Hydroboration of alkynes using catecholborane and $H_3B{:}N(C_2H_5)_2Ph$ complex.[a]

Entry No.	Substrate	Product	Yield(%)[d]
1.	$n\text{-}C_6H_{13}\text{-}C{\equiv}CH$	$n\text{-}C_6H_{13}\text{-}CH_2\text{-}CHO$	65[b]
2.	$n\text{-}C_8H_{17}\text{-}C{\equiv}CH$	$n\text{-}C_8H_{17}\text{-}CH_2\text{-}CHO$	76[b]
3.	$n\text{-}C_{14}H_{29}\text{-}C{\equiv}CH$	$n\text{-}C_{14}H_{29}\text{-}CH_2\text{-}CHO$	81[b]
4.	$H_3COOC\text{-}(CH_2)_8\text{-}C{\equiv}CH$	$H_3COOC\text{-}(CH_2)_9\text{-}CHO$	68[b]
5.	$n\text{-}C_8H_{17}\text{-}C{\equiv}CH$	$n\text{-}C_8H_{17}$ 	65[c]
6.	$n\text{-}C_{14}H_{29}\text{-}C{\equiv}CH$	$n\text{-}C_{14}H_{29}$ 	67[c]

a) Reactions were carried out under N_2 atmosphere using catecholborane (10 mmol) and substrate (16 mmol) in the presence of N,N-diethylaniline-borane complex (1 mmol) as catalyst.

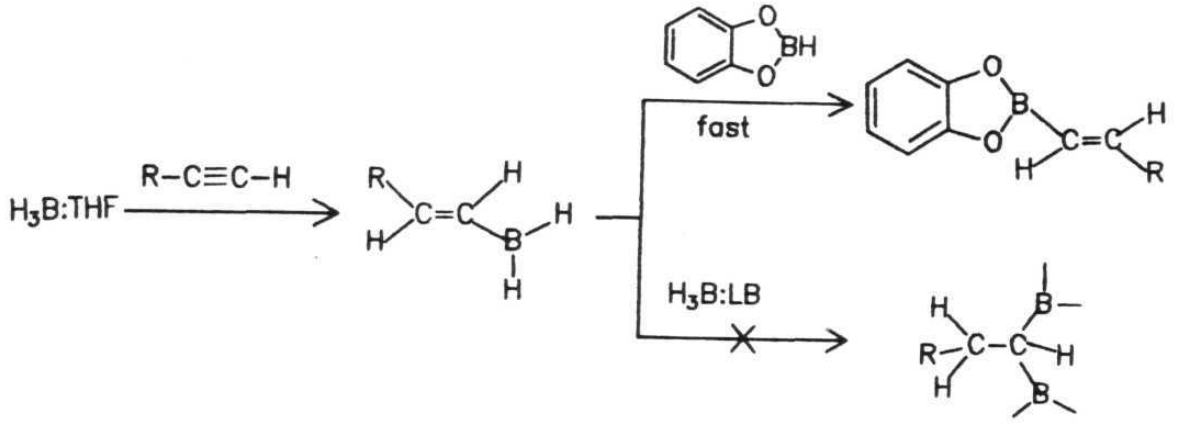
b) Products obtained after oxidation using 3N $NaOAc/H_2O_2$.

c) Products obtained after iodination using 3N NaOH and I_2.

d) Yields are of isolated and purified products calculated on the basis of catechol utilized. The products were identified by spectral data (IR, ^1H and ^{13}C NMR) and comparison with the data of authentic samples.

The experiments of catecholborane and N,N-diethylaniline-BH_3 with 1-alkynes indicate that alkenyl transfer reaction, to give alkenyl-catecholborane is faster than the formation of gem-dibora compounds.

SCHEME 10:



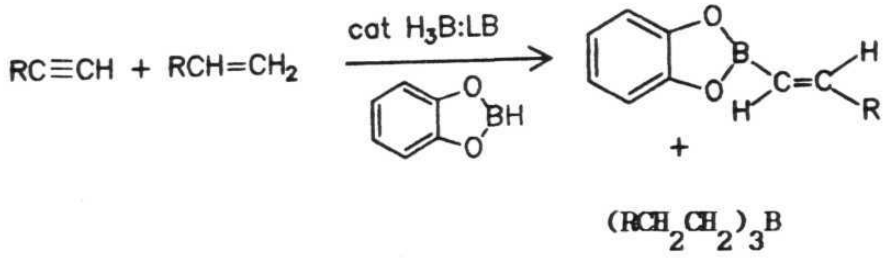
Similar results were observed with the reagent prepared by passing excess B_2H_6 through a mixture of N,N-diethylaniline (1 mmol) and catechol (10 mmol) in benzene at 25°C.

Selective hydroborations were also achieved using this reagent system, as expected. For example, methyl 10-undecynoate was converted to the corresponding aldehyde (Table 2.3). The ester group is not affected, since the experiment is carried out at 25°C.

In order to examine whether alkynes can be selectively hydroborated in the presence of alkenes, 1-decyne (16 mmol) and 1-decene (16 mmol) in a reaction with catecholborane (10 mmol) and

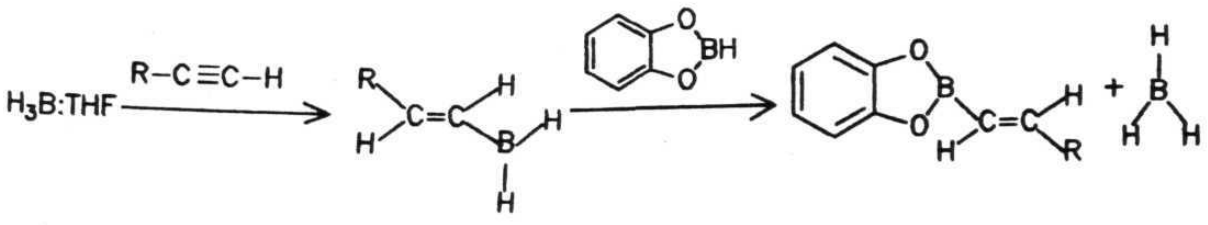
N,N-diethylaniline-BH_3 (1 mmol) were employed. In this case, only 4.5 mmol of 1-decanal was formed besides 2 mmol of 1-decanol (Scheme 11). The decanol formed most probably results from the hydroboration of 1-decene by N,N-diethylaniline-BH_3. The low yield of 1-decanal obtained in this case when compared to the reaction carried out using 1-decyne alone, implies that the BH_3 species to some extent is used up in the hydroboration of 1-decene. Hence, an equivalent amount of catecholborane remained unreacted even after 24h. This rate retardation is not unexpected, since the formation of trialkylborane would remove the "BH_3" species.

SCHEME 11:

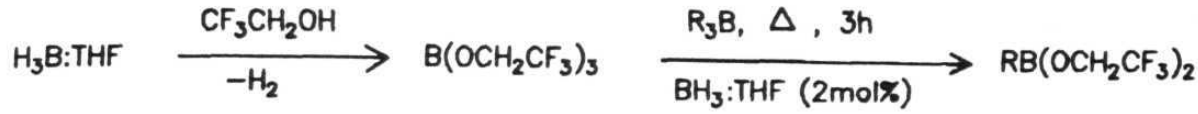


Similar exchange results were also observed using 10 mol % of BH_3:THF (Scheme 12).

SCHEME 12:



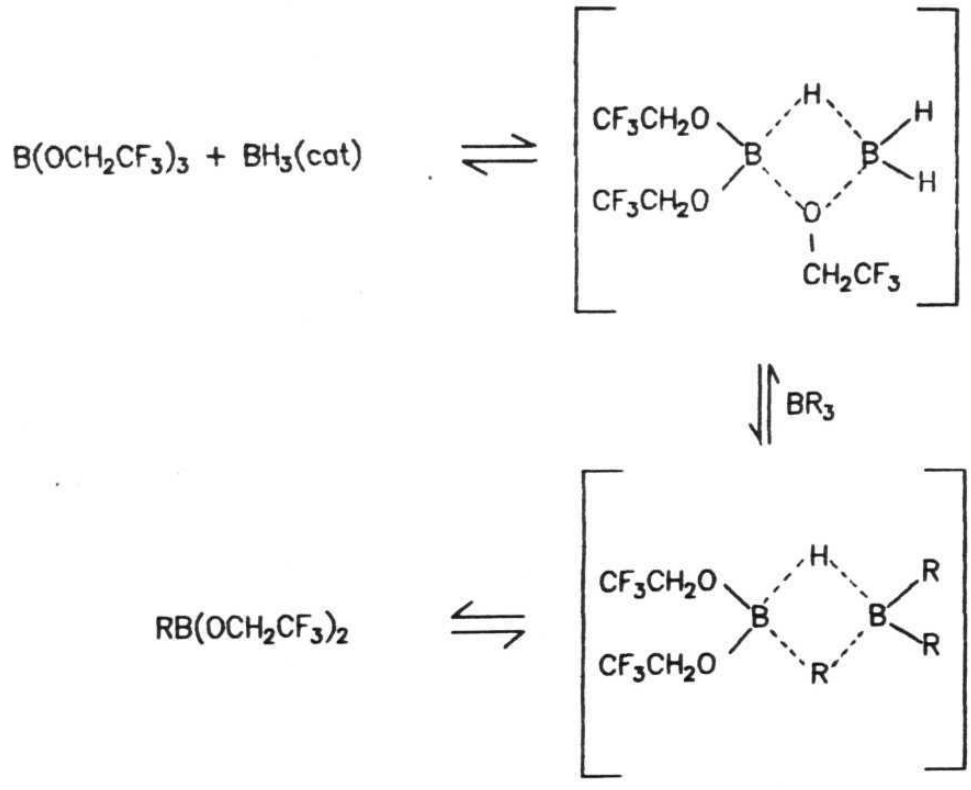
Recently, Corey *et al.*[27] reported the reaction of R_3B with $B(OCH_2CF_3)_3$ in the presence of BH_3:THF (2 mol%) (eq. 7).



—— (7)

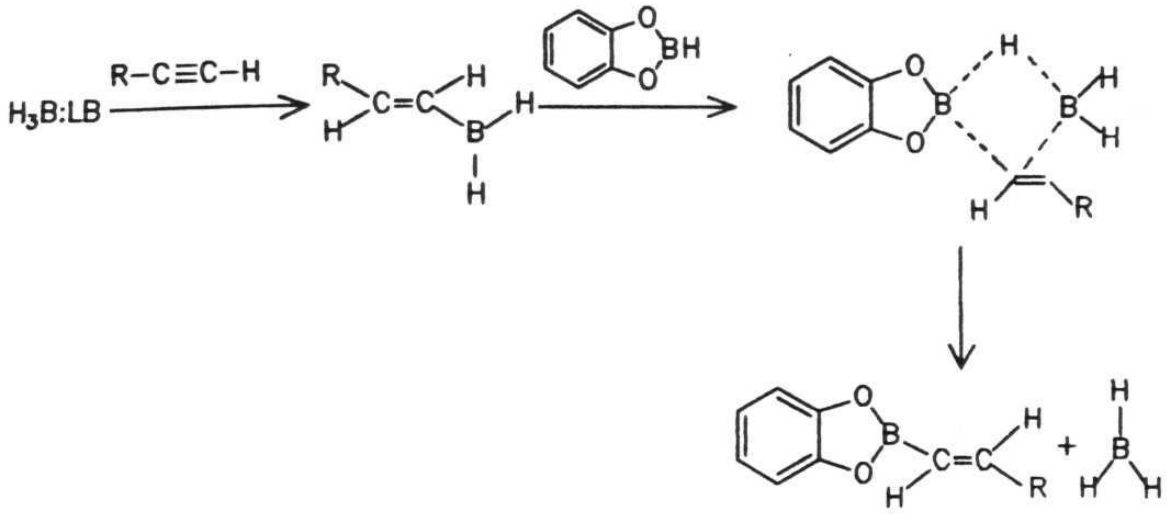
They suggested the mechanism shown in Scheme 13.

SCHEME 13:



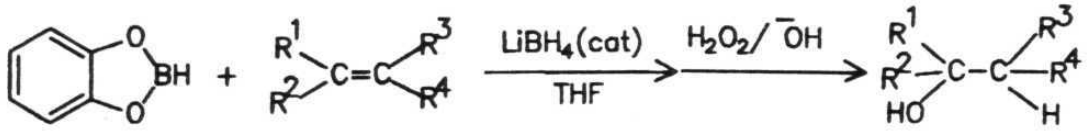
Presumably, the hydroboration with catecholborane/N,N-diethylaniline-BH_3 combination may also go through a similar process. (Scheme 14).

SCHEME 14:



Very recently, Arase and co-workers,[28] reported that the hydroboration of alkenes using catecholborane takes place at room temperature with $LiBH_4$ as catalyst (Scheme 15).

SCHEME 15:



A wide variety of alkenes were hydroborated in quantitative yields. Dialkoxyboranes in the presence of 1% $LiBEt_3H$ hydroborate alkenes under mild conditions.[29] It was found that in the absence of $LiBEt_3H$, the hydroboration of 1-hexene with dibutoxyborane $(BuO)_2BH$ are very sluggish compared to that in the presence of a catalytic amount of

$LiBEt_3H$ (less than 1%). They also found that addition of $LiBEt_3H$ in the dibutoxyborane formation stage, also promoted the hydroboration as well as the formation of dibutoxyborane, providing a quantitative yield of hexanols (eq. 8). These methods add another interesting useful reagent system to the pool of hydroborating agents available to the organic chemists.

$$H_3B \xrightarrow{LiBEt_3H(1\%)} \xrightarrow{2ROH} (RO)_2BH \xrightarrow{alkene} \xrightarrow{H_2O_2/^-OH} R^1OH \qquad \text{—— (8)}$$

Hydroboration of Alkenes and Alkynes using $PhOH/H_3B{:}N(C_2H_5)_2Ph$ System:

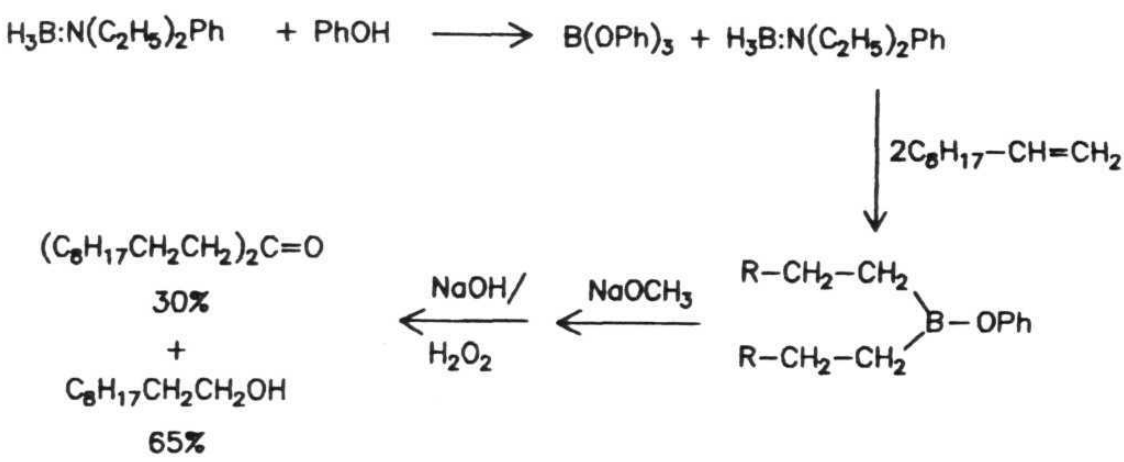
As discussed previously, ArO_2BH and R_2BH species may be the intermediates in exchange reactions of trialkoxyboranes with trialkylboranes, in the presence of catalytic amount of BH_3:THF. It was of interest to examine the possibility of preparing diphenoxyborane by passing B_2H_6 through a suspension of phenol in benzene. However, in these cases the solution IR spectrum of the reaction mixture showed the absence of -OH and >BH absorptions, indicating the formation of aryloxyboranes without >BH bonds. This may be due to the instability of >BH bonds in alkoxy and aryloxy boranes (eq. 9).[19]

$$6(RO)_2BH \rightleftharpoons B_2H_6 \uparrow + 4(RO)_3B \qquad \text{—— (9)}$$

However, it was of interest to examine whether dialkylmono-phenoxyborane can be prepared by adding appropriate amounts of phenol

to $H_3B{:}N(C_2H_5)_2Ph$ in benzene, followed by 1-decene. Several experiments were carried out in order to examine this possibility (Scheme 16).

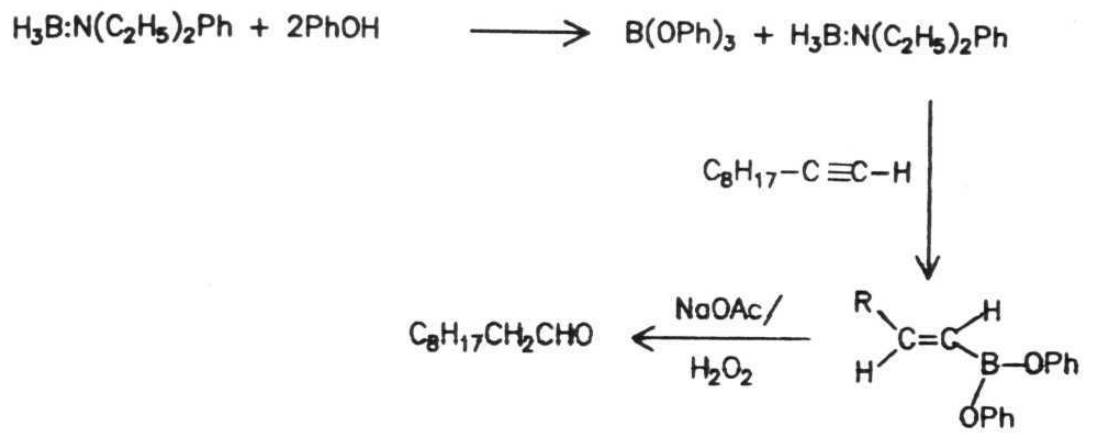
SCHEME 16:



The experiment was carried out under several conditions of temperature and time. However, there was no change observed in the product ratio. The formation of dialkylketone in low yields in the reaction with $NaOCH_3/CHCl_3$ followed by oxidation,[30] indicates that the reaction does not give clearly dialkylborane species.

In order to examine whether alkenyldiphenoxyborane can be prepared using phenol in a similar way, an experiment by taking appropriate amounts of phenol, $H_3B{:}N(C_2H_5)_2Ph$ and 1-decyne (Scheme 17) was carried out.[31]

SCHEME 17:



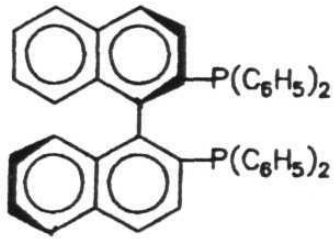
The aldehyde was obtained only in 55% yield and the alkyne (32%) was recovered. The experimental conditions were altered in several ways, for example, taking more of the substrate, heating the reaction mixture to allow the exchange to be complete, changing the solvent from benzene to toluene, but no variation in the product ratio was observed. However, 1-decanol was not formed. This indicates that the gem-dibora derivative is not formed although the yield of the aldehyde is relatively less compared to the experiments with catecholborane.[31]

Attempted preparation of binaphtholborane:

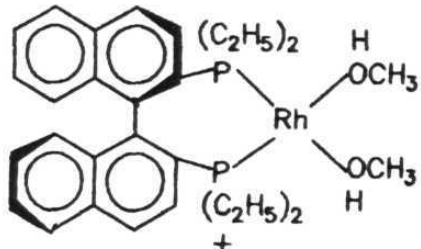
Efficient creation of optically active organic molecules from prochiral compounds by chemical means is a challenging task. Numerous efforts by synthetic organic chemists led to the discovery of a number of chiral auxiliaries (Figure 2). Binaphthol moiety based ligands have

been found to be effective in chiral transformations.[32] For example, BINAP complexes are used in asymmetric hydrogenation, hydroboration, *etc.*[33,34]

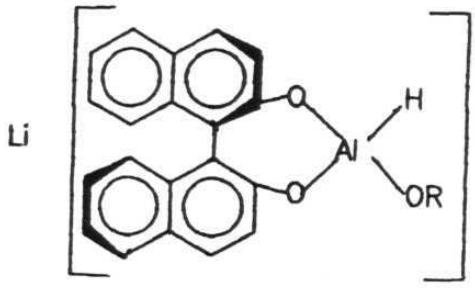
FIGURE 2:



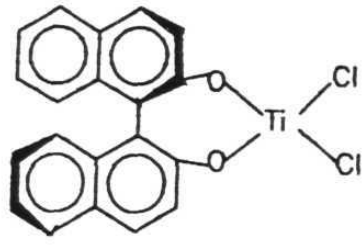
(R)–BINAP



(S)–BINAP–Rh Complex



(S)–BINAL–H

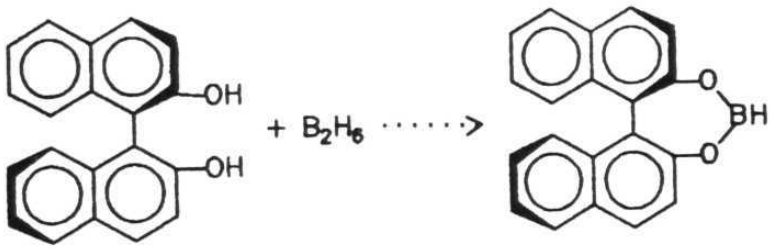


The chiral reducing agent BINAL-H, exhibits exceptionally high enantioface differentiating ability in the stoichiometric reduction of prochiral ketones having an aromatic, olefinic, or acetylenic substitution.[35,36,37] Titanium complex of binaphthol is used in asymmetric Diels-Alder reactions.[38]

In view of the synthetic importance of the binaphthyl reagents,

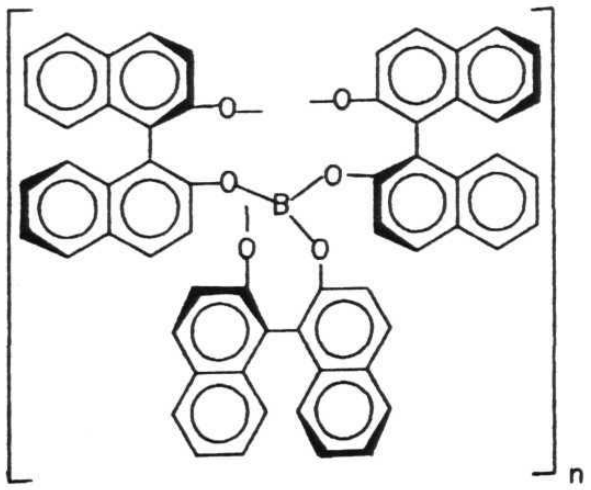
we attempted the preparation of binaphtholborane by bubbling excess of B_2H_6 through a benzene solution of binaphthol (Scheme 18).

SCHEME 18:



Unfortunately, no >B-H absorption was observed in solution IR spectroscopic studies.

FIGURE 3:



We anticipated the formation of a polymer (Figure 3) and hence

attempted to depolymerize it through complexation with Lewis bases such as amines. It has been observed that precipitation occurs when the reaction mixture was treated with triethylamine. The precipitate did not melt even at 250°C.

In order to examine whether such precipitation could be helpful in resolving binaphthol by complexing with chiral Lewis bases, chiral amines such as α-methyl benzyl amine, ephidrine and cinchonine were added in individual runs to the solution of the aryloxy polymer in benzene. In all these cases, we obtained a white precipitate which did not melt even at 250°C. The precipitate was decomposed with dil. HCl. The resulting binaphthol was found to be racemic. Presumably, the amine complexes are still polymeric in nature.

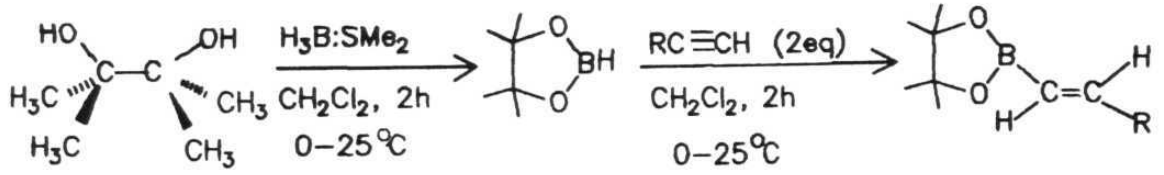
Attempted Hydroboration of Alkenes and Alkynes with Catecholborane in benzene in the presence of added Lewis bases:

It has been reported that there is a large variation in the rate of hydroboration reactions utilizing catecholborane in different solvents. For example, 1-octene in chloroform does not react with catecholborane, whereas in THF it undergoes hydroboration.[19] There is a possibility that complexation of the catecholborane with THF may increase its reactivity towards alkenes. We have carried out the hydroboration of

1-decene by catecholborane in benzene adding THF, $(CH_3)_2S$, and $N(Et)_2Ph$ in individual runs. However, we found that the catecholborane does not react with 1-decene at room temperature even after 48h.

Very recently Knochel *et al.*[39] have prepared a new hydroborating agent, pinacolborane, by the addition of borane-dimethyl sulfide to a solution of pinacol in dry dichloromethane. The pinacolborane can be isolated by distillation or used *in situ* for hydroboration of alkyne at 25°C in CH_2Cl_2 (Scheme 19). Two equivalents of pinacolborane are required and the reaction is complete in 2h at 25°C.

SCHEME 19:

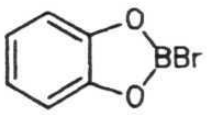


It is suprising that this reagent hydroborates alkynes at 25°C in 2h. The greater stability and reactivity of this reagent compared to the borane heterocycles given in Fig.1 (p-40) is not understood. Presumably, the hindered nature of pinacolborane prevents the formation of alkoxyborane polymers. However, greater reactivity of this borane is unexpected.

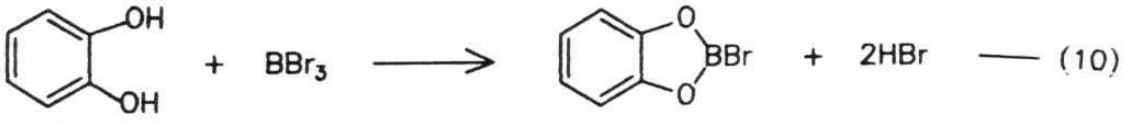
Attempted preparation and utilization of iodocatecholborane:

Recently, Kelly *et al.*[40] have prepared bromocatecholborane[41] which has structurally and conformationally defined site of Lewis acidity (Figure 4).

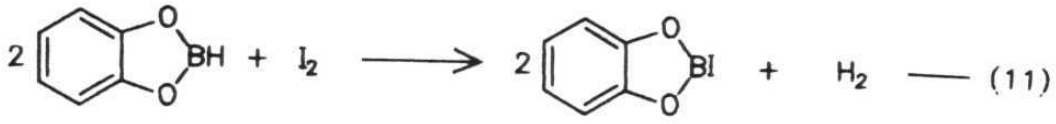
FIGURE 4:



The potential of bromocatecholborane to function as a Lewis acid catalyst was suggested by its ability to cleave ethers.[42,43] It is also very effective as a catalyst with a wide variety of dienophiles in the Diels-Alder reaction. Unfortunately, preparation of bromocatecholborane involves the use of BBr_3, which is difficult to handle and also is not readily accessible (eq.10).[40]

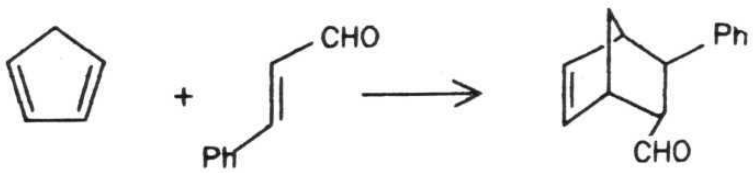


It was thought that iodocatecholborane would have similar properties. We envisaged the preparation of the iodocatecholborane by the reaction of iodine with catecholborane in benzene (eq. 11).



Catecholborane (10 mmol) was prepared in dry benzene (40 mL) from catechol and B_2H_6. Iodine in dry benzene (20 mL) was added under N_2 atmosphere. It was found that iodine reacts very slowly at 25°C. In order to examine whether iodocatecholborane is formed, the Diels-Alder reaction (Scheme 20) of cyclopentadiene and cinnamaldehyde at -78°C was carried out in the presence of iodocatecholborane, prepared in this way. It has been observed that the corresponding Diels-Alder adduct is obtained in 29% yield.

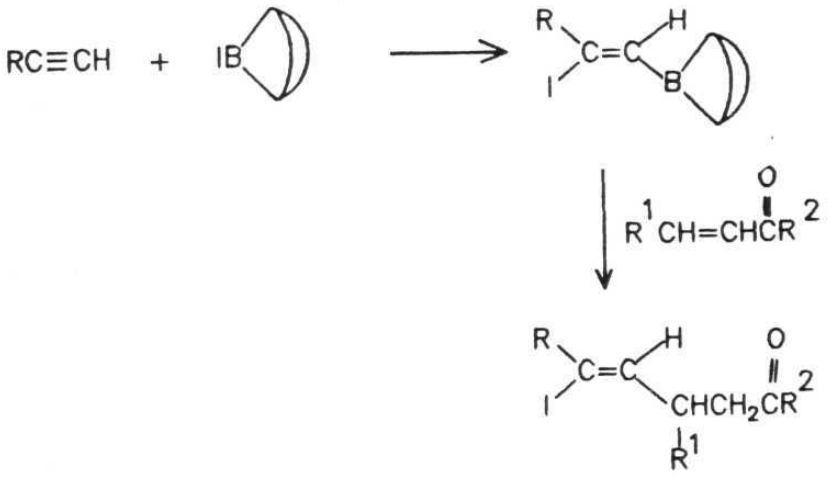
SCHEME 20:



It has been reported that cyclopentadiene does not react with cinnamaldehyde without the catalyst even for 24h at 25°C.[40] Certainly, the iodocatecholborane formed, catalyzes this reaction. However, the yield is poor. So, we have decided to look into other types of reactivity of the >BI moiety. It is well known that, haloboration of alkynes can be achieved using B-halo-9-BBN. They react with acyclic

α,β-unsaturated ketones to give Z-δ-halo-γ,δ-unsaturated ketones (Scheme 21)[44] in stereochemically pure form (> 98%).

SCHEME 21:



An experiment was carried out in order to examine whether iodocatecholborane prepared under the present conditions could iodoborate alkynes. It was found that the only product obtained after oxidation was 2-iodo-1-decene and the 2-iodo-aldehyde was not formed. This may be due to the instability of the corresponding iodoalkenylborane. Also, as mentioned previously, catecholborane reacts slowly with iodine. It is possible that HI may be initially formed by the reaction of I_2 with catecholborane. So, the 2-iodo-1-decene may result from the addition of some left out HI to 1-decyne. Very recently, it has been found in this laboratory, that the HI generated using BI_3/CH_3COOH system is useful for hydroiodination of alkenes and alkynes.[45]

We have also attempted the preparation of iodocatecholborane in different ways. N,N-Diethylaniline-BI_3 complex was prepared from N,N-diethylaniline-BH_3 and iodine[46] and was treated with catechol in order to get iodocatecholborane. Excess of triethylamine was added to eliminate HI in the form of quaternary salt. The formation of iodocatecholborane was examined by the solution IR spectrum (No >BH and -OH absorptions). Attempted iodoboration of 1-decyne at 25°C using this reagent system, gave only 9% of the expected 2-iodo-1-decanal along with the starting material (72%). Heating the reaction mixture to 80°C after the addition of 1-decyne did not improve the yield of the 2-iodo-1-decanal. However, the iodocatecholborane prepared in this way gave reasonable yield (74%) of the adduct in the Diels-Alder reaction between cyclopentadiene and cinnamaldehyde.

CONCLUSIONS

A simple method for preparation of catecholborane by passing B_2H_6 through a suspension of catechol in benzene has been developed. The reagent prepared in this way is used for hydroboration-oxidation of representative alkenes and alkynes at 80°C. The preparation of alkenylcatecholboranes can be achieved at 25°C by performing the reaction in the presence of 10 mol % of $H_3B{:}N(C_2H_5)_2Ph$ or $H_3B{:}THF$. Alkenylcatecholboranes on iodination with I_2/NaOH give the corresponding E-1-iodo-1-alkenes in good yields. Attempts have been made to prepare monophenoxydialkylborane and diphenoxyalkylborane using appropriate amounts of phenol and $H_3B{:}N(C_2H_5)_2Ph$. Attempts were also made to prepare iodocatecholborane for use as a Lewis-acid catalyst in Diels-Alder reactions and also in iodoboration of alkynes.

EXPERIMENTAL SECTION

General Information:

All melting points reported are uncorrected and were determined using a Buchi-510 capillary point apparatus. Infrared spectra were recorded on Perkin-Elmer IR Spectrophotometer Model-3010 with polystyrene as reference. ^{1}H NMR 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). Gas chromatography analyses were carried out on a Packard model-42 instrument equipped with a flame ionisation detector on a SE-30 or carbovax 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 sulphate 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).

All glassware was pre-dried in an air oven, assembled at hot conditions and cooled under a stream of dry nitrogen. Unless otherwise mentioned, all operations/transformations of reagents/ reactions were carried out using standard syringe, septum techniques, recommended for

handling organoboranes.[1] Reagents prepared *in situ* in solvents were transformed using double-ended stainless steel (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 to an acetone bubbler whose outlet was connected by a long tube to the atmosphere.

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

Benzene, toluene, diglyme and THF were distilled over benzo-phenone-sodium. DCM was distilled over P_2O_5. All alkenes utilized were commercial samples, supplied by Fluka, Switzerland. All alkynes except 1-heptyne were prepared by bromination followed by dehydrobromination of the corresponding olefins following the procedure

reported in the literature.[47] 1-Heptyne utilized was supplied by Fluka, Switzerland. Sodium borohydride (97%, 100 g) supplied by LOBA-Cheme, India and Fluka, Switzerland were utilized and kept under nitrogen in a dessicator, after opening the bottle. Resublimed iodine was used. N,N-Diethylaniline and triethylamine were distilled over anhydrous KOH in small quantities (10 mL) and kept under nitrogen for utilization.

Catechol supplied by SD's, India was sublimed to obtain in white crystalline form, which was utilized in all the experiments. Binaphthol was prepared starting from β-naphthol, using the reported procedure.[48] It was recrystallized two times from water to get white crystalline solid which was then utilized for experiments. Freshly distilled phenol utilized was supplied by SD's, India. Dicyclopentadiene was supplied by Fluka, Switzerland. Cinnamaldehyde utilized was supplied by E.Merck, India.

Diborane was generated by dropwise addition of iodine in diglyme to sodium borohydride in diglyme at 10°C using apparatus recommended for utilization in the hydroboration of organoboranes.[16]

Generation of diborane utilizing the $I_2/NaBH_4$ system and preparation of catecholborane:

A solution of iodine (6.35 g, 25 mmol) in diglyme (20 mL) was introduced dropwise during 3h from an addition funnel into a generation flask (100 mL RB flask with a side arm and a side septum) containing $NaBH_4$ (2.0 g, 50 mmol) in diglyme (10 mL) at room temperature (tap water cooling) under a static nitrogen atmosphere. The generated diborane and hydrogen were carried off through a side tube and bubbled through a solution of catechol (1.1 g, 10 mmol) in benzene (40 mL) in another flask at room temperature (250 mL RB flask with a side septum, side arm and a condenser). The outlet from the latter flask was vented through a mercury bubbler and a trap containing adequate amount of acetone to destroy excess diborane. When the bubbling of the gases in the reaction flask had ceased, the bubbler was removed under nitrogen and replaced by a glass stopper. The bubbler was connected to an acetone trap and the traces of diborane remained in the generation flask was driven away by a stream of dry nitrogen. The diborane in the gas phase above the benzene solution in the reaction flask was also flushed out with a stream of nitrogen. The catecholborane solution thus prepared was utilized for further reactions. IR (benzene)ν_{max}: 2680 cm^{-1}. The >B-H stretching absorption of that reported for catecholborane is 2680 cm^{-1}.[18]

Hydroboration-Oxidation of 1-decene using catecholborane prepared in benzene:

The procedure followed for the hydroboration - oxidation of 1-decene with catecholborane is representative.

Catecholborane (10.5 mmol) was prepared by passing diborane through a solution of catechol in benzene over 3h at 25°C. 1-Decene (10 mmol, 1.4 g) was added and temperature was raised to 80°C. The mixture was refluxed for 12h. The contents were brought back to room temperature and the excess hydride (if any) was carefully destroyed by adding water (2 mL) while cooling the flask externally with cold water. THF (20 mL) was added and the organoborane was oxidized by the addition of 3N NaOH (15 mL) followed by dropwise addition of H_2O_2 (16%, 25 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic extract was washed with 1N NaOH solution (3 x 20 mL) to remove catechol followed by water and saturated NaCl solution (15 mL). It was then dried over anhydrous $MgSO_4$, the solvent was removed on a rotary evaporator and the residue was distilled under reduced pressure to obtain 1-decanol (1.39 g, 88%). IR spectrum of this product showed 1:1 correspondence with the spectrum reported in the literature.[49]

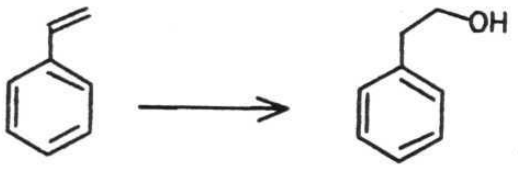
$CH_3(CH_2)_7CH=CH_2 \longrightarrow CH_3(CH_2)_8CH_2OH$

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

B.P. : 106°C/7 mm, Lit.[49] 120°C/12 mm

^{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 above procedure for hydroboration was followed for the conversion of a few other olefins into corresponding alcohols and the results are presented below and also in Table 2.1.



Yield : 80% (0.98 g)

B.P. : 90-91°C/10 mm, Lit.[50] 100-103°C/12 mm

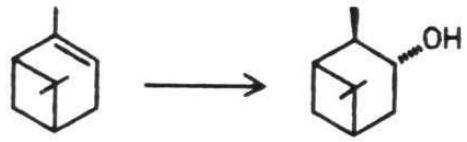
IR (neat)ν_{max} : 3300, 1020 cm^{-1}

^1H NMR(100 MHz, $CDCl_3$) : δ ppm 1.4 (d, $-CH_3$), 2.7 (t, $-CH_2$), 2.8 (br s, -OH), 3.6 (t, $-CH_2-O$), 4.7 (q, CH-O), 7.2 (m, aromatic hydrogens).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 35.1, 63.3, 125.3, 127.1, 128.8, 138.7.

^1H NMR spectrum indicated the presence of isomeric 1-phenyl-

ethanol upto 8%.



Yield : 85% (1.31 g)

B.P. : 98°C/10 mm, Lit.[51,52] 217°C/760 mm

IR (neat)ν_{max} : 3350, 1120 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 20.8, 23.8, 27.9, 34.1, 38.3, 42.1, 47.8, 48.0, 48.2, 71.7.

The data of the compound are identical to that reported in the literature.[50]

Hydroboration-Oxidation of 1-decyne using catecholborane in benzene:

Catecholborane (10.5 mmol) was prepared by passing B_2H_6 through a solution of catechol in benzene (40 mL). 1-Decyne (1.38 g, 10 mmol) was added and the temperature was raised to 80°C. The mixture was stirred for 12h to obtain the catechol ester of 1-decenylboronic acid.[10] The contents were brought back to room temperature and the excess hydride (if any) was destroyed by adding water (2 mL). THF (20

mL) was added and oxidation of the organoborane was carried out using 3N NaOAc (15 mL) and H_2O_2 (16%, 25 mL) following the procedure recommended for oxidation of organoboranes.[1] The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic extract was washed with 1N NaOH (3 x 20 mL) to remove catechol, followed by water and saturated NaCl solution (15 mL). It was then dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. The product eluted with hexane/ethyl acetate (95:5) was identified as 1-decanal (1.4 g, 90%).

$$CH_3(CH_2)_7C\equiv CH \longrightarrow CH_3(CH_2)_8-CHO$$

B.P. : 85°C/10 mm, Lit.[53] 208-9°C/760 mm

IR (neat)ν_{max} : 2700, 1720 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$), 1.5 (m, $-CH_2-$), 2.3 (m, $-CH_2-CHO$), 9.2 (br s, -CHO).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.0, 22.7, 29.1, 29.4, 29.7, 31.9, 43.9, 202.8.

The reaction with 1-dodecyne (1.64 g, 10 mmol) was also carried out following the procedure outlined above, to obtain 1-dodecanal.

$CH_3(CH_2)_9C{\equiv}CH \longrightarrow CH_3(CH_2)_{10}-CHO$

Yield : 91% (1.67 g)

B.P. : 108°C/5mm, Lit.[53] 185/100 mm

IR (neat) ν_{max} : 2700, 1720 cm^{-1}

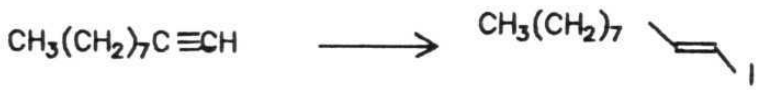
^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$), 1.5 (m, $-CH_2-$), 2.3 (m, $-CH_2-CHO$), 9.2 (br s, -CHO).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.2, 22.1, 22.9, 29.1, 29.3, 29.5, 29.7, 29.9, 31.9, 43.9, 202.6.

Hydroboration-Iodination of 1-decyne using catecholborane in benzene:

Catecholborane (10.5 mmol) was prepared from catechol and B_2H_6 in benzene (40 mL). 1-Decyne (1.38 g, 10 mmol) was added under nitrogen atmosphere and the temperature was raised to 80°C. The mixture was stirred for 12h to obtain the catechol ester of 1-decenylboronic acid.[10] The mixture was cooled to room temperature and stirred with water (10 mL) for 1h, to effect the hydrolysis of the ester. The benzene solvent was distilled out under nitrogen to afford a white solid which was washed with ice-cold water (3 x 10 mL), to obtain boronic acid free of catechol. The boronic acid was then dissolved in ether (20 mL) and cooled to 0°C. 3N NaOH (10 mL) was then added

followed by iodine (1.52 g, 12 mmol) in ether (30 mL), while stirring at $0^{o}C$ over 15 min. The mixture was stirred for 1h at $0^{o}C$. The excess iodine was then destroyed with aqueous sodium thiosulphate solution. The ether layer was separated, washed with 1N NaOH (2 x 20mL), water, and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. The product eluted with hexane was identified as E-1-iodo-1-decene (1.86 g, 70%).



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

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$), 1.4 (m, $-CH_2-$), 1.9 (m, $-CH_2$ adjacent to olefin), 5.8-6.6 (m, olefinic hydrogens)

^{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

Mass (m/e) : 266 (M^+, 40%), 83 (100%).

The E-1-iodo-1-decene has been reported in the literature.[55] However the data are not given.

Similarly, when 1-dodecyne was hydroborated with catecholborane followed by iodonolysis with $NaOH/I_2$, E-1-iodo-1-dodecene was

obtained.

Yield : 72% (2.1 g)

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

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 1.4 (m, $-CH_2-$), 1.9 (m, $-CH_2$ adjacent to olefin), 5.8-6.6 (m, olefinic hydrogens) (Spectrum no. 1).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 28.4, 28.9, 29.1, 29.3, 29.5, 31.9, 36.1, 74.4, 146.7 (Spectrum no. 2).

Mass (m/e) : 294 (M^+, 22%), 97(100%).

The E-1-deuterio-1-iodo-1-dodecene has been reported.[56] The ^1H NMR data of this compound is similar to the data reported here but for the difference in the signals for olefinic protons.

Preparation of N,N-diethylaniline-borane complex:

To a solution of N,N-diethylaniline (1.49 g, 10 mmol) in dry benzene (40 mL), diborane was passed over 1h at 10°C. The N,N-diethylaniline-BH_3 complex thus prepared was utilized for further

reactions. IR (benzene)ν_{max} : 2235, 2280, 2340 cm^{-1}. The $(C_2H_5)_3N:BH_3$ complex has >B-H stretching absorption in the same region are appears as a symmetrical triplet.[57]

Hydroboration of 1-decyne using N,N-diethylaniline-borane complex:

N,N-Diethylaniline-borane complex (10 mmol) was prepared from N,N-diethylaniline and B_2H_6. 1-Decyne (1.38 g, 10 mmol) was added and stirred for 24h at 25°C. The reaction was quenched with water (2 mL). THF (10 mL) was added and oxidized with $NaOAc/H_2O_2$. The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 mL). The combined organic extract was washed with 1N HCl (3 x 10 mL) followed by water and brine. It was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was purified on a silica gel column, to obtained 1-decanol (0.74 g, 47%). No 1-decanal was obtained. The spectral data are superimposable with the spectrum of the authentic sample.

Reaction of 1-decyne with catecholborane in the presence of catalytic amount of N,N-diethylaniline-borane complex (0.1 eq):

Catecholborane (10 mmol) was prepared from catechol and B_2H_6 in dry benzene (40 mL). N,N-diethylaniline-borane complex (1 mmol) in

benzene was transferred to the flask under nitrogen atmosphere with the help of a double-ended needle at 25°C. 1-Decyne (2.21 g, 16 mmol) was added and stirred for 24h at room temperature. The excess hydride (if any) was destroyed by adding water (2 mL). THF (20 mL) was added and oxidation of the organoborane was carried out using 3N NaOAc (15 mL) and H_2O_2 (16%, 25 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic extract was washed with 1N HCl (2 x 15 mL) and 1N NaOH (3 x 20 mL), to remove the amine and catechol respectively followed by water and saturated NaCl solution (15 mL). It was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column. The product eluted with hexane/chloroform (60:40) was identified as 1-decanal (1.19 g, 76% yield, based on catecholborane). IR spectrum of the product showed 1:1 correspondence with the samples obtained previously. The 1-decanol was not formed and the excess alkyne was recovered (0.97 g).

In order to examine the generality of the reaction, the reaction with various other alkynes was carried out following the above procedure and the organoborane was oxidized using $NaOAc/H_2O_2$.

$$CH_3(CH_2)_{13}C{\equiv}CH \longrightarrow CH_3(CH_2)_{14}-CHO$$

Yield : 81% (1.94 g)

B.P. : 150°C/5 mm , Lit.[58] 200-202°C/29 mm

IR (neat)ν_{max} : 2700, 1720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 1.5 (m, $-CH_2-$), 2.3 (m, $-CH_2-CHO$), 9.2 (br s, -CHO) (Spectrum no. 3).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.0, 22.7, 29.1, 29.4, 29.7, 31.9, 43.9, 202.8 (Spectrum no. 4).

$CH_3(CH_2)_5C\equiv CH \longrightarrow CH_3(CH_2)_6-CHO$

Yield : 65% (0.83 g)

B.P. : 70°C/25 mm , Lit.[59] 171°C/760 mm

IR (neat)ν_{max} : 2700, 1720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 1.5 (m, $-CH_2-$), 2.3 (m, CH_2-CHO), 9.2 (br s, -CHO).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.7, 24.8, 29.0, 29.1, 31.7, 34.2, 202.6.

$H_3COOC(CH_2)_8C\equiv CH \longrightarrow H_3COOC(CH_2)_9-CHO$

Yield : 68% (1.45 g)

IR (neat)ν_{max} : 2700, 1740, 1720 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.2 (m, $-CH_2$ hydrogens), 1.5 (m, $-CH_2-COOCH_3$), 2.3 (m, $-CH_2-CHO$), 3.75 (s, $-OCH_3$), 9.8 (br s, -CHO).

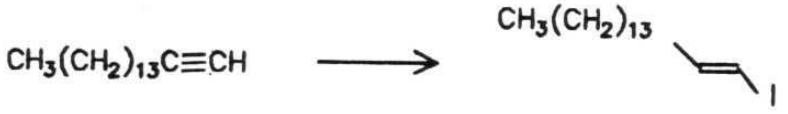
^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 18.0, 24.5, 28.2, 28.4, 28.6, 28.8, 33.6, 50.9, 173.3, 201.5.

Hydroboration-Iodination of 1-decyne with catecholborane in the presence of catalytic amount of N,N-diethylaniline-borane complex (0.1 eq):

Catecholborane (10 mmol) was prepared from catechol and B_2H_6.N,N-Diethylaniline-borane complex (1 mmol) in benzene was transferred under nitrogen atmosphere with the help of a double ended needle at 25°C. 1-Decyne (2.21 g, 16 mmol) was added and stirred at 25°C for 24h, to obtain the catechol ester of 1-decenylboronic acid. The mixture was stirred with water (10 mL) for 1h, to effect the hydrolysis of the ester. The benzene solvent was distilled out under nitrogen atmosphere to afford a white solid which was washed with ice-cold water (3 x 10 mL) to obtain boronic acid free of the catechol. The boronic acid was then dissolved in ether (20 mL) in a 100 mL 2-necked RB flask and cooled to 0°C. 3N NaOH (10 mL) was then added

followed by iodine (1.52 g, 12 mmol) in ether (30 mL), while stirring at 0°C over 15 min. The mixture was stirred for 1h at 0°C. The excess iodine was then destroyed with aqueous sodium thiosulphate solution. The organic layer was separated and washed with 1N HCl (2 x 15 mL) and 1N NaOH (3 x 20 mL) to remove the amine and catechol, respectively followed by water (20 mL) and saturated NaCl solution (15 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. The product eluted with hexane was identified as E-1-iodo-1-decene (1.73 g, 65%). The spectral data were in accordance with the sample obtained previously.

Similarly, when 1-hexadecyne was hydroborated with catechol-borane, followed by iodonolysis with $NaOH/I_2$, E-1-iodo-1-hexadecene was obtained.



Yield : 67% (2.35 g)

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

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 1.4 (m, $-CH_2-$), 1.9 (m, $-CH_2$ adjacent to olefin), 5.8-6.6 (m, olefinic hydrogens).

^{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.

Mass (m/e) : 350 (M^+, 18%), 43 (100%) (Spectrum no 5).

Reaction of 1-decyne with catecholborane in the presence of catalytic amount of borane-tetrahydrofuran complex (0.1 eq):

Catecholborane (10 mmol) was prepared from catechol and B_2H_6. Borane-tetrahydrofuran complex (1 mmol) in THF was transferred under nitrogen atmosphere with the help of a double-ended needle at 25°C. 1-Decyne (2.21 g, 16 mmol) was added and stirred at 25°C for 24h. The excess hydride was destroyed by adding water (2 ml) and oxidation of the organoborane was carried out using 3N NaOAc (15 mL) and H_2O_2 (16%, 25 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic extract was washed with 1N NaOH (3 x 20 mL), to remove catechol followed by water and saturated NaCl solution (15 mL). It was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column. The product eluted with hexane/chloroform (60:40) was identified as 1-decanal (1.13 g, 72%) yield. Spectral data of the 1-decanal obtained in this experiment were identical with the data in the earlier experiments.

Reaction of 1-decyne with the borane reagent prepared by passing B_2H_6 through catechol and N,N-diethylaniline in benzene:

Catechol (1.1 g, 10 mmol) was taken in benzene (40 mL) and N,N-diethylaniline (0.15 g, 1 mmol) was added. Diborane (25 mmol) was bubbled into the benzene solution. 1-Decyne (2.21 g, 16 mmol) was added and stirred at 25°C for 24h. The excess hydride was destroyed by adding water (2 mL). THF (20 mL) was added and oxidation of the organoborane was carried out using 3N NaOAc (15 mL) and H_2O_2 (16%, 25 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic extract was washed with 1N HCl (2 x 15 mL) followed by 1N NaOH (3 x 20 mL) to remove the amine and catechol respectively. It was further washed with water, saturated NaCl solution (15 mL) and was dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. The product eluted with hexane/chloroform (60:40) was identified as 1-decanal (1.16 g, 74%). Spectral data were identical with the data obtained for this product in the earlier experiments.

Attempted selective hydroboration of 1-decyne over 1-decene using

catecholborane in the presence of catalytic amount of N,N-diethyl-aniline-borane complex (0.1 eq.):

Catecholborane (10 mmol) was prepared from catechol and B_2H_6 in dry benzene (40 mL). N,N-diethylaniline-borane complex (1 mmol) in benzene was transferred under nitrogen with the help of a double-ended needle at 25°C. 1-Decyne (2.21 g, 16 mmol) and 1-decene (2.24 g, 16 mmol) were added and stirred at 25°C for 24h. The excess hydride was destroyed by adding water (2 mL). THF (20 mL) was added and oxidation of the organoborane was carried out using 3N NaOAc (15 mL) and H_2O_2 (16%, 25 mL). The organic layer was separated and the aqueous layer was washed with 1N HCl (2 x 15 mL) and 1N NaOH (3 x 20 mL) to remove the amine and catechol respectively, followed by water and saturated NaCl solution (15 mL). The solution was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromotagraphed on a silica gel column. The products obtained were identified as 1-decanal (0.70 g, 45%) and 1-decanol (0.32 g, 20%).

The spectral data of 1-decanal and 1-decanol showed 1:1 correspondence with those obtained earlier.

Attempted preparation of binaphtholborane from binaphthol using diborane:

Binaphthol was prepared by the coupling of β-naphthol with $FeCl_3$ following the reported procedure.[48] Binaphthol (2.88 g, 10 mmol) was taken in dry benzene (40 mL) in an RB flask with a side septum and bubbled excess diborane at 25°C over 3-4h under nitrogen atmosphere. The bubbler was replaced by a stopper and solution IR spectrum of the contents was recorded which indicated the absence of >B-H and -OH absorptions.

An attempt towards the preparation of PhO_2BH and/or $PhOBH_2$ by passing B_2H_6 through a solution of phenol in benzene also gave similar results.

Hydroboration of 1-decene with the borane reagent prepared from N,N-diethylaniline-borane complex and phenol:

N,N-diethylaniline-borane (10 mmol) complex was prepared using N,N-diethylaniline and B_2H_6 in dry benzene (40 mL) at 10°C. Phenol (0.94 g, 10 mmol) in benzene (20 mL) was added under nitrogen atmosphere with the help of a double ended needle. Evolution of H_2 gas

was observed. After the evolution ceased, 1-decene (2.8 g, 20 mmol) was added and the contents were stirred for 12h at 25°C and for 2h at 80°C . THF (10 mL) was added and the excess hydride (if any) was destroyed using water (2 mL). The organoborane species was oxidized using H_2O_2/NaOH. The organic layer was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N HCl (2 x 20 mL), followed by water and brine solution. The residue was chromatographed using hexane/ethyl acetate (95:5) as eluent, to yield 1-decanol (1.52 g, 96%).

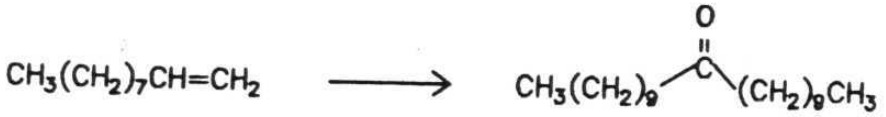
Reaction of $CHCl_3$/$NaOCH_3$ with alkylborane reagent prepared using phenol (1 eq.), BH_3:N,N-diethylamine complex (1eq.) and 1-decene (2 eq.):

N,N-diethylaniline-borane complex (10 mmol) was prepared in benzene (40 mL) at 10°C. Phenol (0.94 g, 10 mmol) in benzene (20 mL) was added under nitrogen atmosphere. After the evolution of H_2 gas ceased, 1-decene (2.8 g, 20 mmol) was added and the contents were stirred for 12h at 25°C and for 2h at 80°C. The contents were brought to 25°C and THF (30 mL) was added. The excess hydride was destroyed carefully with methanol (1 mL). To the reaction mixture, chloroform (10 mL) was added. NaOMe (2.16 g, 40 mmol) was added from a solid addition flask during 1h and the contents were further stirred at 55°C

for 2h. It was brought to 25°C and water (2 mL) was added. The organoborane species was oxidized using H_2O_2/NaOH. The contents were neutralized with 2N HCl (phenophthalein indicator) and extracted with ether (3 x 30 mL). The ether layer was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$.

The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane/chloroform as eluent to obtain di-1-decylketone (0.76 g, 30%) and 1-decanol (1.03 g, 65%).

The above experiment was repeated taking 40 mmol of 1-decene instead of 20 mmol. No improvement in the yield of di-1-decylketone was observed.



M.P. : 64°C, Lit.[60] 62°C

IR(KBr)ν_{max} : 1710 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.8 (t, $-CH_3$), 1.2 (m, $-CH_2$), 1.5 (m, $-CH_2$), 2.3 (m, $-CH_2-CO$).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.6, 23.9, 29.3, 29.5, 29.6, 31.9, 42.8, 211.9.

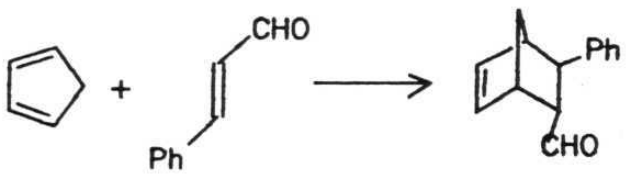
Reaction of the borane reagent prepared using BH_3:$N(C_2H_5)_2Ph$ (1 eq.) and phenol (2 eq.) with 1-decyne (1 eq.):

N,N-diethylaniline-borane complex (10 mmol) was prepared in benzene (40 mL) at 10°C. Phenol (1.88 g, 20 mmol) in benzene (20 mL) was added under nitrogen atmosphere. After the evolution of gas ceased, 1-decyne (1.38 g, 10 mmol) was added and the contents were stirred for 12h at 25°C. THF (10 mL) was added and the excess hydride was quenched with water (2 mL). The organoborane species was oxidized using H_2O_2/NaOAc. The organic layer was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N HCl (2 x 20 mL), 1N NaOH (3x 20 ml), followed by water and brine solution. The layer was dried over anhydrous $MgSO_4$. The solvent was evaporated and the compound was separated on a silica gel column using hexane/chloroform (60:40) as eluent to obtain 1-decanal (0.86 g, 55%). Some amount of the starting material was recovered (0.44 g, 34%).

Changing the reaction conditions in several ways like heating the reaction mixture to 80°C after the addition of 1-decyne, increasing the amount of the substrate added, changing the solvent to toluene, did not help in improving the yield of the product.

Attempted Diels-Alder reaction of iodocatecholborane:

Catecholborane (10 mmol) was prepared from catechol and diborane. Iodine (1.27 g, 5 mmol) was added in benzene (20 mL) and stirred for 3h. Dry DCM (20 mL) was added and the system was cooled to -78°C. Cinnamaldehyde (1.32 g, 10 mmol) was added, followed by cyclopentadiene (1.98 g, 30 mmol) and stirred for 4h. Water was added followed by hexane (10 mL). Saturated sodium bicarbonate solution was added and extracted with ether (2 x 20 mL). The organic layer was washed with $Na_2S_2O_3$ solution (2 x 20 mL), 1N NaOH solution (3 x 20 mL), water (10 mL) and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was separated on a silica gel column using hexane/ethyl acetate (95:5) as eluent to yield the Diels-Alder product (0.57 g, 29%).[40]



IR (neat) ν_{max} : 1720, 1620, 1600 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.1 (q, $-CH_2$), 3.3-3.8 (m, -CH), 6.5-6.9 (m, olefinic hydrogens), 7.7 (m, aromatic hydrogens), 9.2 (br s, -CHO) (Spectrum no. 6).

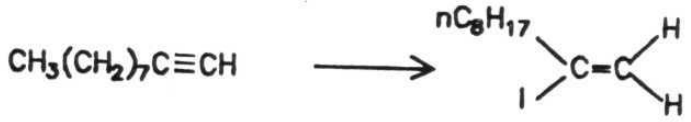
^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 41.9, 45.5, 46.9, 48.2, 60.7, 126.2, 127.3, 128.6, 133.8, 139.2, 143.6, 203.4 (Spectrum no. 7).

The product has been reported in the literature.[40]

The above reaction was tried in dry toluene also, but there was no improvement in the yield of the product obtained. Raising the reaction temperature conditions also did not help.

Attempted iodoboration-protonolysis of 1-decyne using iodocatechol-borane:

Iodo-catecholborane was prepared from catecholborane (10 mmol) and iodine (5 mmol). 1-Decyne (1.38 g, 10 mmol) was added and stirred for 24h at 25°C. Acetic acid (1.2 g, 20 mmol) was added and stirred for 1h. Sodium bicarbonate solution was added slowly and stirred for 10 mts. Hexane was added and the organic layer was separated. It was washed successively with saturated $Na_2S_2O_3$ solution (2 x 20 mL), 1N HCl solution (20 mL), 1N NaOH solution (3 x 20 mL), water (20 mL) and saturated NaCl solution. It was dried over anhydrous $MgSo_4$ and the solvent was evaporated. The residue was separated on a silica gel column using hexane as eluent to obtain 2-iododecene.



Yield : 72% (1.9 g)

IR (neat)ν_{max} : 3020, 1620 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, $-CH_2$), 2.0-2.5 (m, $-C=C-CH_2$), 5.7 (s, olefinic hydrogen), 6.0 (s, olefinic hydrogen).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.8, 22.3, 27.8, 28.8, 28.9, 31.5, 45.0, 112.8, 124.8.

Comparison of the ^{13}C NMR with that reported previously[45] confirms the structural assignment.

Attempted iodoboration-oxidation of 1-decyne using iodo-catechol-borane:

Iodo-catecholborane was prepared from catecholborane (10 mmol) and iodine (5 mmol). 1-Decyne (1.38 g, 10 mmol) was added and stirred for 24h at 25°C. THF (20 mL) was added and quenched with water (2 mL). The organoborane species was oxidized with 1N NaOH solution followed by dropwise addition of H_2O_2. The organic layer was separated, washed with saturated $Na_2S_2O_3$ (20 mL) and 1N HCl (2 x 20 mL). It was further

washed with 1N NaOH (3 x 20 mL), to remove catechol and saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/ethyl acetate as on eluent. The only product isolated was 2-iodo-1-decene (1.85 g, 70%). No iodo-aldehyde was obtained. The spectral data were identical with the data obtained in the previous experiment.

Attempted iodoboration of 1-decyne using iodocatecholborane:

N,N-diethylaniline-borane was prepared from B_2H_6 and N,N-diethylaniline (0.75 g, 5 mmol) in dry benzene (40 mL) at 10°C. To the above solution, iodine (3.81 g, 15 mmol) in dry benzene (30 mL) was added at 25°C and stirred for 12h followed by catechol (0.55 g, 5 mmol). The contents were further stirred for 10h. The solution IR spectrum of the mixture showed the absence of the -OH and >B-H absorption. Excess of triethylamine was added to arrest the reaction due to HI. 1-Decyne (0.69 g, 5 mmol) was added and stirred for 24h at 25°C. To the reaction mixture, water (10 mL) was added followed by oxidation using $NaOAc/H_2O_2$, following the reported procedure.[1] The organic layer was separated and washed with 3N NaOH solution (3 x 10 mL), 3N HCl (3 x 10 mL), water and brine solution. It was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed on a silica gel column to

obtain the 2-iodo-1-decanal (0.26 g, 9%). The starting material was recovered (0.49 g, 72%).

$$CH_3(CH_2)_7C{\equiv}CH \longrightarrow CH_3(CH_2)_7-\underset{\displaystyle I}{\overset{\displaystyle |}{C}}H-CHO$$

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

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$), 1.8 (m, $-CH_2$), 4.4 (m,-CH), 9.2 (d, -CHO).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.6, 28.8, 29.1, 31.8, 31.8, 36.8, 191.9.

The spectral data of the product showed 1:1 correspondence with the data of the sample reported previously.[46]

The above reaction was tried by heating the reaction mixture at 70°C for 24h after the addition of 1-decyne. No improvement in the yield of the product was observed.

Diels-Alder reaction of cyclopentadiene and cinnamaldehyde using iodo-catecholborane as a catalyst:

B-Iodocatecholborane (5 mmol) was prepared using N,N-diethylaniline-BI_3 complex and catechol. Cinnamaldehyde (0.66 g, 5

mmol) in dry DCM (20 mL) was added to the reagent at -20°C. Cyclopentadiene (0.66 g, 10 mmol) was added and further stirred for 6h. The reaction was quenched with water. The organic layer was separated and washed with 3N HCl (3 x 10 mL), followed by water (10 mL), 3N NaOH (3 x 10 mL), brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane/ethyl acetate (95:5) as eluent to yield the Diels-Alder product (1.48 g, 74%). The spectral data showed 1:1 correspondence with the compound obtained earlier.

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CHAPTER - 3

Studies on the reductions and hydroborations with reagents prepared using catechol and $NaBH_4$.

INTRODUCTION

Sodium borohydride is a convenient and useful reducing agent because it is easy to handle and it is readily accessible. Part of the convenience associated with sodium borohydride lies in the fact that unlike most other complex hydrides, it is not affected by moisture and atmospheric oxygen under ambient conditions. Generally, reductions can be carried out in solvents like water and alcohols. Various functional groups such as aldehydes,[1] ketones,[2] acid chlorides,[3] oximes,[4] lactones,[5] imines[6] can be reduced by sodium borohydride. However, it fails to reduce functional groups such as carboxylic acids, carboxylic salts, esters, amides, imides, nitriles, halides, nitro compounds and olefins under ambient conditions.

The reactivity of sodium borohydride can be enhanced using Lewis acids in which case, diborane is generated (eq. 1-4).

$$3NaBH_4 + BCl_3 \xrightarrow{\text{diglyme}} 3NaCl + 2B_2H_6 \quad \text{---- (1)}$$

$$3NaBH_4 + 4BF_3{\cdot}OEt_2 \xrightarrow{\text{diglyme}} 3NaBF_4 + 2B_2H_6 \quad \text{---- (2)}$$

$$2NaBH_4 + Hg_2Cl_2 \xrightarrow[25^oC]{\text{diglyme}} 2Hg + 2NaCl + H_2 + B_2H_6 \quad \text{---- (3)}$$

$$2NaBH_4 + I_2 \xrightarrow[25^oC]{\text{diglyme}} 2NaI + H_2 + B_2H_6 \quad \text{---- (4)}$$

In ethereal solvents, diborane gas dissolved to give BH_3:etherate

complexes. These complexes reduce functionalities such as acids, esters, amides, imides, nitriles and olefins.[8,9]

The reaction of MBH_4 with mineral acids also yields diborane (eq. 5-7).[10-13]

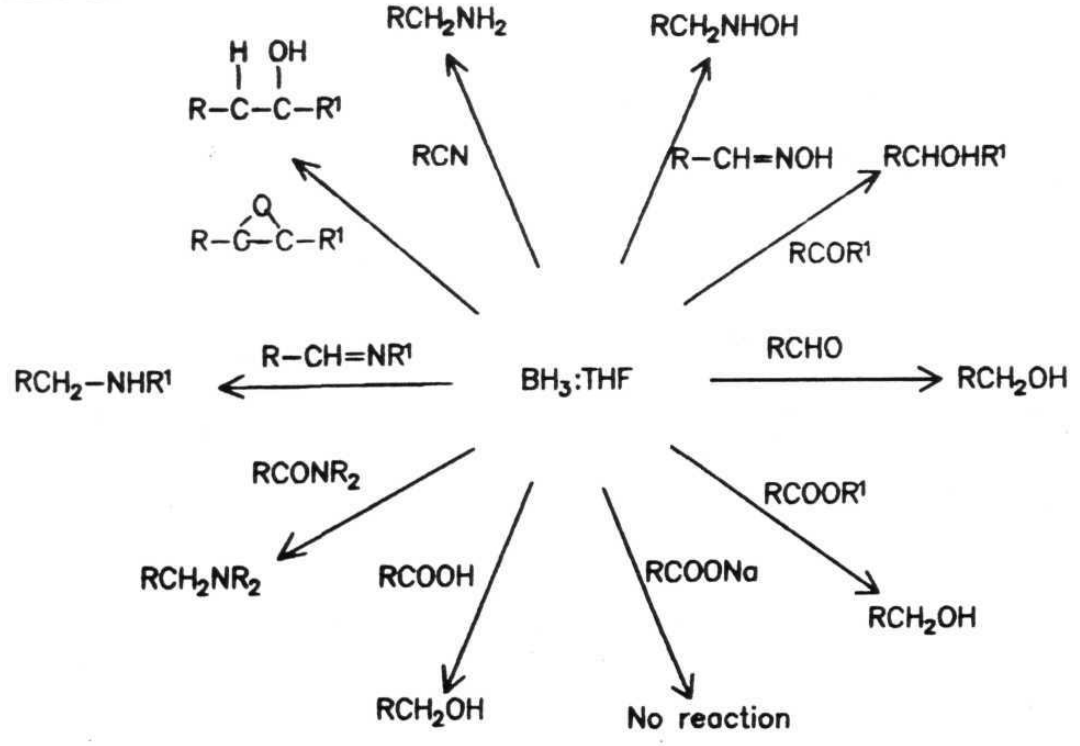
$$2NaBH_4 + H_2SO_4 \xrightarrow{\text{diglyme}} Na_2SO_4 + 2H_2 + B_2H_6 \quad (5)$$

$$2KBH_4 + 2H_3PO_4 \longrightarrow 2KH_2PO_4 + 2H_2 + B_2H_6 \quad (6)$$

$$2NaBH_4 + Me_2SO_4 \longrightarrow Na_2SO_4 + 2CH_4 + B_2H_6 \quad (7)$$

The diborane generated using the above methods can be used to prepare BH_3:THF, which is now commercialized and widely used for the reduction of a variety of functionalities (Chart 1).[14]

CHART 1:



Carboxylic acids are normally not reduced by sodium borohydride

in protolytic solvents. However, a number of aromatic and aliphatic carboxylic acids are reduced to alcohols using sodium borohydride at 300°C. Hydroboration of 1-alkenes using sodium borohydride and acetic acid givesan organoborane, which on alkaline peroxide oxidation gives good yield of the corresponding alcohol (eq.8).

$$n\text{-}C_4H_9CH{=}CH_2 \xrightarrow[2\cdot\ NaOH/H_2O_2]{1\cdot\ NaBH_4/AcOH} n\text{-}C_4H_9CH_2CH_2OH \quad \text{---} \quad (8)$$

This can be explained by the formation of the following acyloxyborohydride species (eq. 9).

$$NaBH_4 + X\ RCOOH \longrightarrow NaBH_{4-x}(OOCR)_x + XH_2 \quad \text{---} \quad (9)$$

X=1 to 3

Originally, it was observed that upon reaction of sodium borohydride (1 eq) with CH_3COOH (1 eq), a material analyzed for '$NaBH_3OAc$' crystallizes out of THF.[15] The reaction of this material with water liberates 3 moles of hydrogen. The material gives $(RO)_3PBH_3$ in good yields on treatment with trialkylphosphates.[15]

It has been observed that the reaction of isobutyric acid (1 eq) and sodium borohydride (1 eq) in THF actually gives a suspension, in which $NaBH_4$ is in equilibrium with the mono-, di-, tri- and tetra-acyloxyborohydride species (eq. 10).[16]

$$NaBH_4 \rightleftharpoons NaBH_3OAc \rightleftharpoons NaBH_2(OAc)_2 \rightleftharpoons$$

$$NaB(OAc)_4 \rightleftharpoons NaBH(OAc)_3 \quad \text{—— (10)}$$

Among the above acyloxyborohydride species, the following hydride delivering ability order was observed (eq. 11).[17]

$$^{-}BH_3OCOR > ^{-}BH_2(OCOR)_2 > ^{-}BH(OCOR)_3 \quad \text{—— (11)}$$

The $RCOOH/NaBH_4$ system prepared in neat carboxylic acids or in solvents such as benzene, THF, dioxane, DMF, dichloroethane, dichloromethane *etc.* have been utilized for several useful synthetic transformations. An excellent review has appeared recently.[17] The reagent system has been utilized for reduction of enamines,[18-21] and related substrates,[22-29] reductions of imines,[18] indoles,[30] amines,[18,31-38] reductive nitrogen heterocycles,[18,35,39-43] oximes[44-46] and related substrates, reduction of hydrazones,[47] nitriles,[48] amides,[48] carbamates,[37,49] reduction of alkenes,[50-54] alcohols,[50] ketones,[55-57] selective reduction of aldehydes[58,59] in the presence of ketones,[60-62] asymmetric reduction of ketones,[16,52,63-66] and for many other applications.

In recent years, there is an increased interest in enhancing the

reactivity of $NaBH_4$ using various additives and by partial substitution of borohydride. For example, $Zn(BH_4)_2$[67] and benzyltriethylammonium borohydride[68] were used for selective reductions of different functional groups. In this laboratory, it was found that the iodine/$NaBH_4$ system can be used for obtaining interesting applications.[69] As discussed previously, interesting reactivities were observed for the RCOOH/$NaBH_4$ systems. We have decided to examine the reactivity of the reagent generated utilizing the RCOOH/$NaBH_4$/catechol system and undertook the investigation discussed in this chapter.

RESULTS AND DISCUSSION

Reduction of carboxylic acids using catechol/$NaBH_4$ system:

It has been reported that the $NaBH_4$ reduces carboxylic acids to the corresponding alcohols under THF reflux conditions.[70] However, the yield is only about 50%.[70,71,72] It was suggested that the reaction may involve the formation of acyloxyborane intermediate (Scheme 1).[73]

SCHEME 1:

$$RCOOH + NaBH_4 \xrightarrow{\text{fast}} RCOOBH_3Na + H_2$$

$$RCOOBH_3Na \longrightarrow (RCOO)_2BH_2Na + NaBH_4$$

$$(RCOO)_2BH_2Na \longrightarrow RCOOBH_2 + RCOONa$$

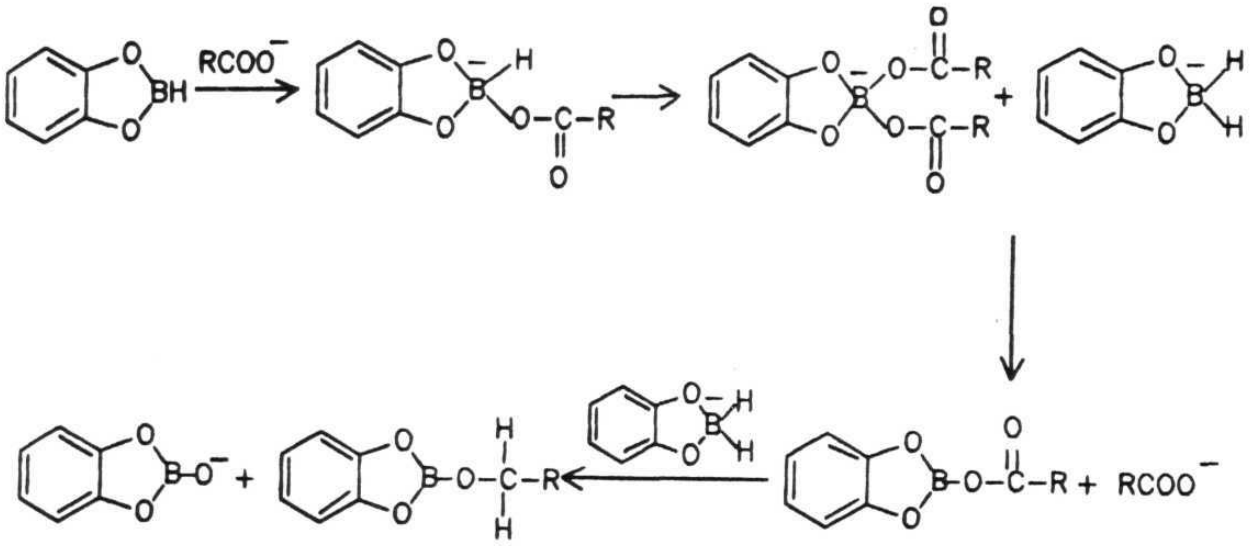
$$\downarrow \text{fast}$$

$$RCH_2O-B\!\!<$$

Kabalka *et al.*[74] have found that the sodium salt of stearic acid is reduced by catecholborane to the corresponding alcohol in THF at room temperature in 6.5h. This result is surprising because borane itself is inert towards the sodium salt of an acid.[75] The facile reduction of the carboxylate anion by catecholborane at 25°C must go through the initial formation of the ate complex, *i.e.* $RCOO^-$ could form a coordination complex with catecholborane, which might then react with another molecule of catecholborane to give the reduced product.

The sequence of reactions shown in Scheme 2 can be considered on the basis of the results obtained.

SCHEME 2:

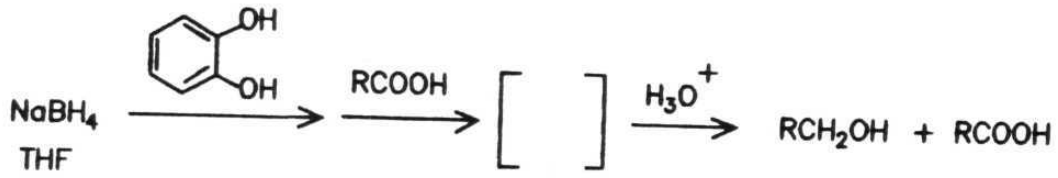


The reaction went to completion, since Kabalka utilized 2 mole equivalents of catecholborane per mole of the carboxylate anion.

It occured to us that if the above reaction sequences are true, it could be possible to reduce carboxylic acids using catechol and sodium borohydride at room temperature. In order to examine this, we performed a reaction by adding 1-decanoic acid (10 mmol) to the suspension of $NaBH_4$ (20 mmol) and catechol (20 mmol) in dry THF at $0^{\circ}C$ (scheme 3). It was further stirred for 4h at $25^{\circ}C$. After work up (see experimental section), 1-decanol was isolated (48%) besides the unreacted acid. No improvement in the yield of the product was observed by increasing the amounts of $NaBH_4$ and/or catechol.

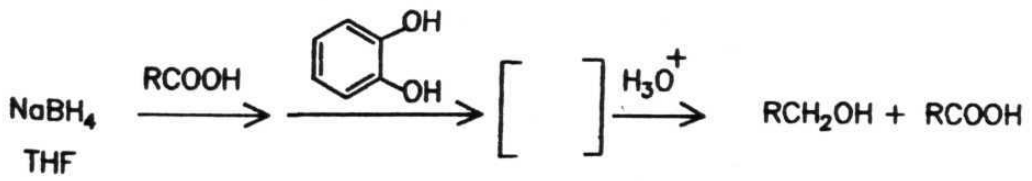
Increasing the reaction time or the reaction temperature did not help. There was no improvement in the product on increasing the amount of the substrate.

SCHEME 3:



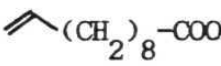
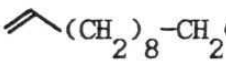
The reaction was carried out by changing the sequence of addition.[76] For example, $NaBH_4$ (20 mmol) was taken in dry THF and 1-decanoic acid (10 mmol) was added followed by the addition of catechol (20 mmol) at 0°C (Scheme 4). The mixture was stirred for 4h at 25°C. Again, 1-decanol was obtained only in 47% yield, besides the unreacted 1-decanoic acid. There was no improvement in the yield of the product formed when the experiment was carried out under various reaction conditions similar to those discussed above. Although the conversion is only upto 50%, the yield is high if the recovered acid is taken into account. When catechol was replaced by phenol (2 eq), no reduced product was obtained.

SCHEME 4:



The reagent system was used for the reduction of few other acids (Table 3.1). In all cases, the yield obtained was only about 50%.

Table 3.1: Reduction of carboxylic acids using $NaBH_4$/catechol system.[a]

Entry No.	Substrate [RCOOH]	Time[h]	Product	Yield(%)[b]
1.	$CH_3(CH_2)_7-COOH$	4	$CH_3(CH_2)_7-CH_2OH$	47
2.	$CH_3(CH_2)_8-COOH$	4	$CH_3(CH_2)_8-CH_2OH$	48
3.	$CH_3(CH_2)_{14}-COOH$	4	$CH_3(CH_2)_{14}-CH_2OH$	49
4.	$H_3COOC(CH_2)_8-COOH$	4	$H_3COOC(CH_2)_8-CH_2OH$	47
5.		4		49

a) Reactions were carried out using $NaBH_4$ (20 mmol), catechol (20 mmol) and RCOOH (10 mmol) in THF (40 mL) under N_2 atmosphere.

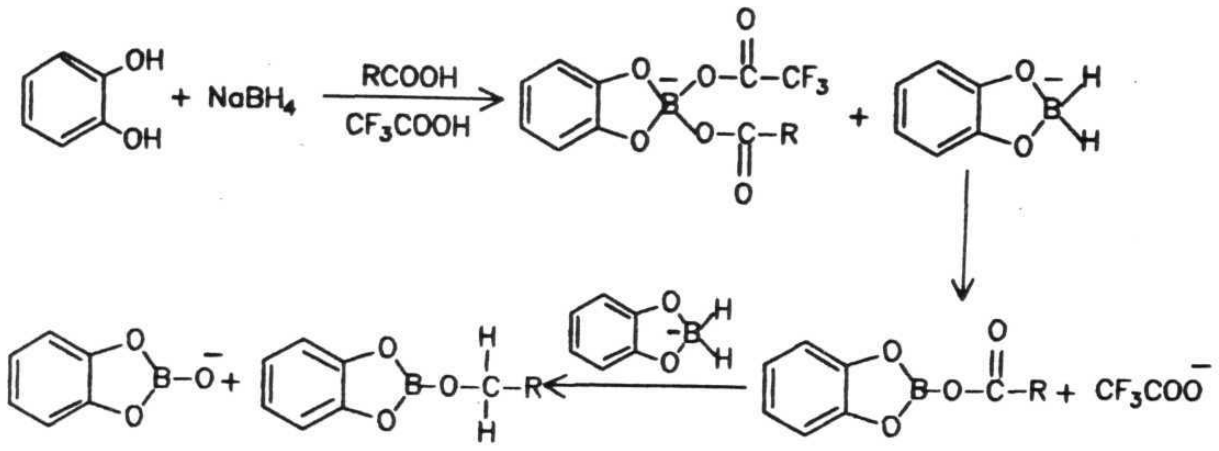
b) Yields are of products isolated by distillation and/or by column chromatography on silica gel using hexane/ethyl acetate as eluent. The products were identified by spectral data (IR, ^1H NMR, ^{13}C NMR) and comparison with the data of authentic samples.

However, the procedure is useful for reduction of molecules which have other functional groups such as an olefin or an ester along with the carboxylic acid moiety. For example, the half ester of sebacic acid is converted to the corresponding alcohol in 47% yield besides the unreacted starting material (entry no. 4, Table 3.1). Also, 10-undecenoic acid was converted to 10-undecenol in 49% yield (entry no. 5, Table 3.1) leaving the olefinic group intact. Benzoic acid gave very low yields (9%) of benzyl alcohol under these conditions.

Assuming that the reaction conditions outlined in Scheme 3 and 4 would lead to the same intermediates as outlined in Scheme 2, the results can be tentatively explained. Since there is no free catecholborane present in our reaction conditions, one half equivalent of $RCOO^-$ will remain unreacted (Scheme 1). It occured to us that if a mixture of two carboxylic acids are used and if one of them could readily dissociate to give $RCOO^-$, then the reduction of the other acid can be achieved to more extent.

It was thought that CF_3COOH would serve our purpose, since the CF_3COO^- species is expected to be relatively stable, good leaving and poorly coordinating group. A 1:1 mixture of RCOOH and CF_3COOH was utilized for this purpose (Scheme 5).

SCHEME 5:



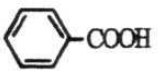
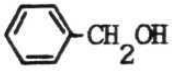
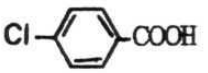
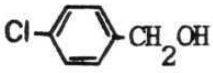
It was indeed found that the conversion of carboxylic acid into alcohol is more efficient in this case. The generality of the reaction was tested with a number of acids. It was found that the aliphatic acids are reduced to the corresponding alcohols in good yields (87-94%, Table 3.2).

When the reduction of benzoic acid was attempted, it was found that benzyl alcohol is obtained in low yield (20%). However, the result is better with p-chlorobenzoic acid. The reduction of phenylacetic acid, diphenylacetic acid and 3,5-dimethylbenzoic acid also gave poor yields of the corresponding alcohols (see the experimental section).

The low yield of benzyl alcohol obtained suggested the possibility of reducing aliphatic acids in the presence of benzoic acid. An experiment was carried out for 4h at 25°C, using 0.5 eq. of benzoic acid and 0.5 eq. of capric acid, to examine this possibility as

described in Table 3.2. 1-Decanol was isolated in 72% yield. GC analysis of the crude product revealed the absence of benzyl alcohol.

Table 3.2: Reduction of carboxylic acids using $NaBH_4$/catechol/ CF_3COOH system.[a]

Entry No.	Substrate [RCOOH]	Time(h)[b]	Product	Yield(%)[e]
1.	$CH_3(CH_2)_7COOH$	4	$CH_3(CH_2)_7CH_2OH$	87
2.	$CH_3(CH_2)_8COOH$	4	$CH_3(CH_2)_8CH_2OH$	88
3.	$CH_3(CH_2)_{10}COOH$	4	$CH_3(CH_2)_{10}CH_2OH$	91
4.	$CH_3(CH_2)_{12}COOH$	4	$CH_3(CH_2)_{12}CH_2OH$	91
5.	$CH_3(CH_2)_{14}COOH$	4	$CH_3(CH_2)_{14}CH_2OH$	92
6.	$CH_3(CH_2)_{16}COOH$	4	$CH_3(CH_2)_{16}CH_2OH$	94
7.		12		20
8.		12		62
9.	$HOOC-(CH_2)_8-COOH$[c]	12	$HOH_2C-(CH_2)_8-CH_2OH$	68
10.	$H_3COOC(CH_2)_8-COOH$[d]	12	$H_3COOC(CH_2)_8-CH_2OH$	89

a) Reactions were carried out using RCOOH (10 mmol), $NaBH_4$ (20 mmol), catechol (20 mmol) and CF_3COOH (10 mmol) in THF (40 mL) under N_2 atmosphere, (see experimental section).

....contd.

b) Time taken after adding CF_3COOH (see experimental section).

c) 5 mmol of the carboxylic acid was utilized.

d) In this case, CF_3COOH (10 mmol) was added 10 h after stirring the $RCOOH/NaBH_4$/catechol mixture.

e) Yields are of products isolated by distillation and/or by column chromatography on silica gel using hexane/ethyl acetate as eluent. The products were identified by spectral data (IR, ^1H NMR, ^{13}C NMR) and comparison with the data of authentic samples.

In order to further examine the selectivity of the reagent, the reduction of half ester of sebacic acid was carried out.

In this case, selective reduction of the carboxylic group in the presence of the ester moiety was achieved (entry no. 10, Table 3.2). The yield of the 1,10-decanediol (entry no. 9, Table 3.2) formed in the reduction of sebacic acid is somewhat low. However, it has been reported that dicarboxylic and hydroxycarboxylic acids, occasionally react with borane reagent to give insoluble, polymeric intermediates.[14] The formation of these insoluble polymers leads to incomplete reduction.

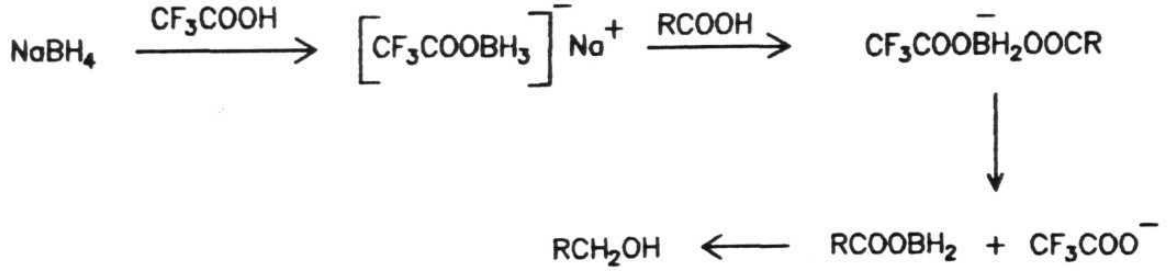
In the reduction of 10-undecenoic acid, the olefinic group also underwent hydroboration. This is surprising, since catecholborane does

not hydroborate olefins at room temperature.

Reduction of RCOOH to RCH_2OH using $NaBH_4/CF_3COOH$ system:

As mentioned previously, it has been reported that acyloxyborohydride in refluxing THF gives reduction to an extent of 50% (Scheme 1).[70,71,72] It was of interest to examine whether use of 0.5 eq. of CF_3COOH would help in carrying out such reductions to more extent at ambient conditions. If this is the case, then the use of catechol can be avoided and the hydride can be utilized in a more efficient manner (Scheme 6).

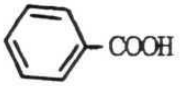
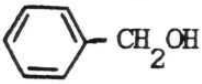
SCHEME 6:



This was indeed observed when CF_3COOH (10 mmol) was added to RCOOH (10 mmol) and $NaBH_4$ (10 mmol) and stirred for 4h at 25°C (Table 3.3).

The results obtained are similar to those obtained using catechol. In this case also the yield of benzyl alcohol obtained after the reduction of benzoic acid was somewhat low (30%). These results

Table 3.3: Reduction of carboxylic acids using $NaBH_4/CF_3COOH$ system.[a]

Entry No.	Substrate [RCOOH]	Time(h)[b]	Product	Yield(%)[d]
1.	$CH_3(CH_2)_7COOH$	4	$CH_3(CH_2)_7CH_2OH$	93
2.	$CH_3(CH_2)_8COOH$	4	$CH_3(CH_2)_8CH_2OH$	95
3.		12		30
4.	$HOOC-(CH_2)_8-COOH$[c]	12	$HOH_2C-(CH_2)_8-CH_2OH$	65
5.	$H_3COOC(CH_2)_8-COOH$	12	$H_3COOC(CH_2)_8-CH_2OH$	78

a) Reactions were carried out using RCOOH (10 mmol), $NaBH_4$ (10 mmol) and CF_3COOH (10 mmol) in THF (40 mL) under N_2 atmosphere (see experimental section).

b) Time taken after the addition of CF_3COOH.

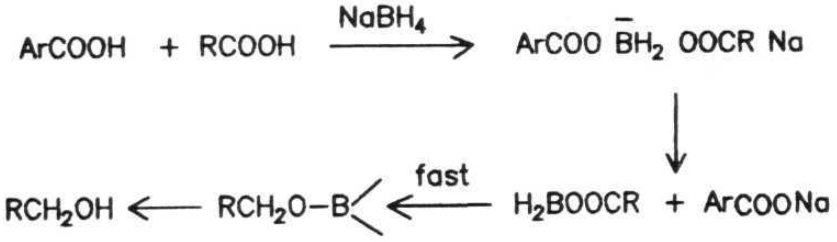
c) 5 mmol of acid was utilized.

d) Yields are of products isolated by distillation and/or by column chromatography on silica gel using hexane/ethyl acetate as eluent. The products were identified by spectral data (IR, ^1H NMR, ^{13}C NMR) and comparison with the data of authentic samples.

again indicate the possibility of achieving selective reduction of an aliphatic carboxylic acid over an aromatic acid.

In order to examine this, an experiment using capric acid (5 mmol) and benzoic acid (5 mmol) was carried out. In this case, the 1-decanol was obtained in 72% yield and the benzyl alcohol was not formed. GC analysis of the crude product also indicated the absence of benzyl alcohol. This result is similar to that observed by Cho and Yoon,[77] in the reduction of aliphatic acid over aromatic acid by $NaBH_4$ in THF at reflux temperature (Scheme 7).

SCHEME 7:



Hydroboration of alkenes and alkynes using $NaBH_4$/catechol/CF_3COOH:

We have found that in the case of 10-undecenoic acid, the olefinic moiety was also hydroborated when the reagent system $NaBH_4$/catechol/CF_3COOH was used. This observation prompted us to further explore the reactivity of this system.

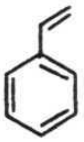
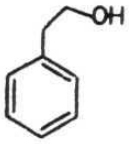
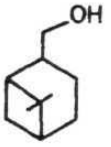
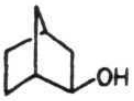
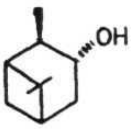
To a mixture of catechol (10 mmol) and $NaBH_4$ (10 mmol) in THF at $0^{\circ}C$, 1-decene (10 mmol), and CF_3COOH (10 mmol) were added. The mixture was further stirred at $25^{\circ}C$ for 12h and was oxidized using H_2O_2/OH^-, to

give 1-decanol in 92% yield.

The generality of the reaction was examined with several other olefins such as 1-octene, 1-dodecene, norbornene, styrene, α-pinene, β-pinene and cyclohexene. The results are summarized in Table 3.4. It was found that, whereas the yields of the hydroborated product obtained in the case of terminal olefins are reasonable (77-92%), the internal olefins give lesser yields. However, in the case of norbornene, the yield was good as expected.

When the reaction was carried out in the absence of CF_3COOH, no hydroborated product was obtained and the starting material was recovered quantitatively. When benzoic acid was used instead of CF_3COOH, under the same conditions, in the hydroboration of 1-decene, 1-decanol was obtained in only 46% yield. Similar reaction was attempted by taking phenol (2 eq) instead of catechol, in which case only the starting material was recovered. The low reactivity of the $NaBH_4$/catechol/CF_3COOH system towards internal olefins when compared with the terminal olefins prompted us to carry out a reaction using 1-decene and α-pinene. 1-Decanol was obtained in 84% yield in this case. The GC analysis of the mixture showed that isopinocampheol is present in less than 5%. ^{13}C NMR also showed the absence of the isopinocampheol.

Table 3.4: Hydroboration of olefins using $NaBH_4$/catechol/CF_3COOH system.[a]

Entry No.	Substrate (olefin)	Time(h)[b]	Product[c]	Yield(%)[d]
1.	$CH_3(CH_2)_5-CH=CH_2$	12	$CH_3(CH_2)_6CH_2OH$	88
2.	$CH_3(CH_2)_7-CH=CH_2$	12	$CH_3(CH_2)_8-CH_2OH$	92
3.	$CH_3(CH_2)_9-CH=CH_2$	12	$CH_3(CH_2)_{10}-CH_2OH$	85
4.		12		71
5.		12		77
6.		12		63
7.		12		45
8.		12		46

....contd.

a) Reactions were carried out using $NaBH_4$ (10 mmol), catechol (10 mmol), CF_3COOH (10 mmol) and olefin (10 mmol) in THF (40 mL) under N_2 atmosphere (see experimental section).

b) Time taken after the addition of CF_3COOH (see experimental section).

c) Oxidation was carried out using $NaOH/H_2O_2$.

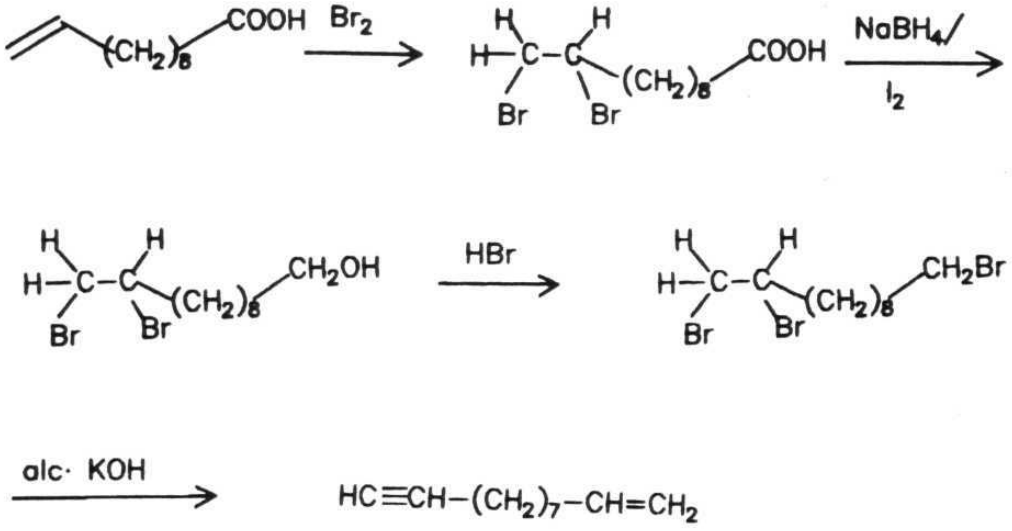
d) Yields are of products isolated by distillation and/or column chromatography on silica gel using hexane/ethyl acetate as eluent. The products were identified by spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with the data of authentic samples.

It is surprising to note that when 1-decene was replaced by 1-decyne under the same reaction conditions, only 15% of 1-decanal was obtained. The starting material was recovered in 81% yield. It is apparent that the reagent system is somewhat different from catecholborane, which hydroborates alkynes much faster than alkenes. This reverse reactivity was used in the selective reduction of 1-decene (10 mmol) in the presence of 1-decyne (10 mmol). In this case, 1-decanol was obtained as the major product in 79% yield. 1-Decanal was obtained in 9% yield.

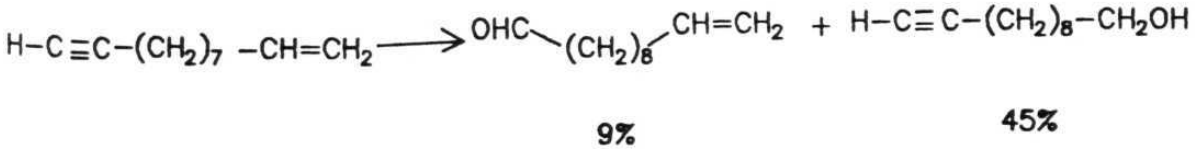
It appeared that it may be possible to hydroborate 1-alkene in the presence of a terminal alkyne. In order to examine this, undeca-1-en-10-yne was prepared from 10-undecanoic acid in 4 steps

(Scheme 8, for details see experimental section).[69,78]

SCHEME 8:

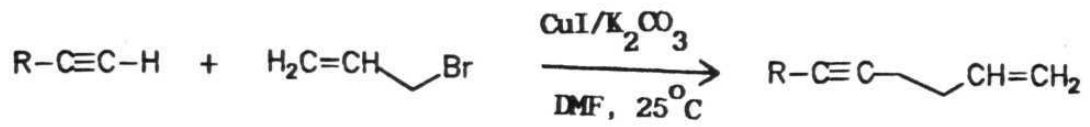


When this terminal enyne (10 mmol) was added to catechol/$NaBH_4$ system (10 mmol), the acetylenic alcohol was obtained in 45%, along with 9% of the olefinic aldehyde and the starting material was recovered in 36% yield. There was not much improvement in the amount or the ratio of the product, when the reaction time was increased to 36h.

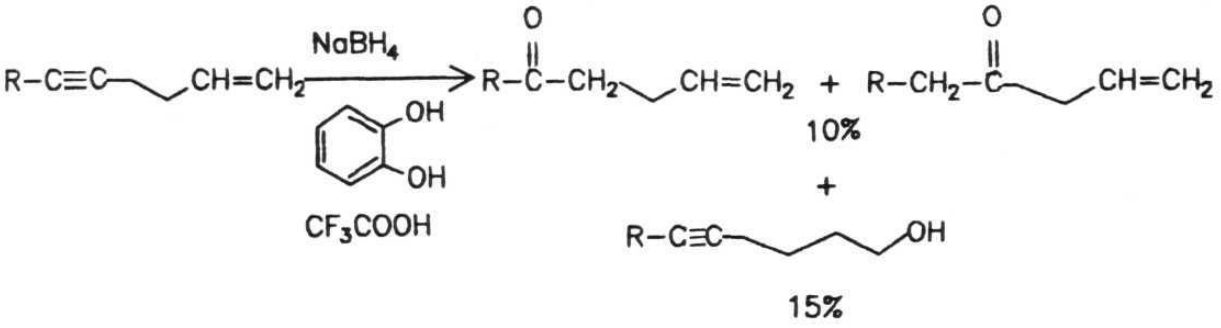


In order to examine the reactivity of an internal alkyne-terminal alkene combination, an enyne from 1-decyne and allyl bromide (Scheme 9) was prepared.[79]

SCHEME 9:

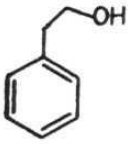
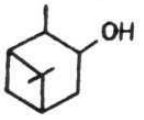


In this case, the acetylenic alcohol was obtained in 15% yield and the olefinic ketones in 10% yield. The starting material was recovered in 66% yield. Again, increasing the reaction time did not improve the yield.



The hydroboration with this reagent system in the absence of catechol was then examined. To a mixture of $NaBH_4$ (1 eq) and CF_3COOH (1 eq) in dry THF at 0°C, 1-decene (3 eq) was added and stirred for 4h at 25°C. 1-Decanol was obtained in 97% yield. In order to examine the generality of the reaction, the hydroboration of styrene, and α-pinene was examined (see Table 3.5). In all the cases, the alcohols were obtained in good yields. Hence, from these results it is clear that this reagent is more reactive than the $NaBH_4$/catechol/ CF_3COOH system. This is obvious from the reactivity observed using α-pinene.

Table 3.5: Hydroboration of olefins using $NaBH_4/CF_3COOH$ system.[a]

Entry No.	Substrate (olefin)	Time(h)	Product[c]	Yield(%)[b]
1.	$CH_3(CH_2)_7CH=CH_2$	4	$CH_3(CH_2)_8-CH_2OH$	97
2.		4		95
3.		4		91

a) Reactions were carried out using $NaBH_4$ (5 mmol), CF_3COOH (5 mmol) in and olefin (15 mmol, 10 mmol in the case of α-pinene)in THF (40 mL).

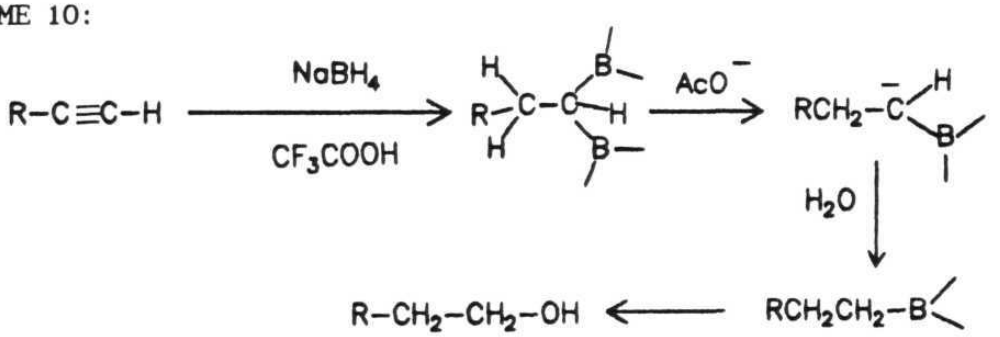
b) Yields are of products isolated by distillation and/or by column chromatography on silica gel using hexane/ethyl acetate as eluent. The products were identified by spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with the data of the authentic samples.

c) Oxidation was carried out using $NaOH/H_2O_2$.

The hydroboration of α-pinene with $NaBH_4/CF_3COOH$ gave isopinocampheol in 91% yield. But with $NaBH_4$/catechol/CF_3COOH, the alcohol

was obtained in only 45% yield even after 12h. The reactivity of this reagent was further examined using 1-decyne (3 eq). It was found that the reaction gave only 1-decanol after oxidation with $NaOAc/H_2O_2$, indicating that the reaction does not stop at the mono- hydroboration stage and gives gem-dibora compound, which is known to give 1-decanol (Scheme 10). The product was obtained in 47% yield. The starting material was recovered in 44% yield.

SCHEME 10:



This is the major difference between the $NaBH_4$/catechol/CF_3COOH and $NaBH_4/CF_3COOH$ systems.

The reactivity of the $NaBH_4$/catechol/CF_3COOH is interesting. The hydroboration by this system may be due to the presence of small amount of BH_3:THF or $CF_3COO\bar{B}H_3$ species in the reaction mixture which may hydroborate alkenes and alkynes. The alkyl and alkenyl groups could then be transfered to the catecholborane species in ways similar to that discussed in Chapter-2. However, precise nature of the species involved in these transformations is not clearly understood.

CONCLUSIONS

The reagent systems $NaBH_4$/catechol, $NaBH_4$/catechol/CF_3COOH and $NaBH_4$/CF_3COOH in THF are useful in the reduction of carboxylic acids to the corresponding alcohol with some selectivities. The systems $NaBH_4$/catechol/CF_3COOH and $NaBH_4$/CF_3COOH are also useful in the hydroboration of olefins again with certain selectivities. Although the nature of the intermediate species is not clear, the synthetic methods developed utilizing these readily accessible reagents should be useful.

EXPERIMENTAL SECTION

General Details:

Several items given in the experimental section of Chapter 2 are also applicable for the experiments outlined here.

All carboxylic acids utilized are commercial materials. Trifluoroacetic acid utilized was supplied by Fluka, Switzerland. Half-ester acid of sebacic acid was prepared from sebacic acid following literature procedure.[80] Cobalt naphthenate supplied by Fluka, Switzerland was utilized for the oxidation of mesitylene to 3,5-dimethylbenzoic acid.[81]

Undeca-1-en-10-yne was prepared starting from 10-undecanoic acid in 4 steps.[69,78] Trideca-1-en-4-yne was prepared from 1-decyne and allyl bromide following a reported procedure.[79] Sodium borohydride was purified by dissolving it in dry DME and collecting the precipitate at 0°C by the addition of dry ether. The precipitate was dried under nitrogen atmosphere and used immediately.

Reduction of capric acid (1 eq) using $NaBH_4$/catechol (1:1 eq):

Sodium borohydride (0.4 g, 10 mmol) in dry THF (20 mL) was taken

in a 2 necked RB flask. To the slurry, catechol (1.1 g, 10 mmol) in dry THF (20 mL) was added slowly under N_2 atmosphere over 15 min at 0°C with the help of a double-ended needle. After the evolution of H_2 gas ceased, capric acid (1.72 g, 10 mmol) dissolved in dry THF (20 mL) was added slowly under N_2 atmosphere at 0°C. Evolution of H_2 gas was again observed. The reaction mixture was stirred at 25°C for 4h and quenched carefully with 3N HCl (5 mL). The aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was succesively washed with 1N NaOH solution (3 x 20 mL), water (20 mL) and saturated NaCl solution (20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/ethyl acetate (95:5) as eluent. 1-Decanol was isolated (0.74 g, 47%). IR spectrum of the product showed 1:1 correspondence with the authentic sample obtained earlier (Chapter-2).

The aqueous layer was neutralized using 3N HCl and extracted with ether (3 x 20 mL). The combined organic extract was washed with brine and dried over anhydrous $MgSO_4$. The solvent was evaporated to yield the unreacted capric acid in 40% yield.

Similar results were obtained when catechol was added after the addition of capric acid.

Reduction of capric acid (1 eq) using $NaBH_4$/catechol (2:2 eq):

Sodium borohydride (0.8 g, 20 mmol) was taken in dry THF (20 mL) and catechol (2.2 g, 20 mmol) in dry THF (20 mL) was added slowly under N_2 atmosphere over 15 min. at 0°C. After H_2 gas evolution ceased, capric acid (1.72 g, 10 mmol) in dry THF (20 mL) was added slowly under N_2 atmosphere at 0°C. The reaction mixture was stirred at 25°C for 4h and was quenched carefully with 3N HCl solution (5 mL). The aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was washed successively with 1N NaOH solution (3 x 20 mL), water (20 mL) and saturated NaCl solution (20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/ethyl acetate (95:5) as eluent to yield 1-decanol (0.76 g, 48%). The IR spectrum showed 1:1 correspondence with that of the product obtained earlier.

When the reaction was carried out by adding catechol after the addition of capric acid, the result obtained was almost the same as obtained in the previous experiment.

There was no improvement in the yield even at 80°C. The procedure of reduction using carboxylic acid (1 eq), $NaBH_4$ (2 eq) and

catechol (2 eq) was followed for the conversion of several other acids into the corresponding alcohols and the results are summarized below and also in Table 3.1.

$CH_3(CH_2)_7COOH \longrightarrow CH_3(CH_2)_7COOH$

Yield : 47% (0.70 g)

B.P. : 117°C/15 mm , Lit.[82] 213°C/760 mm

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 3.6 (t, $-CH_2$), 4.2 (br s, -OH).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 25.7, 29.3, 29.6, 31.9, 32.8, 63.1.

$CH_3(CH_2)_{14}COOH \longrightarrow CH_3(CH_2)_{14}CH_2OH$

Yield : 49% (1.18 g)

M.P. : 48-49°C, Lit.[83] 50°C

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 3.6 (t, $-CH_2$), 4.2 (br s, -OH).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 25.7, 29.3, 29.6, 31.9, 32.8, 63.1.

Yield : 49% (0.84 g)

B.P. : 130°C/15 mm , Lit.[84] 132-133°C/15 mm

IR (neat)ν_{max} : 3350, 1620, 1060 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.2 (m, $-CH_2$ hydrogens), 1.5 (br s, -OH), 1.9 (m, $-CH_2$ attached to olefin), 3.6 (t, $-CH_2-O$), 4.8-5.9 (m, olefinic hydrogens).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 25.7, 28.8, 29.0, 29.3, 29.4, 32.5, 33.6, 62.4, 114.0, 139.0 **(Spectrum no. 8).**

Yield : 47% (0.95 g)

B.P. : 121°C/0.5 mm, Lit.[85] 156°C/45 mm

IR (neat)ν_{max} : 3375, 1730, 1060 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.2 (m, $-CH_2$ hydrogens), 1.5 (br -s, -OH), 2.1 (m, $-CH_2$ attached to $-COOCH_3$), 3.4 (t, $-CH_2-O$), 3.6 (s, $-OCH_3$).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.4, 25.3, 28.7, 28.8, 32.1, 33.5, 33.7, 50.9, 61.9, 173.6 **(Spectrum no. 9).**

Attempted reduction of benzoic acid (1 eq) using $NaBH_4$ (2 eq) and catechol (2 eq):

Sodium borohydride (0.8 g, 20 mmol) was taken in dry THF (20 mL) and catechol (2.2 g, 20 mmol) in dry THF (20 ml) was added over 15 min. The mixture was stirred for 1h and benzoic acid (1.22 g, 10 mmol) in dry THF (20 mL) was added at $0^{\circ}C$. The reaction mixture was stirred for 4h at $25^{\circ}C$ and was carefully quenched with 3N HCl solution (5 mL). The organic layer was extracted with ether (3 x 10 mL) and the combined extract was successively washed with 1N NaOH solution (3 x 20 mL), water (20 mL), saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane/ethyl acetate (95:5) as eluent to obtain benzyl alcohol in 9% yield. The aqueous extract was neutralized using 3N HCl and extracted with ether (3 x 10 mL). The combined organic layer was successively washed with brine, dried over anhydrous $MgSO_4$ and evaporated to isolate unreacted benzoic acid (1.04 g, 85%).

B.P. : $92^{\circ}C$/10 mm, Lit.[86] $205^{\circ}C$/760 mm

IR (neat)ν_{max} : 3010, 1600, 1060 cm^{-1}

Reduction of capric acid using $NaBH_4$/catechol system in the presence of CF_3COOH.

To a suspension of sodium borohydride (0.8 g, 20 mmol) in dry THF (20 mL), catechol (2.2 g, 20 mmol) in dry THF (20 ml)was added at 0°C over 15 min. Evolution of H_2 gas was observed. The mixture was stirred for 1h and capric acid (1.72 g, 10 mmol) in dry THF was added followed by CF_3COOH (1.14 g, 10 mmol) at 0°C. The mixture was stirred for 4h at 25°C, carefully quenched with 3N HCl (5 mL) and extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N NaOH solution (3 x 20 mL). It was further washed with water (20 mL), saturated NaCl solution (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain 1-decanol (13.9 g, 88%). The spectral data showed 1:1 correspondence with the data of the authentic sample.

The above procedure was followed for the conversion of several other acids into the corresponding alcohols and the results are summarized below and also in Table 3.2.

With 1-nonanoic acid, the 1-nonanol was obtained (1.25 g, 87%). The spectral data showed 1:1 correspondence with the data of the product obtained earlier.

$CH_3(CH_2)_{10}COOH \longrightarrow CH_3(CH_2)_{10}CH_2OH$

Yield : 91% (1.69 g)

B.P. : 188°C/15 mm, Lit.[87] 256°C/760 mm

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 2.2 (br -s, -OH), 3.6 (t, $-CH_2$).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 25.8, 29.4, 29.7, 32.0, 32.8, 63.1.

$CH_3(CH_2)_{12}COOH \longrightarrow CH_3(CH_2)_{12}CH_2OH$

Yield : 91% (1.94 g)

M.P. : 39°C, Lit.[87] 38°C

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 2.4 (br -s, -OH), 3.6 (t, $-CH_2$).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.9, 22.6, 25.7, 28.8, 29.5, 29.6, 31.9, 32.6, 62.5.

$$CH_3(CH_2)_{14}COOH \longrightarrow CH_3(CH_2)_{14}CH_2OH$$

With 1-hexadecanoic acid, the 1-hexadecanol was obtained (2.22 g, 92%). The spectra were superimposable with the spectra obtained earlier.

$$CH_3(CH_2)_{16}COOH \longrightarrow CH_3(CH_2)_{16}CH_2OH$$

Yield : 94% (2.53 g)

M.P. : 58°C, Lit.[88] 50.9°C

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 2.3 (br -s, -OH), 3.6 (t, $-CH_2$).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.7, 25.8, 28.9, 29.4, 29.5, 31.8, 32.4, 62.8.

Reduction of sebacic acid using $NaBH_4$/catechol system in the presence of CF_3COOH:

To a suspension of sodium borohydride (0.8 g, 20 mmol) in dry THF

(20 mL), catechol (2.2 g, 20 mmol) in dry THF (20 mL) was added at 0°C. After the evolution of gas ceased, sebacic acid (1.01 g, 5 mmol) in dry THF (20 mL) was added followed by CF_3COOH (1.14 g, 10 mmol) at 0°C and stirred for 12h at 25°C. The mixture was quenched with 3N HCl (5 mL) carefully and extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N NaOH solution (3 x 20 mL). It was further washed with water (20 mL), saturated NaCl solution (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain the corresponding diol, which was purified by column chromatography.

$$HOOC-(CH_2)_8-COOH \longrightarrow HOCH_2-(CH_2)_8-CH_2OH$$

Yield : 68% (0.59 g)

M.P. : 72°C, Lit.[89] 72-75°C

IR : 3350, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.2 (m, all $-CH_2$ hydrogens), 3.2 (t, $-CH_2-OH$), 3.8 (br -s, -OH).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 25.5, 29.1, 32.4, 62.6.

Reduction of half ester of sebacic acid using $NaBH_4$/catechol system in the presence of CF_3COOH:

Sodium borohydride (0.8 g, 20 mmol) was taken in dry THF (20 mL) and catechol (2.2 g, 20 mmol) in dry THF (20 mL) was added at 0°C over

15 min. The mixture was stirred for 1h and the ester acid (2.16 g, 10 mmol) was added to dry THF (20 mL) at 0°C. The reaction mixture was stirred for 10h, CF_3COOH (1.14 g, 10 mmol) was added at 0°C and stirred for 2h at 25°C. The mixture was quenched with 3N HCl (5 mL) carefully and extracted with ether (3 x 10 mL). The combined organic extract was washed successively with 1N NaOH (3 x 20 mL), water (20 mL), saturated NaCl and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane/ ethyl acetate (95:5) as eluent to obtain methyl-10-hydroxydecanoate (1.8 g, 89%). The spectral data showed 1:1 correspondence with the data obtained earlier.

When the aliphatic acid was replaced by an aromatic acid (benzoic acid) in the above experiment, the benzyl alcohol was obtained (0.22 g, 20%). The yields are relatively low with most of the aromatic acids.

Yield : 62% (0.89 g)

M.P. : 73°C, Lit.[90] 75°C

IR (neat)ν_{max} : 3350, 1600, 1060 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 64.1, 128.2, 128.5, 133.2, 139.2.

Yield : 39% (0.48 g)

B.P. : 97°C/10 mm, Lit.[91] 120°C/12 mm

IR (neat)ν_{max} : 3360, 1600, 1050 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.9 (br -s, -OH), 2.9 (t, $-CH_2$), 3.9 (t, $-CH_2$), 7.3 (m, aromatic hydrogens).

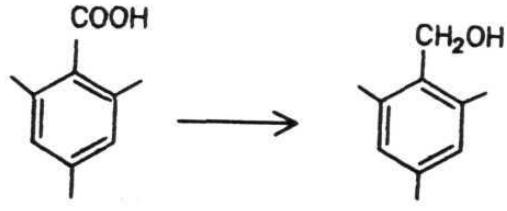
^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 38.9, 63.3, 125.3, 128.2, 128.8, 138.7.

Yield : 41% (0.77 g)

M.P. : 51°C, Lit.[92] 52°C

IR (neat)ν_{max} : 3350, 1610, 1040 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 53.5, 66.3, 126.8, 127.1, 128.4, 128.8, 139.0, 141.5.



Yield : 34% (0.46 g)

B.P. : 104°C/7 mm, Lit [93] 220°C/760 mm

IR (neat)ν_{max} : 3350, 1620, 1060 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 2.3 (br -s, -OH), 2.4 (s, $-CH_3$ attached to phenyl), 4.6 (s, CH_2-O), 7.0 (s, aromatic).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 21.2, 65.1, 125.0, 129.2, 138.1, 141.2.

Selective reduction of capric acid over benzoic acid using $NaBH_4$/catechol system in the presence of CF_3COOH:

To a suspension of sodium borohydride (0.8 g, 20 mmol) in dry THF (20 mL), catechol (2.2 g, 20 mmol) in dry THF (20 mL) was added slowly over 15 min. at 0°C. The mixture was stirred for 1h. Capric acid (0.86 g, 5 mmol) and benzoic acid (0.61 g, 5 mmol) in dry THF (20 mL) were added at 0°C, followed by CF_3COOH (1.14 g, 10 mmol). The reaction mixture was stirred for 4h at 25°C. The mixture was quenched with 3N HCl (5 mL) carefully and extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N NaOH solution (3 x 20 mL). It was further washed with water (20 mL), saturated NaCl solution (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. 1-Decanol was obtained (1.14 g, 72%). GC analysis of the crude reaction mixture revealed the absence of benzyl alcohol.

Reduction of capric acid with $NaBH_4$ in the presence of CF_3COOH:

To a suspension of sodium borohydride (0.4 g, 10 mmol) in dry THF (20 mL), capric acid (1.72 g, 10 mmol) was added. After the evolution of gas ceased, CF_3COOH (1.14 g, 10 mmol) was added slowly over 15 min. at 0°C and stirred for 4h at 25°C. The mixture was quenched with 3N HCl (5 mL) carefully and extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N NaOH (3 x 20 mL), water (20 mL), saturated NaCl solution (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using n-hexane/ethyl acetate (95:5) as eluent to yield 1-decanol (1.5 g, 95%). IR spectrum of the product showed 1:1 correspondence with that obtained earlier.

The reduction of pelargonic acid (10 mmol) also occured in good amounts giving the corresponding alcohol (1.34 g, 93%). Sebacic acid (5 mmol) was reduced in 65% (0.56 g) yield. With the $NaBH_4/CF_3COOH$ system also, the conversion of benzoic acid (10 mmol) to benzyl alcohol was only 30% (0.32 g). The spectra of all the products were superimposable with that of the spectra reported earlier.

Similar procedure was followed for the monomethyl ester of sebacic acid, to observe the selectivity of $NaBH_4/CF_3COOH$ system

towards esters. The alcoholic ester of sebacic acid was obtained (1.58 g, 78%). The spectral data showed 1:1 correspondence with the data of the product obtained earlier.

Hydroboration of 1-decene using $NaBH_4$/catechol system in the presence of CF_3COOH:

Sodium borohydride (0.4 g, 10 mmol) was taken in dry THF (20 mL) and catechol (1.1 g, 10 mmol) in dry THF (20 mL) was added at 0°C under N_2 atmosphere. The mixture was stirred for 1h at 25°C. 1-Decene (1.4 g, 10 mmol) was added at 0°C followed by CF_3COOH (1.14 g, 10 mmol) and stirred for 12h at 25°C. The reaction mixture was quenched with water (2 mL) while externally cooling with cold water.The organoborane was oxidized by adding 3N NaOH (15 mL) followed by dropwise addition of H_2O_2 (16%, 25 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic extract was washed with 1N NaOH solution (3 x 10 mL), to remove catechol followed by water (20 mL) and saturated NaCl solution (20 mL). It was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/ethyl acetate (95:5) as eluent to obtain 1-decanol (1.45 g, 92%).

The hydroboration of 1-octene and 1-dodecene also gave good yields of the corresponding alcohols. The results are summarized below and also in Table 3.4.

$$CH_3(CH_2)_5CH=CH_2 \longrightarrow CH_3(CH_2)_6CH_2OH$$

Yield : 88% (1.14 g)

B.P. : 100°C/20 mm, Lit [94] 194°C/760 mm

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$ hydrogens), 2.4 (br -s, -OH), 3.6 (t,$-CH_2$).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.8, 25.9, 29.5, 31.8, 32.7, 63.3.

$$CH_3(CH_2)_9CH=CH_2 \longrightarrow CH_3(CH_2)_{10}CH_2OH$$

Yield : 85 % (1.58 g)

The spectral data of the product showed 1:1 correspondence with the data obtained earlier.

Several other olefins were hydroborated using the $NaBH_4/CF_3COOH$

reagent and the resulting organoborane species were oxidized with H_2O_2/OH^-.

Yield : 63% (1.41 g)

M.P. : 126°C, Lit.[95] 125°C

IR (neat)ν_{max} : 3350, 1060 cm^{-1}

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

Yield : 71% (0.87 g)

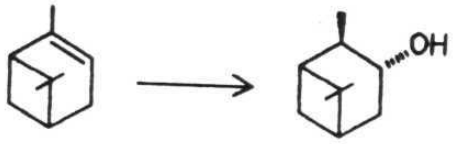
B.P. : 90°C/10 mm, Lit.[91] 100-103°C/12 mm

IR (neat)ν_{max} : 3300, 1020 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.4 (d, $-CH_3$), 2.7 (t, $-CH_2$), 2.8 (br s, -OH), 3.6 (t, $-CH_2-O$), 4.7 (q, CH-O-). 7.2 (m, aromatic hydrogens).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 24.9, 35.1, 63.3, 65.9, 125.3, 126.1, 127.1, 128.2, 128.8, 138.7.

^{1}H NMR signal showed the presence of isomeric 1-phenylethanol upto 20%.



Yield : 45% (0.69 g)

The data were identical to the data obtained earlier in Chapter-2.

Yield : 77% (1.19 g)

B.P. : 88-89°C/2 mm, Lit.[96] 65°C/0.2 mm

IR (neat)ν_{max} : 3360, 1600, 1050 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.1 (s, $-CH_3$), 2.0 (m, $-CH_2$'s), 2.3 (m, -OH), 3.6 (d, CH_2-OH).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 18.2, 22.7, 25.4, 27.3, 32.6, 37.9, 40.9, 42.3, 43.6, 66.7.

Yield : 46% (0.46 g)

B.P. : 60°C/20 mm, Lit.[97] 160°C/760 mm

IR (neat)ν_{max} : 3350, 1050 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.4 (m, $-CH_2$'s), 2.8 (br -s, -OH), 3.3 (m, -CH).

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

Preparation of undeca-1-en-10-yne:

i) **Preparation of 10,11-dibromoundecanoic acid:**[78]

10-Undecanoic acid (9.4 g, 50 mmol) was taken in CCl_4 (50 mL) and cooled to 0°C. Bromine (11.1 g, 70 mmol) in CCl_4 (20 mL) was added in portions over 1h and was stirred for 1h. Excess bromine was destroyed using saturated $NaHSO_3$ solution. The organic layer was separated and washed with water (20 mL) and brine solution. It was then dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. IR spectrum of the crude showed the absence of olefinic peaks.

ii) **Reduction of 10,11-dibromoundecanoic acid using $NaBH_4/I_2$:**[69]

Sodium borohydride (2.4 g, 60 mmol) in dry THF (120 mL) was taken in a 2 necked RB flask and iodine (6.4 g, 25 mmol) in THF (60 mL) was added slowly during 2.5h through a pressure equilizer at 0°C. To this

10,11-dibromoundecanoic acid (17.2 g, 50 mmol) in THF (30 mL) was added with the help of a double-ended needle. The contents were further stirred for 1h at 25°C. 3N HCl (20 mL) was added carefully and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic layer was washed with 3N NaOH solution (3 x 10 mL) and saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated to yield essentially pure 10,11-dibromodecanol. The compound was used without further purification.

Yield : 90% (15 g)

IR (neat)ν_{max} : 3325, 2900, 2850, 1450, 1050 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 62.1, 58.2, 36.1, 35.7, 32.2, 29.1, 28.5, 26.4, 25.4.

iii) **Preparation of 1,10,11-tribromoundecane.**[78]

10,11-Dibromoundecanol was stirred with excess of HBr (50%, 60 ml) for 2h at 25°C and extracted with hexane. The hexane layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was evaporated to yield 1,10,11-tribromoundecane (16.8 g, 95%).

iv) **Preparation of undeca-1-en-10-yne:**

The 1,10,11-tribromo undecane obtained above was subjected to dehydrobromination as reported in the literature.[78]

Yield : 20% (1.27 g)

IR (neat)ν_{max} : 3300, 2300, 3020, 1620, 900 cm^{-1}

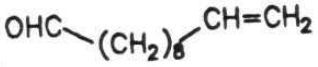
^1H NMR (100 MHz, $CDCl_3$) : δ ppm 1.3 (m, CH_2's), 1.8-2.3 (m, CH_2's attached to unsaturation), 4.8-5.1 (m, $=CH_2$,$\equiv CH$), 5.5-6 (m, olefinic hydrogens).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 18.3, 28.4, 28.7, 28.9, 33.8, 68.1, 84.6, 114.3, 139.2.

Hydroboration of undeca-1-en-10-yne (1 eq) using $NaBH_4$/catechol (1:1 eq) to the presence of CF_3COOH:

To a suspension of sodium borohydride (0.4 g, 10 mmol) in dry THF (20 mL), catechol (1.1 g, 10 mmol) in dry THF (20 mL) was added at 0°C under N_2 atmosphere and the mixture was stirred for 1h at 25°C. The terminal enyne (1.5 g, 10 mmol) was added followed by CF_3COOH (1.14 g, 10 mmol) at 0°C and stirred for 12h at 25°C. The reaction mixture was quenched with water (2 mL) while externally cooling with cold water and the organoborane species was oxidized by adding 3N NaOAc (15 mL) and dropwise addition of H_2O_2 (16%, 25 mL). The organic layer was

separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N NaOH solution (3 x 20 mL) to remove catechol followed by water (20 mL) and saturated NaCl solution (20 mL). The layer was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/ethyl acetate as eluent. The starting material (0.54 g, 36%) was recovered using hexane.The product which eluted next was identified as undeca-10-en-1-al (0.15 g, 9%) and the fraction which followed was identified as undeca-11-yn-1-ol (0.75 g, 45%).

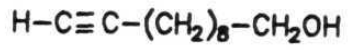


Fraction - 1:

IR (neat)ν_{max} : 3020, 2700, 1720, 1620 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 22.1, 28.9, 29.0, 29.1, 29.2, 33.8, 43.9, 114.2, 139.2, 203.0.

Mass (m/e) : 168 (M^+, 3%), 55 (100%).



Fraction - 2:

IR (neat)ν_{max} : 3350 (broad), 3300 (sharp), 2300, 1050 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 18.0, 25.4, 28.1, 28.3, 28.7, 29.0, 32.8, 62.5, 67.9, 84.5, **(Spectrum no. 10).**

Hydroboration of trideca-1-en-4-yne (1 eq) using $NaBH_4$/catechol (1:1 eq) in the presence of CF_3COOH:

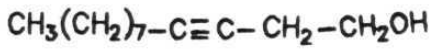
To a suspension of sodium borohydride (0.4 g, 10 mmol) in dry THF (20 mL), catechol (1.1 g, 10 mmol) in dry THF (20 mL) was added at 0°C under N_2 atmosphere and the mixture was stirred for 1h at 25°C. The internal enyne (1.78 g, 10 mmol) was added followed by CF_3COOH (1.14 g, 10 mmol) at 0°C and stirred for 12h at 25°C. The reaction mixture was quenched with water (2 mL) while externally cooling with cold water and the organoborane species was oxidized by adding 3N NaOAc (15 mL) and H_2O_2 (16%, 25 mL).

The organic layer was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was washed with 1N NaOH solution (3 x 20 mL) to remove catechol followed by water (20 mL) and saturated NaCl solution (20 mL). The layer was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatography on a silica gel column using hexane/ethyl acetate as eluent. Starting material was recovered using hexane (1.17 g, 66%). The product which eluted next was identified as a mixture of trideca-1-en-5-one and trideca-1-en-4-one (0.2 g, 10%) and the fraction which followed was identified as trideca-4-yn-1-ol (0.29 g, 15%).

Fraction - 1:

IR (neat)ν_{max} : 3010, 1720, 1620 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 29.2, 29.4, 31.9, 41.7, 42.3, 42.8, 47.7, 115.0, 118.4, 130.7, 137.1, 200.0, 202.0.



Fraction - 2:

IR (neat)ν_{max} : 3300, 2300, 1060 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.7-0.9(t, 3H), 1.1-1.8 (m, 15H), 2.0-2.3 (m, 4H), 3.6-3.7 (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.

Mass (m/e) : 195 (M-1, 1%), 97 (100%).

Hydroboration of 1-decene using $NaBH_4$ and CF_3COOH:

Sodium borohydride (0.2 g, 5 mmol) in dry THF (40 mL) was taken and CF_3COOH (0.57 g, 5 mmol) was added dropwise at 0°C. The mixture was stirred for 10 mts. 1-Decene (2.1 g, 15 mmol) was added at 0°C and stirred for 4h at 25°C. The reaction mixture was quenched with water

(2 mL) while externally species was oxidized using 3N NaOAc/H_2O_2. The organic layer was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic extract was washed with water (20 mL) and saturated NaCl solution (20 mL). It was then dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromotographed on a silica gel column using hexane/ethyl acetate (95:5) as eluent to obtain 1-decanol (2.3 g, 97%). The IR and NMR spectra are superimposable with the spectra obtained previously.

In order to examine the generality of the reaction, the reaction with a few other olefins was also tried and the products were obtained in quantitative yields. The results are summarized in Table 3.5.

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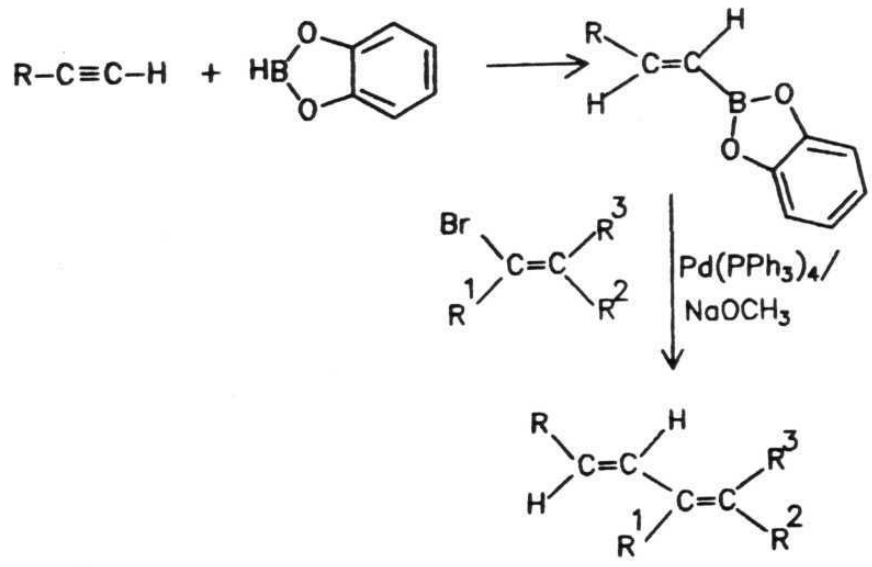
CHAPTER - 4

Studies on the development of C-C bond forming reactions using alkyl and alkenylcatecholboranes

INTRODUCTION

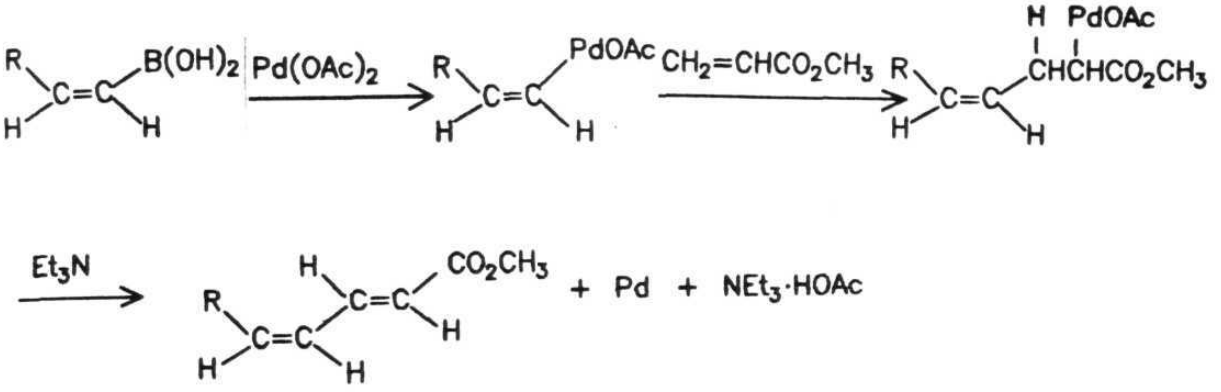
The alkenylcatecholboranes differ from the alkenyldialkylboranes in that, they can be easily hydrolyzed to the corresponding alkenylboronic acids, which are stable and important intermediates in several organic transformations. In recent years, there is an increasing interest in utilizing these alkenylcatecholboranes in the formation of stereospecific C-C bond forming reactions. A most promising use of alkenylcatecholboranes is in the preparation of conjugated dienes (Scheme 1) and enynes in a stereospecific manner upon cross coupling reaction with haloalkenes or haloalkynes with the aid of catalytic amount of a transition metal complex.[1-3]

SCHEME 1:



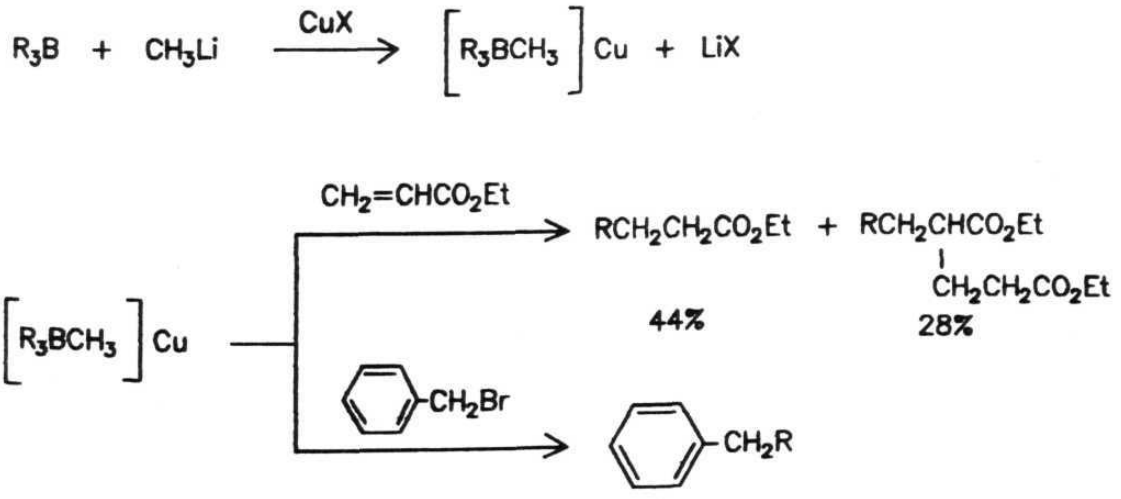
The alkenylboronic acids react with methyl acrylate in the presence of $Pd(OAc)_2$ and triethylamine to produce conjugated dienes. Even though the role of $Pd(OAc)_2$ is not clear, it is believed that an alkenylpalladium intermediate is involved (Scheme 2).[4]

SCHEME 2:



The alkyl and alkenyl groups in boranes can also be made to achieve reactivities similar to the more reactive organocopper species under appropriate conditions as shown in Scheme 3.[5]

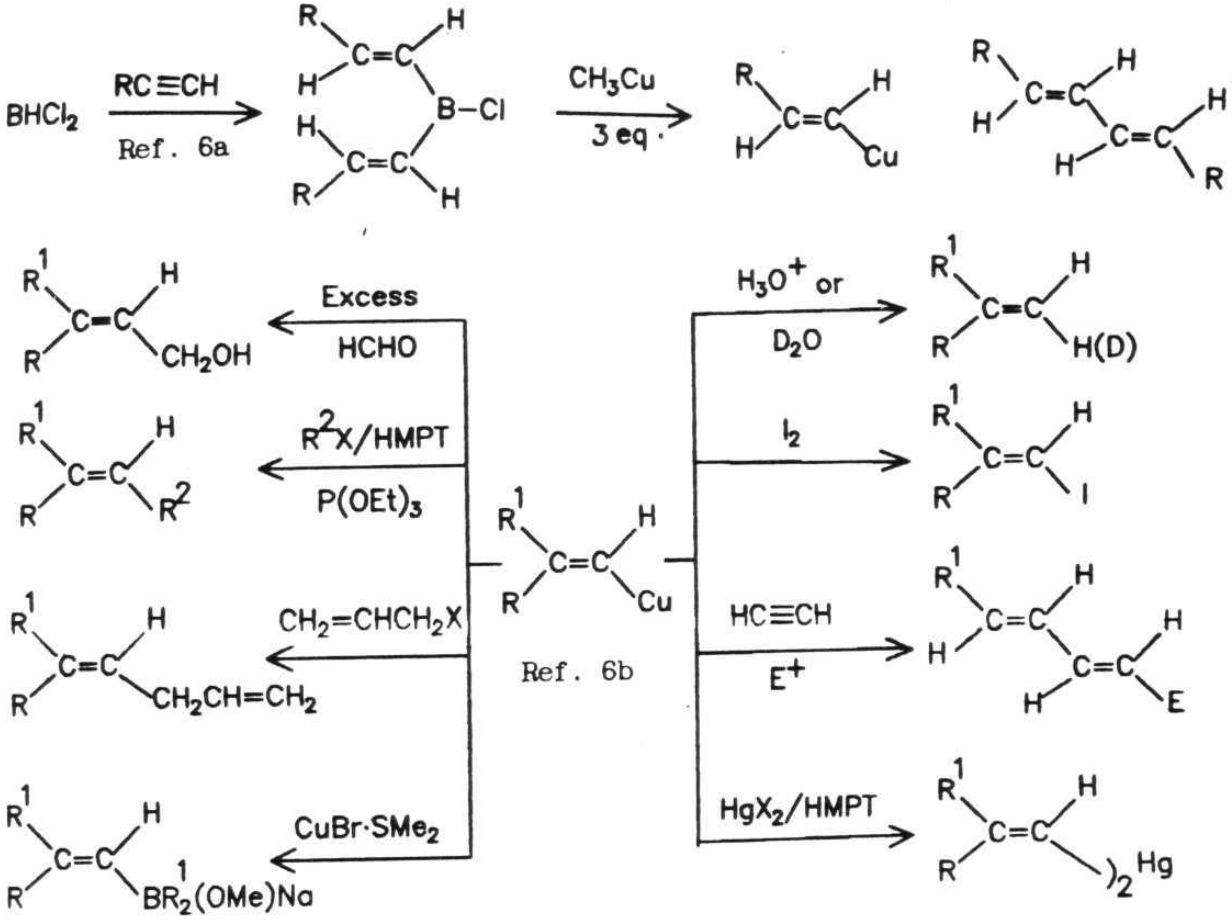
SCHEME 3:



The alkenylcopper derivatives are very useful synthetic

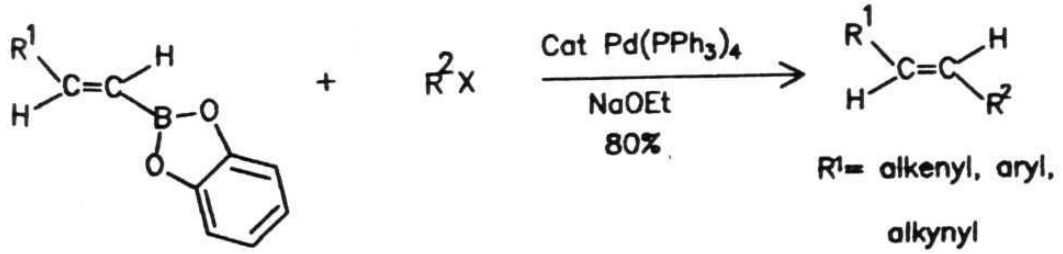
intermediates (Chart 1).[6]

CHART 1:



The alkenylcatecholboranes on protonolysis[7] give cis-alkenes and hence provide an alternative to the catalytic cis hydrogenation of alkynes. When these alkenylcatecholboranes are treated with alkyl halides in presence of catalytic amount of $[Pd(PPh_3)_4]$ and $NaOC_2H_5$, trans-alkenes are formed in good yields (Scheme 4).[8,9]

SCHEME 4:



The corresponding cis-olefins can be prepared by hydroborating alkynes with dialkylborane followed by $NaOH/I_2$ treatment.[10]

As outlined in Chapter-1, we have an easy access to alkyl and alkenylcatecholboranes through hydroboration of alkenes and alkynes using catecholborane prepared in benzene. We have undertaken investigations described in this chapter in order to examine the inter- and intramolecular transfer reactions of the alkyl and alkenyl groups from these derivatives.

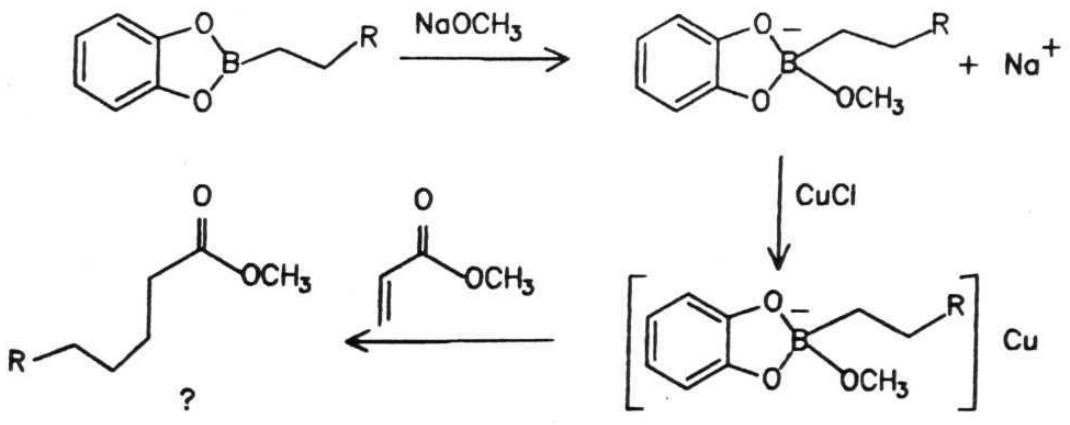
RESULTS AND DISCUSSION

Alkyl and alkenyl transfer reactions using alkyl and alkenylcatecholboranes:

As discussed in the introductory section, vinylcopper is a versatile intermediate for several transformations. Since we have a simple method of preparing alkyl and alkenylcatecholboranes, it is of interest to examine whether these reagents can be transformed to alkyl and alkenylcopper respectively, which are more reactive species.

We have examined the reactivity of the borate complexes, formed by the reaction of $NaOCH_3$ with the alkyl and alkenylcatecholboranes, with methyl acrylate in the presence of CuCl (Scheme 5).

SCHEME 5:



If such a transformation occurs, there is an advantage over the tetraalkyl borate complexes utilized for this purpose by Suzuki and co-workers,[5] since 2 equivalents of alkyl groups will not be utilized. In order to examine this, we have carried out, several experiments utilizing alkyl or alkenylcatecholboranes, $NaOCH_3$, CuCl, and methyl acrylate under various conditions. Unfortunately, in all these conditions, only the alcohols (RCH_2CH_2OH) or aldehydes (RCH_2CHO) derived from the organoboron were formed (upto 78%), besides small amounts of unidentified mixture of carbonyl compounds. Use of $CuBr.SMe_2$ complex and CuCN.2LiCl in the place of CuCl did not help. Also, use of NaOPh instead of $NaOCH_3$ was not helpful.

Since we were unsuccessful in our attempts to transfer alkyl groups to α,β-unsaturated compounds as envisaged in Scheme 5, we turned our attention to examine whether alkyl free radicals would serve this purpose.

Generation of free radicals from organoboranes using Ag^+/KOH, for utilization in reactions with α,β-unsaturated compounds:

Alkyl free radicals can be readily generated from organoboranes in the presence of oxygen.[11]

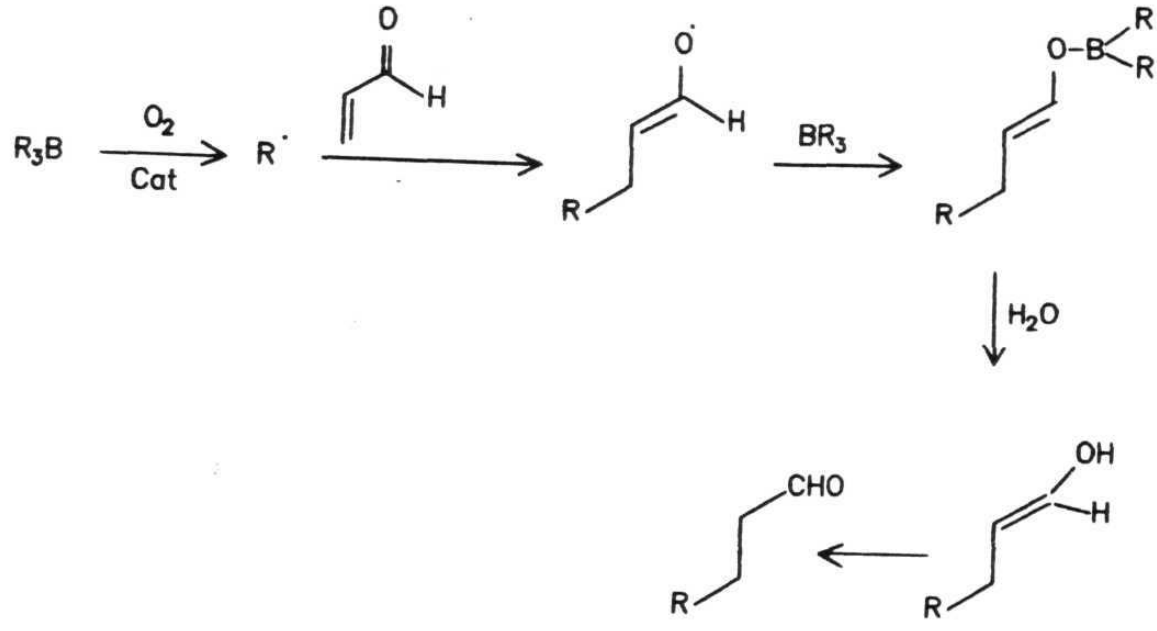
$$R_3B + O_2 \longrightarrow R^{\cdot}$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$$

$$RO_2^{\cdot} + R_3B \longrightarrow RO_2BR_2 + R^{\cdot} \text{ etc}$$

The radical produced in this way reacts with α,β-unsaturated compounds when the reaction is carried out in the presence of water to give the 1,4-addition product (Scheme 6).[12]

SCHEME 6:

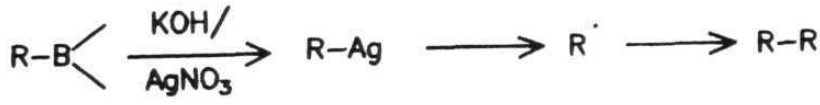


However, in this case only one of the alkyl group of the organoborane is transferred. Also, the transfer reaction does not proceed with less reactive α,β-unsaturated compounds such as methyl acrylate.

It has been reported that the reaction of R_3B with alkaline $AgNO_3$

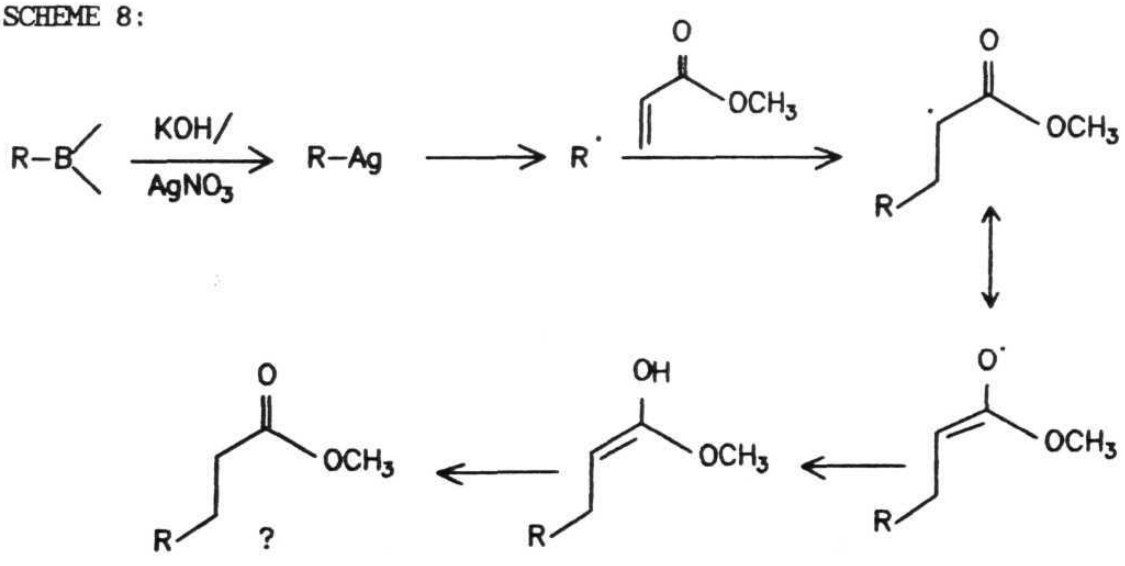
gives R-R (Scheme 7).[13] It was suggested that this reaction goes through the intermediacy of R-Ag and R radicals and that all alkyl groups take part in the reaction.

SCHEME 7:



We decided to examine the utilization of the radicals produced in this way, in the addition reaction with α,β-unsaturated ester (Scheme 8).

SCHEME 8:



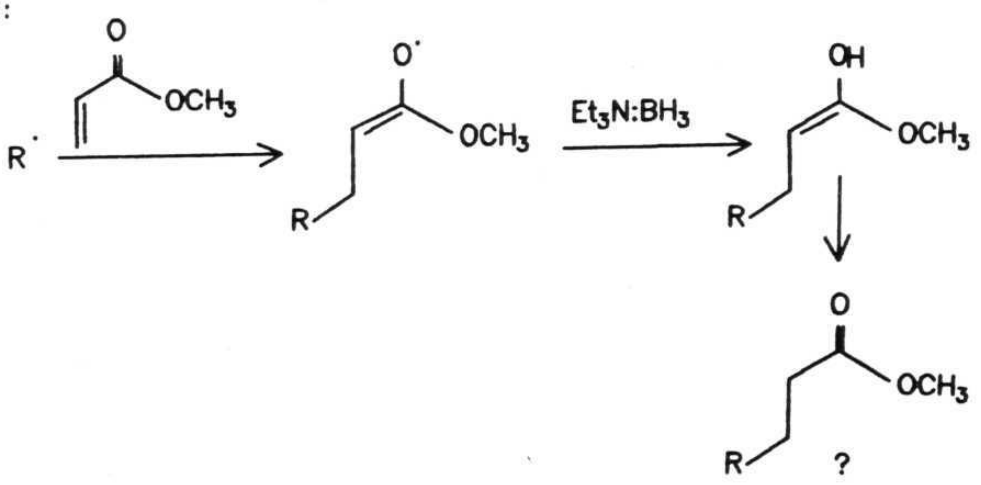
We have performed several experiments utilizing organoborane compounds prepared through hydroboration of 1-decene in THF using $CH_3COOH/NaBH_4$,[14,15] and in benzene using $H_3B{:}N(C_2H_5)_2Ph$[16] through addition of alkaline $AgNO_3$ solution in H_2O to the organoborane and methyl acrylate.

However, in all cases, in addition to small amounts of the R-R product, only a polymeric mixture of carbonyl (ester) compounds were isolated. When the experiment was carried out using methyl crotonate or methyl cinnamate, the hydrocarbon product was obtained as the major product, besides the unreacted starting ester.

We have then undertaken efforts to avoid the formation of polymeric products in reactions using methyl acrylate. It was thought that the presence of a reducing agent such as $Et_3N{:}BH_3$ would help in intercepting the enolic radical obtained by the addition of R radical to methyl acrylate.

We have carried out several experiments under various conditions using excess $Et_3N{:}BH_3$ to trap the radical formed after R radical addition to methyl acrylate (Scheme 9).

SCHEME 9:

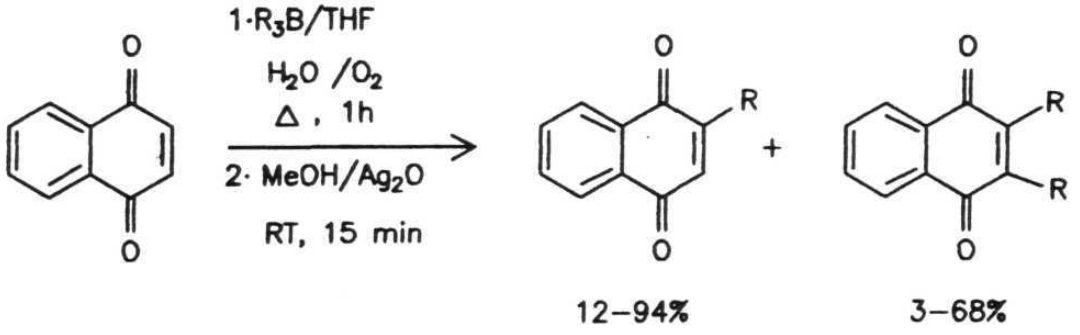


However, in all cases the reaction was found to be incomplete

since some amount of organoborane was also isolated. Presumably, the Ag^+ attacks the amine borane to some extent.

After we have turned our attention to other topics, Laatsch and co-workers reported that the R radicals generated under slightly different conditions, add to 1,4-naphthoquinone to give some useful alkylated products (Scheme 10).[17]

SCHEME 10:



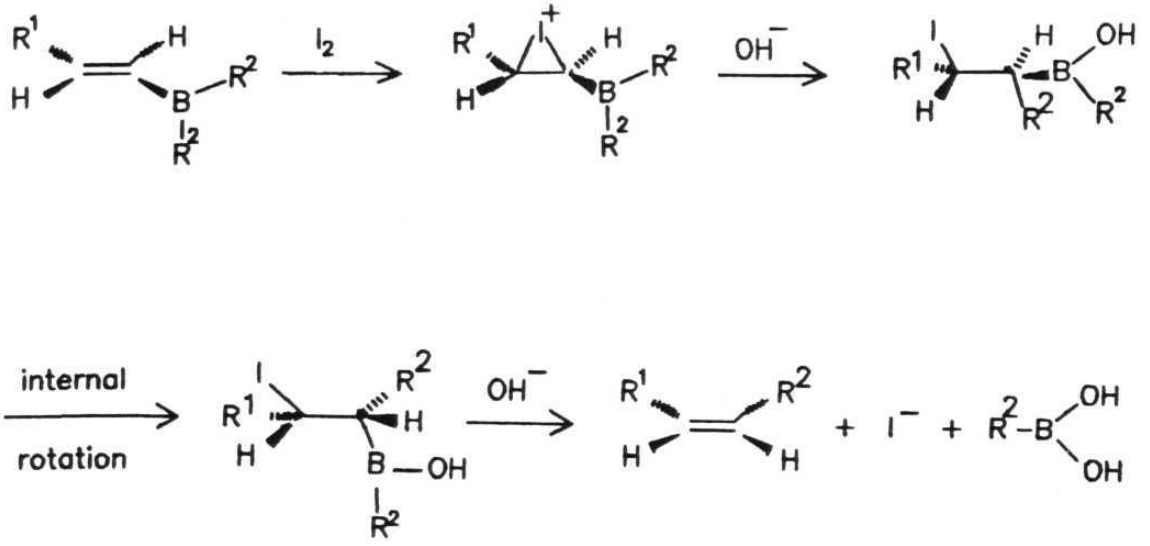
It is interesting to note that alkenyldisiamylboranes and alkenylcatecholboranes give only trace amounts of diene with aqueous alkaline silver nitrate which is an effective reagent for generating radicals from trialkylboranes.[18]

Intramolecular rearrangement reactions using alkenylcatecholboranes:

The reaction of E-1-alkenyldialkylboranes with iodine and base

give stereochemically pure cis-alkenes.[19] The reaction is believed to go through the mechanism shown in Scheme 11.

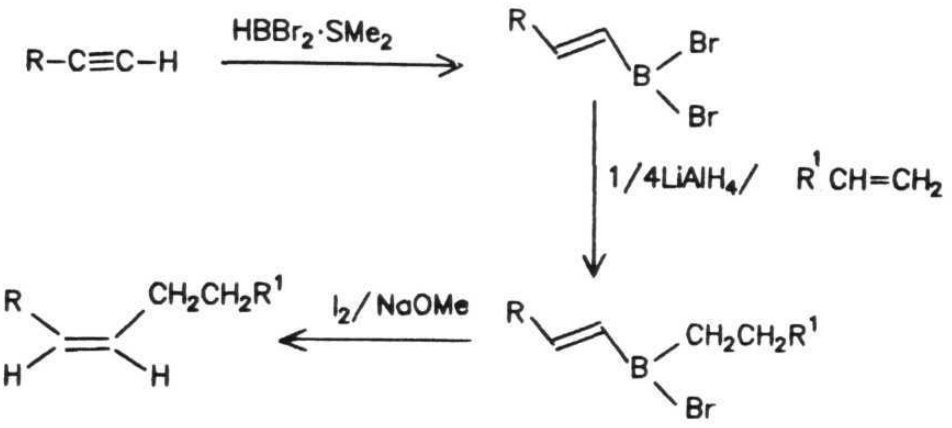
SCHEME 11:



It was also found that the use of cyanogen iodide or bromide in place of iodine and sodium hydroxide, leads to elimination in the final step, resulting in the formation of trans-alkene.[20] The major limitation of this approach is the requirement of dialkylborane for the hydroboration of alkynes.

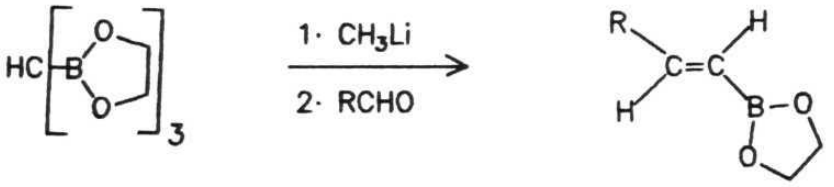
Stepwise hydroborations using $HBBr_2.SMe_2/LiAlH_4$ followed by I_2/NaOMe treatment also lead to formation of cis-olefin from alkynes (Scheme 12).[21]

SCHEME 12:



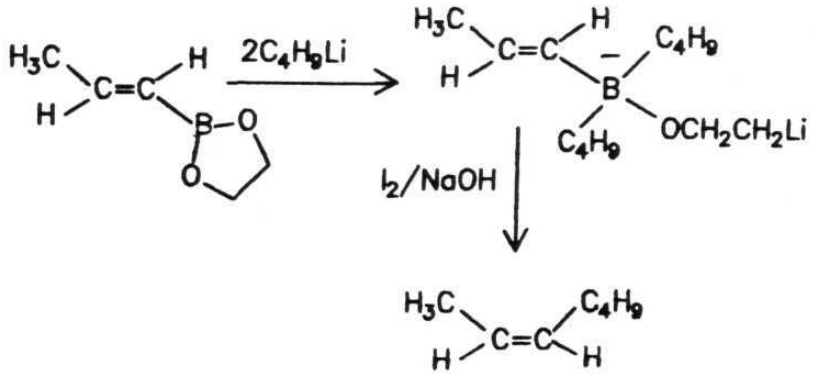
Matteson and co-workers gave an interesting method for the preparation of alkenylboronic esters(Scheme 13).[22]

SCHEME 13:



The reaction of the E-1-(ethylenedioxyboryl)propene obtained in this way with two equivalents of butyllithium followed by I_2/NaOH in THF gives Z-2-heptene (Scheme 14).[22]

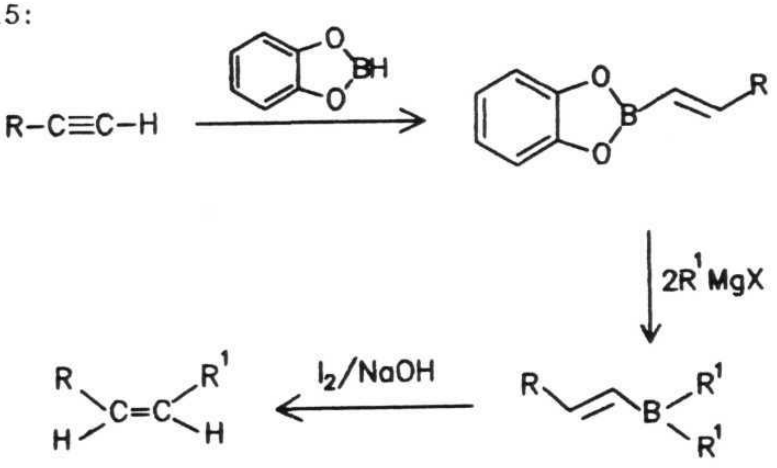
SCHEME 14:



Similarly, E-2-heptene can be prepared starting from the Z-isomer of the boronic ester. Surprisingly, alkenylcatecholboranes readily available through hydroboration of alkynes have not been utilized in such applications.

We have decided to investigate the application of the alkenyl borane compounds prepared using catecholborane and Grignard reagents (Scheme 15) for this purpose.

SCHEME 15:



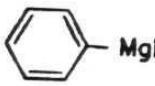
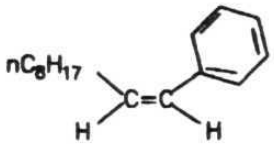
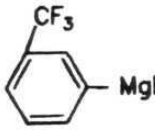
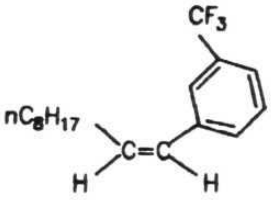
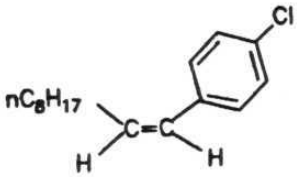
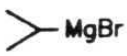
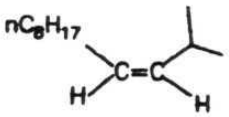
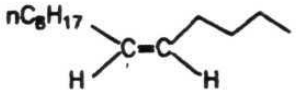
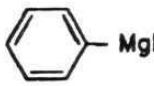
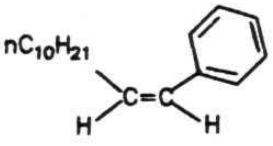
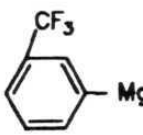
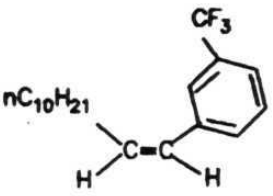
The advantage in such a procedure over those outlined in Schemes 11 and 12, is that it should also be possible to utilize the B-alkyl groups which are not available through hydroborations (ex. B-phenyl, B-isopropyl). Also, we have decided to utilize the more readily accessible Grignard reagents for this purpose.

1-Decenylcatecholborane (5 mmol) was prepared by refluxing 1-decyne with catecholborane (for details see experimental section of

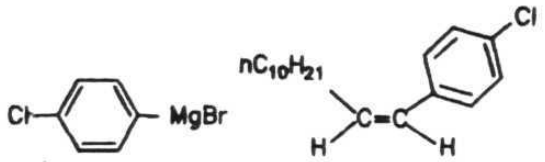
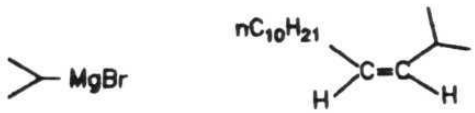
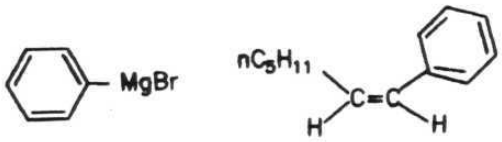
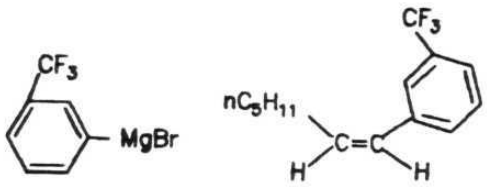
Chapter-2) in benzene (40 ml) for 12h (We have followed this procedure instead of the procedure utilizing H_3B:LB as a catalyst, since there will always be some BH_3:LB present in this procedure). Freshly prepared phenylmagnesium bromide (6 mmol) in THF (40 mL) was added at 0°C and stirred at 25°C for 8h. The iodine induced rearrangement (Scheme 11) was carried out at -10°C, following the reported procedure.[10] Z-1-Phenyl- 1-decene was obtained in 65% yield besides 1-decanal (22%). The yield of the cis-olefin increased to 89%, when 10 mmols of phenylmagnesium bromide was used in the above experiment. In order to examine the generality of this transformation, a few other 1-alkynes such as 1-dodecyne, 1-heptyne were utilized in combination with Grignard reagents such as m-trifluoromethylphenylmagnesium bromide and p-chlorophenylmagnesium bromide. The results are summarised in Table 4-1

When PhMgBr was replaced by isopropylmagnesium bromide (2 eq), Z-1-isopropyl-1-decene was obtained in only 32% yield. With n-butylmagnesium bromide also, the yield was low (30%). However, when the reaction was carried out under reflux conditions for 8h after the isopropyl Grignard addition, (see experimental section for details), the yield of Z-1-isopropyl-1-decene improved to 68% and that of Z-1-n-butyl-1-decene to 62%. Similarly, starting from 1-dodecyl-catecholborane (5 mmol), 67% of Z-1-isopropyl-1-dodecene was obtained.

Table 4.1: Cis-olefination of 1-alkynes with alkyl and aryl Grignards:[a]

Entry No	Alkyne	Grignard Reagent[b]	Product[c]	Yield(%)[d]
1.	$C_8H_{17}C\equiv CH$			89
2.				86
3.				56
4.				68
5.				62
6.	$C_{10}H_{21}C\equiv CH$			82
7.				87

....contd.

8.				52
9.				67
10.	$C_5H_{11}C\equiv CH$			78
11.				83

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a) Reactions were carried out under N_2 atmosphere using catecholborane (5.2 mmol) and 1-alkyne (5 mmol) in benzene (40 mL) at 80°C for 12h (see experimental section).

b) Grignard reagent (10 mmol) in THF (40 mL) was used.

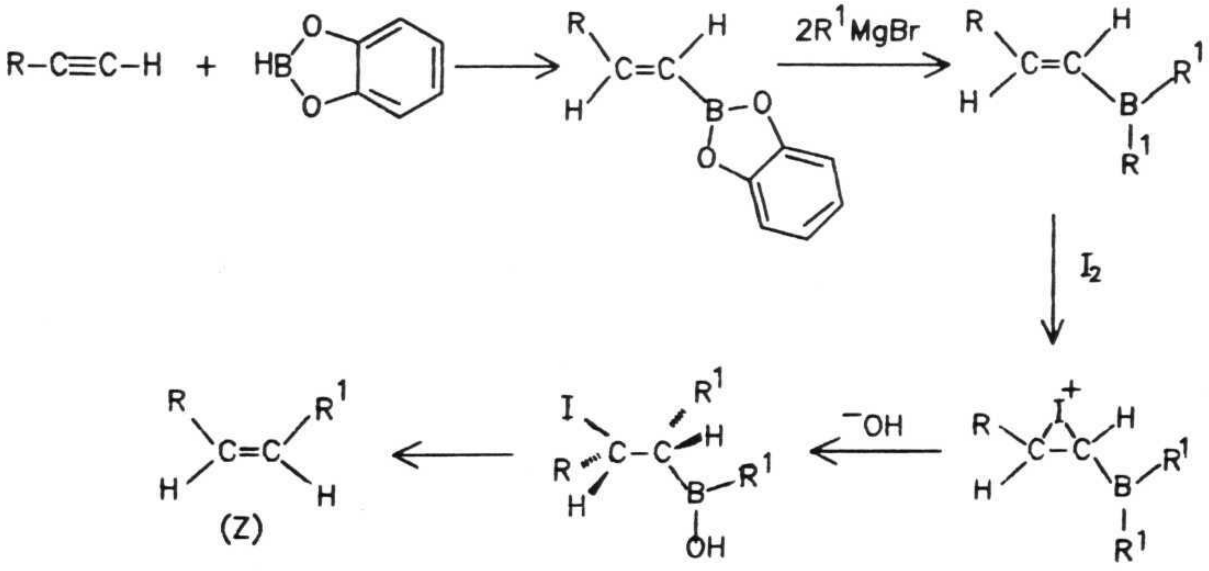
c) Iodination was carried out using 6N NaOH and I_2.

d) Yields are of products isolated by column chromatography on silica gel. The products were identified by spectral data (IR, ^1H and ^{13}C NMR) and comparison with the data of the authentic samples.

When p-methoxyphenylmagnesium bromide (2 eq) was added to 1-decenylcatecholborane, only p-iodoanisole was obtained (81%) besides 1-decanal (20%). Refluxing the reaction mixture after adding the p-methoxyphenylmagnesium bromide, also did not help. Presumably, in this case the anisole group attached to boron reacts preferentially over the alkenyl group.

The stereochemistry of these olefins is expected to be Z- from the mechanism outlined in Scheme 16.

SCHEME 16:



Several of these derivatives have been reported in the literature and spectral data for some of them are also available. Comparison of the spectral data of these derivatives also confirm the stereochemical assignment.

The stereochemistry of Z-1-phenyl-1-decene obtained was further confirmed by converting it to the corresponding E-olefin by a procedure developed in this laboratory,[23] using $CoCl_2/PPh_3/NaBH_4$ (see experimental section for details). The corresponding E-olefin is also a known compound and comparison of the ^1H NMR data again confirms the stereochemical assignment.[24]

In addition to confirming the stereochemical assignments, the isomerization using $CoCl_2/Ph_3P/NaBH_4$ should also be useful in the conversion of 1-alkynes to E-olefins through hydroboration using catecholborane-Grignard addition- $I_2/NaOH$ rearrangement and isomerization sequence.

CONCLUSIONS

The alkyl and alkenylcatecholboranes failed to undergo intermolecular transfer reaction through reaction with $NaOCH_3/CuX$ system. Alkenylcatecholboranes were successfully applied in the Grignard addition-intramolecular rearrangement using $I_2/NaOH$, an alternative to Zwefiel's Z-olefin synthesis. Alkyl and aryl groups which are not available through hydroboration reaction can also be utilized here.

EXPERIMENTAL SECTION

General Details:

Several of the general experimental details outlined in Chapters 2 and 3 are also applicable here.

1,2-Dibromoethane supplied by BDH, England was utilized. Commercial Grignard grade magnesium, supplied by Fluka, Switzerland was utilized. Bromobenzene, methyl acrylate, methyl methacrylate, methyl crotonate, ethyl fumarate and 1,4-napthoquinone supplied by E.Merck, India were utilized. m-Bromobenzotrifluoride, p-bromochloro benzene, p-bromoanisole, n-butyl bromide and isopropyl bromide supplied by Fluka, Switzerland were utilized.

Attempted reaction of methyl acrylate with 1-decylcatecholborane in the presence of $NaOCH_3$/CuCl:

Catecholborane was prepared from catechol (0.57 g, 5.2 mmol) and B_2H_6 in benzene (40 mL) as mentioned in Chapter-2. 1-Decyne (0.69 g, 5 mmol) was added and heated at 80°C for 12h. $NaOCH_3$ (0.54 g, 10 mmol) was added with the help of a solid addition flask at 25°C and stirred for 2h. Methyl acrylate (0.76 g, 10 mmol) was added at 0°C followed by

CuCl (0.98 g, 10 mmol) and stirred for 6h. The reaction was quenched with water and the organic layer was separated. The aqueous layer was extracted with ether (2 x 20 mL). The combined organic layer was washed with 3N NaOH (3 x 20 mL) and the solvent was evaporated. THF (30 mL) was added and the mixture was oxidized with 3N $NaOH/H_2O_2$. The organic layer was extracted with ether and washed with brine solution. The solvent was evaporated and the residue was chromatographed on a silica gel column to yield 1-decanol (1.23 g, 78%). Only trace amounts of an unidentified carbonyl compound was obtained.

There was no improvement in the formation of the carbonyl compound by replacing CuCl with $CuBr.SMe_2$. Use of NaOPh in the place of $NaOCH_3$ also gave similar results.

Use of 1-decenylcatecholborane in the place of 1-decylcatecholborane also gave similar results (i.e, unidentified polar carbonyl compound besides 1-decanol).

Dimerization of alkyl radical generated from trialkylborane in aqueous medium:

N,N-Diethylaniline-borane (5 mmol) was prepared and 1-decene (15 mmol) was added. It was stirred for 2h at 25°C. The temperature was

raised to 50°C and further stirred for 2h. The excess hydride was destroyed with absolute MeOH (2 mL) at 0°C. 2N KOH (18 mL) in MeOH was added, followed by slow addition of 5M $AgNO_3$ (3.6 mL) over 30 min at 0°C. The mixture was stirred for 2h and quenched with 1N HCl (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 1N HCl (2 x 20 mL), followed by water (10 mL) and brine. The mixture was dried over anhydrous $MgSO_4$ and the solvent was evaporated to obtain Eicosane (1.7 g, 82%).[25] 1-Decanol was obtained in trace amounts.

$$CH_3(CH_2)_7CH{=}CH_2 \longrightarrow CH_3(CH_2)_{18}CH_3$$

M.P. : 36°C, lit.[25] 36.8°C.

I.R (neat)ν_{max} : 2960, 2870, 1460, 720 cm^{-1}

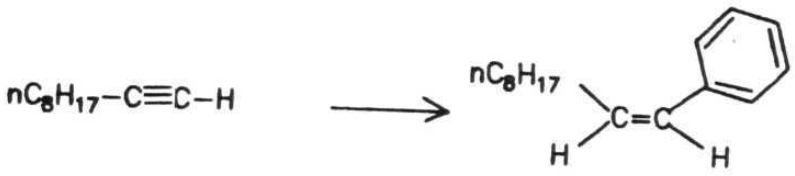
Attempted reaction of trialkylborane with methyl acrylate in the presence of aq. $AgNo_3$/KOH:

The procedure followed was exactly same as the above experiment except that methyl acrylate (1.7 g, 20 mmol) was added before the addition of $AgNO_3$. The product obtained after purification on a silica gel column was found to be polymeric, besides 1-decanol (19%, 0.30 g).

Similar results were obtained with methyl methacrylate, ethyl fumarate and 1,4-naphthoquinone. With methyl crotonate, only 1-decanol was obtained. No addition product was formed.

Preparation of 1-decenylcatecholborane followed by the reaction with phenylmagnesium bromide and I_2/NaOH treatment:

1-Decenylcatecholborane was prepared from 1-decyne (0.69 g, 5 mmol) and catecholborane (5.2 mmol) as mentioned previously. Freshly prepared phenylmagnesium bromide (10 mmol) in THF (40 mL) was added at $0^{\circ}C$ and stirred for 8h at $25^{\circ}C$. The reaction mixture was cooled to $-10^{\circ}C$ and 6N NaOH (10 mL) was added, followed by dropwise addition of iodine (2.54 g, 10 mmol) in THF (10 mL) over 30 min.[10] The contents were stirred for 4h. The reaction was quenched with saturated sodium thiosulphate solution and filtered over celite pad. The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 mL). The combined organic extract was washed with 1N NaOH (3 x 20 mL) followed by water (10 mL) and brine. It was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column. The product eluted with hexane, was identified as Z-1-phenyl-1-decene (0.96 g, 89%). The same experiment when carried out with 6 mmol of the Grignard reagent, gave only 65% of Z-1-phenyl-1-decene besides 1-decanal (0.17g, 22%).



Yield : 89% (0.96 g)

IR (neat)ν_{max} : 3020, 3010, 1620–1600 (broad) cm^{-1}

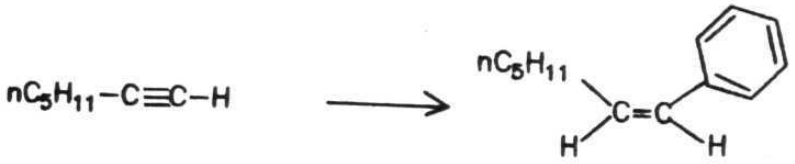
^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$), 2.3, (m, $-CH_2$), 5.5 (m, olefinic H), 6.25 (m, olefinic H), 7.2 (m, aromatic H) (Spectrum no. 11).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 28.6, 29.2, 29.6, 29.9, 31.8, 126.5, 128.2, 129.8, 133.4, 137.9 (Spectrum no. 12).

Mass (m/e): 216 (M^+, 15%), 104 (100%)(Spectrum no. 13).

The Z-1-phenyl-1-decene has been reported in the literature. Comparison of the reported ^{1}H NMR data confirms the stereochemical assignment of the product obtained here.[26]

The procedure was followed for a few other 1-alkynes and the results are summarized below and also in Table 4.1.



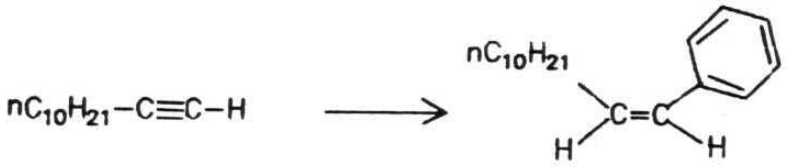
Yield : 78% (0.68 g)

IR (neat)ν_{max} : 3020, 3010, 1620, 1600 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, $-CH_2$), 2.3 (m, $-CH_2$), 5.6 (m, olefinic H), 6.3 (m, olefinic H), 7.3 (m, aromatic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.8, 29.5, 29.6, 32.8, 126.6, 128.7, 128.9, 132.4, 139.0.

The Z-1-phenyl-1-heptene has been reported in the literature. Comparison of the reported ^{1}H NMR data confirms the stereochemical assignment of the product obtained here.[27]



Yield : 82% (1.0 g)

IR (neat)ν_{max} : 3020, 3010, 1620, 1600 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$), 2.0, (m, $-CH_2$), 5.5 (m, olefinic H), 6.2 (m, olefinic H), 7.0-7.8 (m, unsaturated H).

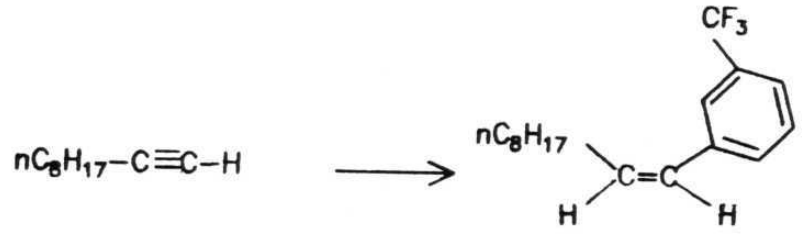
^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.2, 22.8, 29.3, 29.5, 29.8, 32.1, 127.6, 130.1, 130.4, 130.5, 137.7, 139.3.

This compound has been reported in the literature.[28]

Formation of 1-decenylcatecholborane followed by m-trifluorophenylmagnesium bromide addition and I_2/NaOH treatment.

1-Decenylcatecholborane was prepared from 1-decyne (0.69 g, 5 mmol) and catecholborane (5.2 mmol). The procedure followed was as outlined previously, except that freshly prepared m-trifluorophenylmagnesium bromide (10 mmol) in THF (40 mL) was added.

Z-1-m-Trifluoromethylphenyl-1-decene was obtained in 86% (1.21 g) yield.



IR (neat)ν_{max} : 3020, 3010, 1620, 1600 cm^{-1}

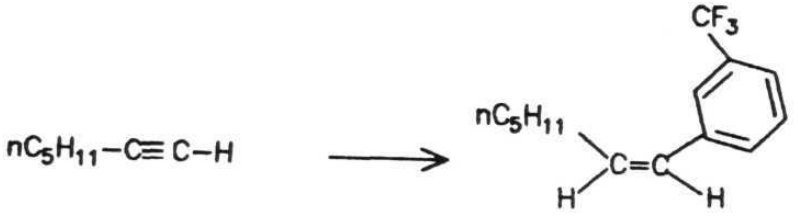
^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, $-CH_2$), 2.3 (m, $-CH_2$), 5.8 (m, olefinic H), 6.4 (m, olefinic H), 7.4 (m, aromatic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 13.7, 22.4, 28.3, 29.1, 29.2, 29.6,

31.6, 122.8, 125.4, 127.4, 128.3, 131.7, 134.8, 138.5 (Signals due to the CF_3 groups were not seen).

Mass (m/e) : 284 (M^+, 2%), 43 (100%)

The transformation was carried out with few other 1-alkynes.

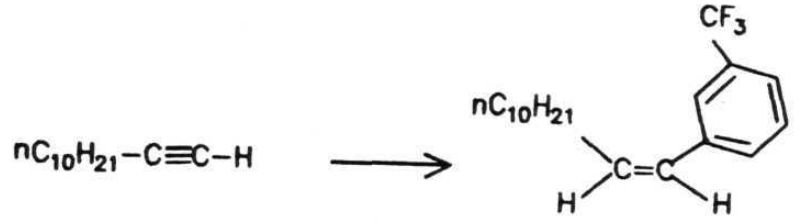


Yield : 83% (1.0 g)

IR (neat)ν_{max} : 3020, 3010, 1620, 1600 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.4 (m, $-CH_2$), 2.3 (m, $-CH_2$), 5.8 (m, olefinic H), 6.4 (m, olefinic H), 7.5 (m, aromatic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 28.6, 29.6, 31.6, 123.4, 125.4, 127.7, 128.7, 132.1, 135.0, 138.8 (Spectrum no. 14).



Yield : 87% (1.35 g)

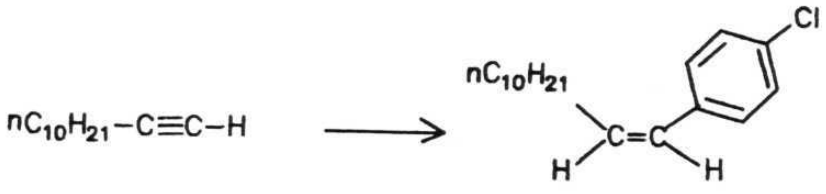
IR (neat)ν_{max} : 3020, 3010, 1620, 1600 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, $-CH_2$), 2.3 (m, $-CH_2$), 5.7 (m, olefinic H), 6.3 (m, olefinic H), 7.2-7.5 (m, aromatic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.8, 28.6, 28.9, 29.5, 29.7, 29.9, 32.0, 122.7, 125.7, 127.7, 128.7, 132.1, 135.1, 138.8.

Formation of 1-dodecenylcatecholborane followed by p-chlorophenylmagnesium bromide addition and I_2/NaOH treatment:

1-Dodecenylcatecholborane was prepared from catecholborane (5.2 mmol) and 1-dodecyne (0.83 g, 5 mmol). Freshly prepared p-chlorophenylmagnesium bromide (10 mmol) in THF (40 mL) was added and rest of the procedure followed was same as described previously.



Yield : 52% (0.72 g)

IR (neat) ν_{max} : 3020, 3010, 1620, 1600 (broad) cm^{-1}

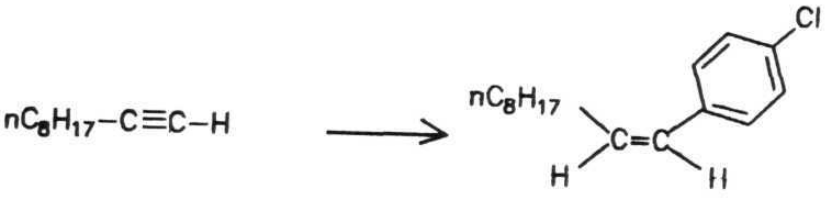
^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, $-CH_2$), 3.2 (m, $-CH_2$), 5.3 (m, olefinic H), 6.3 (m,

olefinic H), 7.4 (m, aromatic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.0, 22.6, 29.3, 29.6, 31.9, 128.2, 128.6, 129.1, 130.6, 138.8.

Mass (m/e) : 280 (M+2, 3%), 278 (M^+, 10%), 57 (100%).

In this case, 1-dodecanal was also obtained (0.23 g, 29%).



Yield : 56% (0.70 g)

IR (neat) ν_{max} : 3020, 3010, 1620, 1600 cm^{-1}

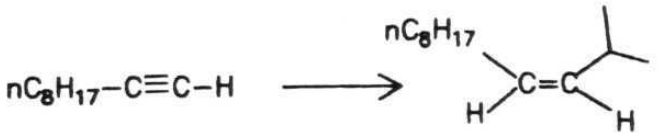
^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.2 (m, $-CH_2$), 3.2 (m, $-CH_2$), 5.3 (m, olefinic H), 6.3 (m, olefinic H), 7.3 (m, aromatic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.6, 29.2, 29.4, 31.8, 126.9, 128.2, 128.6, 129.1, 130.5, 138.8 (Spectrum no. 15).

Preparation of 1-decenylcatecholborane followed by isopropylmagnesium bromide addition and I_2/NaOH treatment:

1-Decenylcatecholborane (5 mmol) was prepared following the

procedure mentioned previously. Freshly prepared isopropylmagnesium bromide (10 mmol) in THF (40 mL) was added at 0°C and the rest of the procedure was similar to the previous experiment. Z-1-isopropyl-1-decene was obtained in only 32% (0.29 g) yield, besides unidentified polar compounds, presumably organoboron compounds.



IR (neat) ν_{max} : 3020, 1620 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.0 (m, $-CH_3$), 1.3 (m, $-CH_2$), 1.7 (m, $-CH_2$), 3.2 (m, -CH), 5.3 (m, olefinic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.2, 29.4, 29.6, 30.9, 32.0, 127.7, 137.6.

This compound has been reported in the literature.[29] However, the data has not been given.

When n-butylmagnesium bromide was used in the place of isopropylmagnesium bromide, Z-1-n-butyl-1-decene was obtained in 30% (0.25 g) yield.

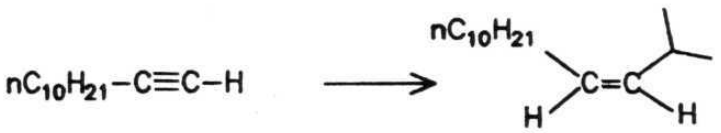
IR (neat) ν_{max} : 3020, 1620 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, CH_2), 2.0 (m, $-CH_2$), 3.1 (m, $-CH_2$), 5.3 (m, olefinic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.8, 29.4, 29.7, 32.0, 32.7, 130.0, 130.5.

This compound has been reported in the literature.[30]

When the above reaction mixtures were heated at 80°C for 8h after the alkyl Grignard addition, the yield of the product improved to 62% (0.51 g) and 68% (0.62 g) for Z-1-n-butyl-1-decene and Z-1-isopropyl-1-decene, respectively. The IR and NMR spectra showed 1:1 correspondence with the spectra obtained earlier. The above reaction was carried out with 1-dodecyne also.



Yield : 67% (0.70 g)

IR (neat) ν_{max} : 3020, 1620 cm^{-1}

^{1}H NMR (100 MHz, $CDCl_3$) : δ ppm 1.0 (m, all CH_3's), 1.3 (m, $-CH_2$), 1.6 (m, $-CH_2$), 3.2 (m, -CH), 5.3 (m, olefinic H).

^{13}C NMR (25.0 MHz, $CDCl_3$) : δ ppm 14.1, 22.7, 23.3, 29.5, 29.7, 30.0, 32.0, 127.7, 137.6 (Spectrum no. 16).

Mass (m/e) : 210 (M^+, 3%), 57 (100%).

Isomerization of Z-1-phenyl-1-decene to E-1-phenyl-1-decene:

A procedure similar to the one reported from this laboratory for the conversion of allylbenzene to E-β-methylstyrene was followed.[23]

$CoCl_2$ (0.21 g, 2 mmol) and PPh_3 (1.57 g, 6 mmol) were taken in dry THF (30 mL). To the magnetically stirred suspension, $NaBH_4$ (0.02 g, 2 mmol) was added under nitrogen atmosphere during 15 min. at $-10^{\circ}C$ and the contents were further stirred for 30 min. The Z-1-phenyl-1-decene (0.43 g, 2 mmol) in THF (10 mL) was added under nitrogen atmosphere with the help of a double ended needle and the mixture was stirred at $-10^{\circ}C$ for 8h. Hexane (20 mL) was added at $-10^{\circ}C$ followed by 2N HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with hexane (2 x 20 mL). The combined organic extract was washed with saturated sodium chloride solution (20 mL) and dried

over anhydrous $MgSO_4$. The solvent was evaporated and hexane (10 mL) was added to the residue to precipitate the $Ph_3P:BH_3$ complex and most of the Ph_3P. The filtrate was evaporated and the residue was purified on a silica gel column using hexane as eluent.

Yield : 81% (0.34 g)

IR (neat) ν_{max} : 3020, 1610, 1600, 960 cm^{-1}

^1H NMR (100 MHz, $CDCl_3$) : δ ppm 0.9 (t, $-CH_3$), 1.3 (m, $-CH_2$), 2.3 (m, $-CH_2$), 6.4 (m, olefinic H), 7.4 (m, aromatic H) (Spectrum no. 17).

Although the ^1H NMR spectral resolution is poor (spectrum no. 17), the data are comparable with the data reported for E-phenyl-1-decene.[26]

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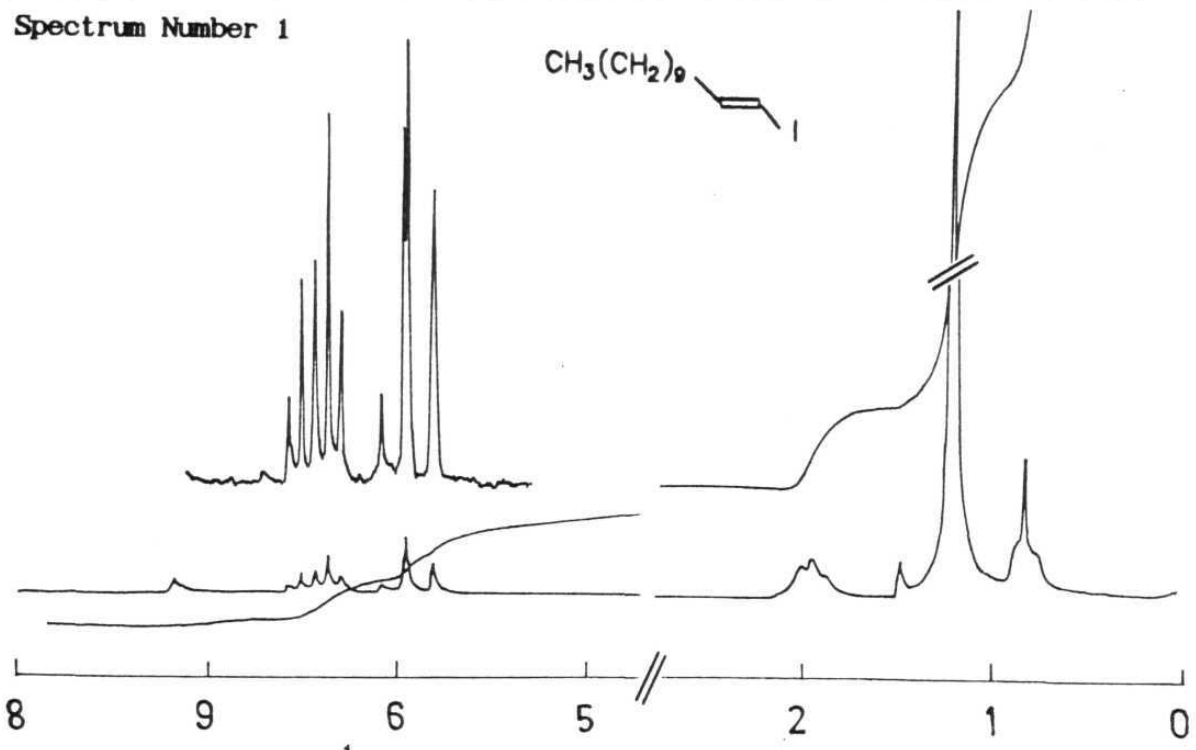
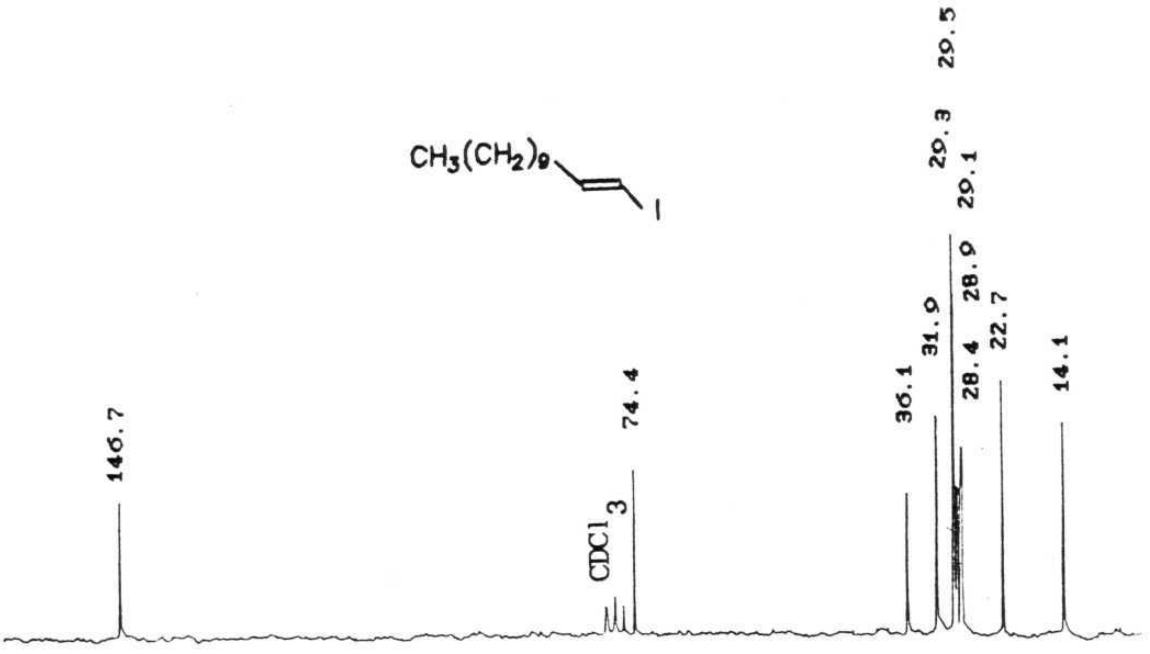
Spectrum Number 1



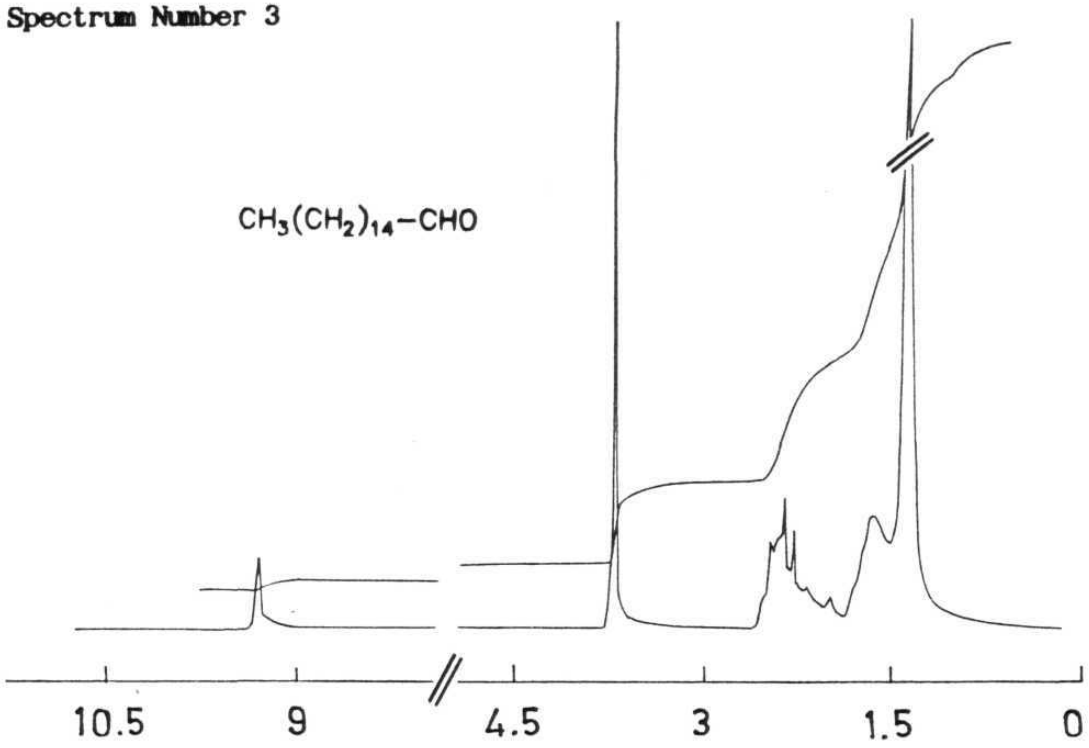
^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 2



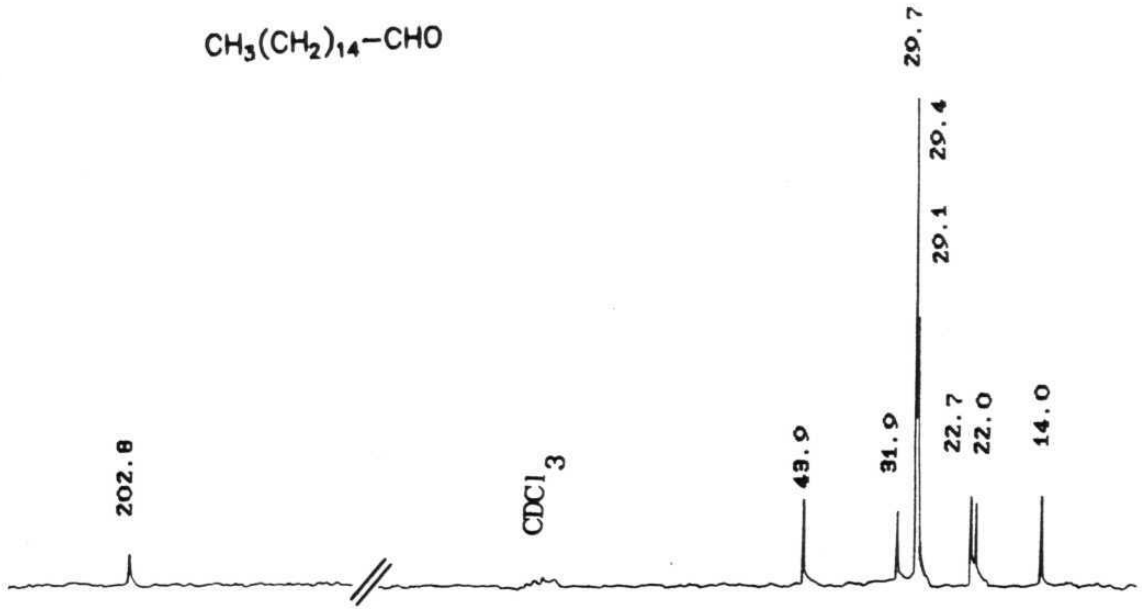
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 3



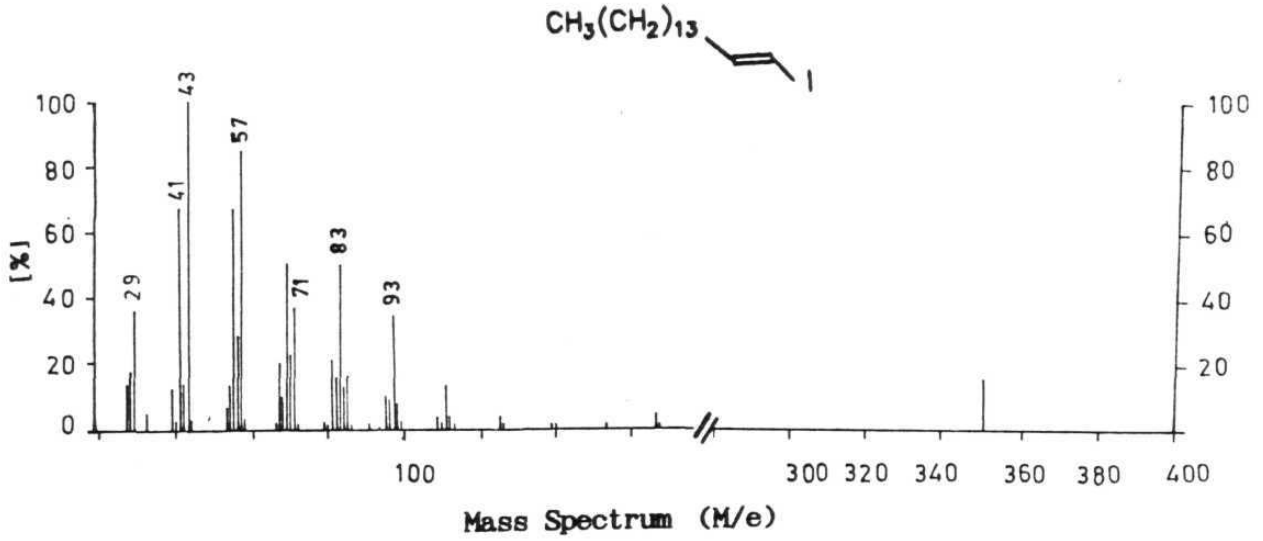
^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 4

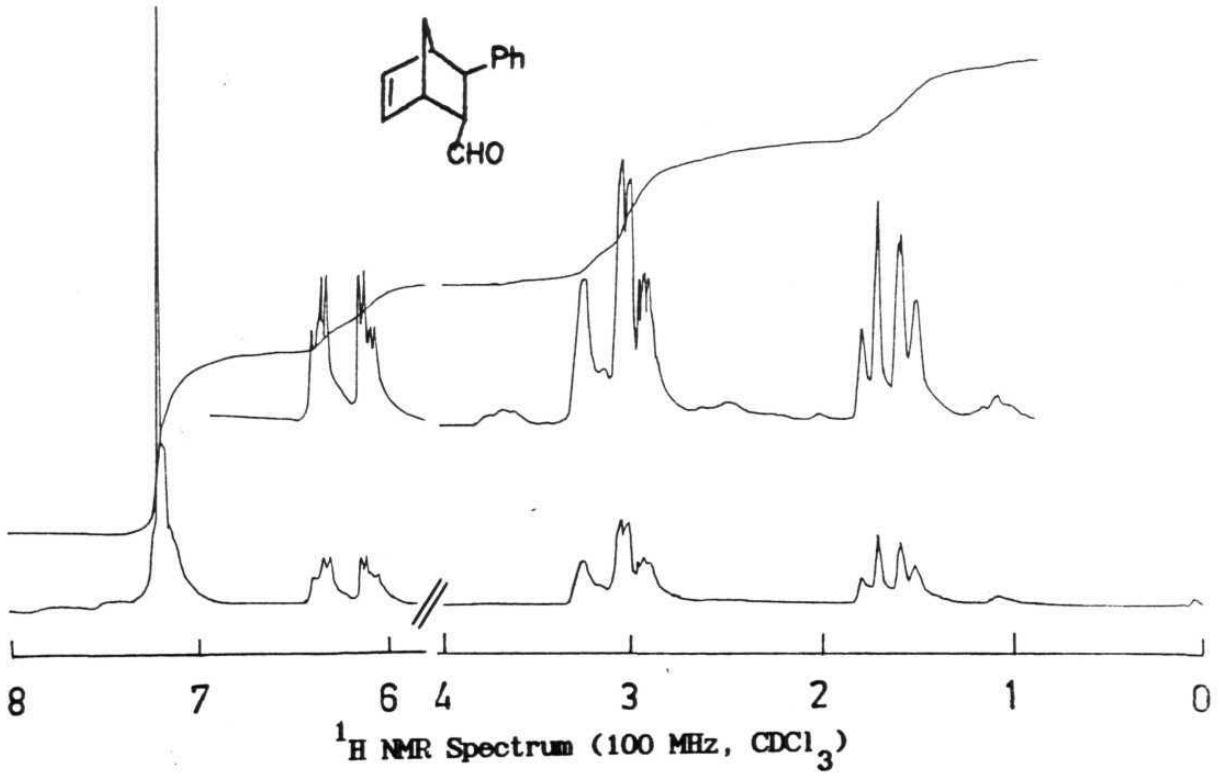


^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

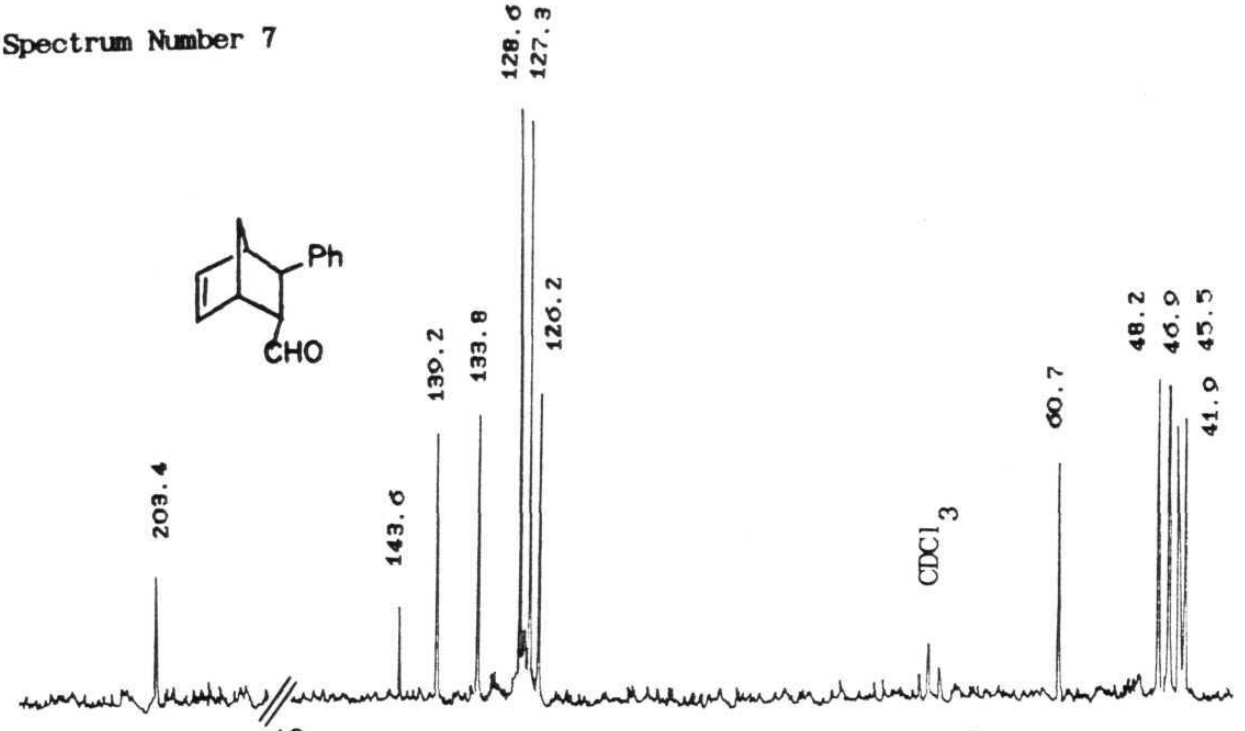
Spectrum Number 5



Spectrum Number 6

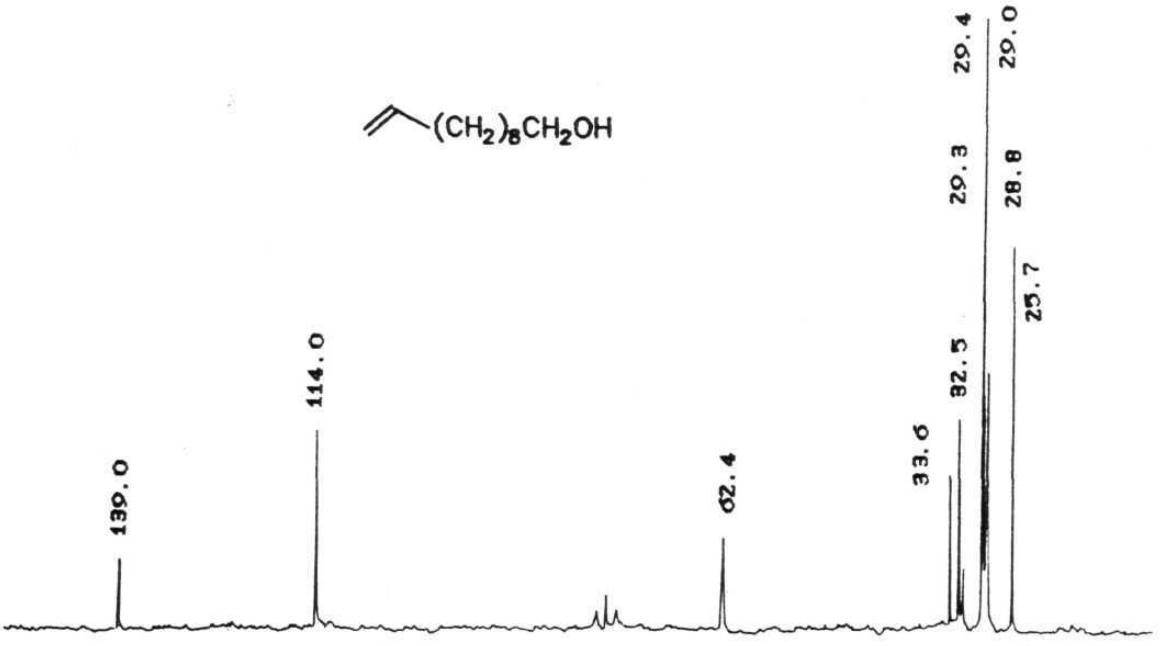


Spectrum Number 7



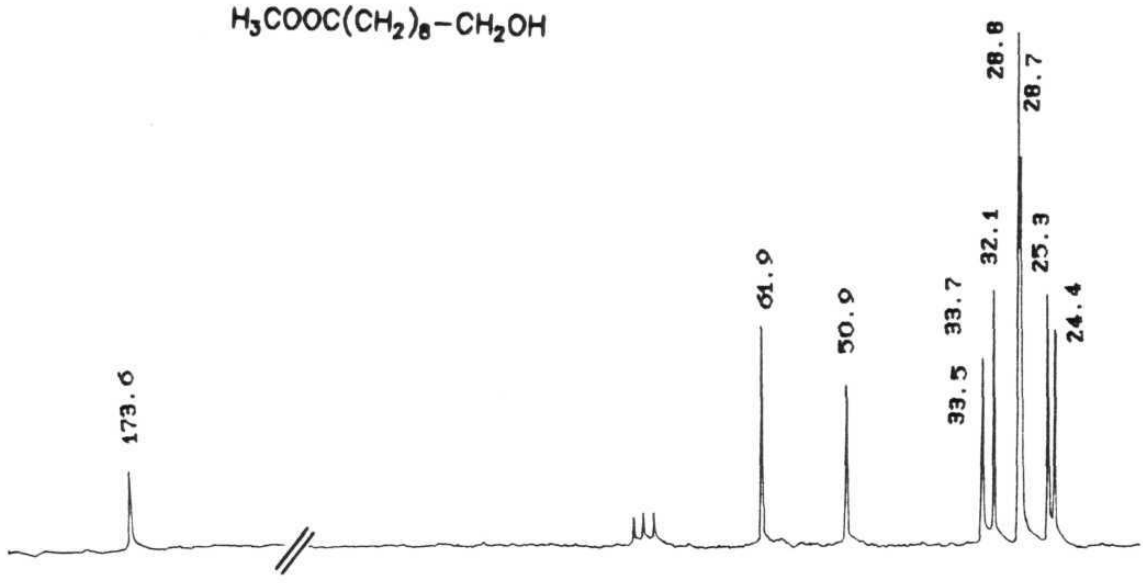
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 8



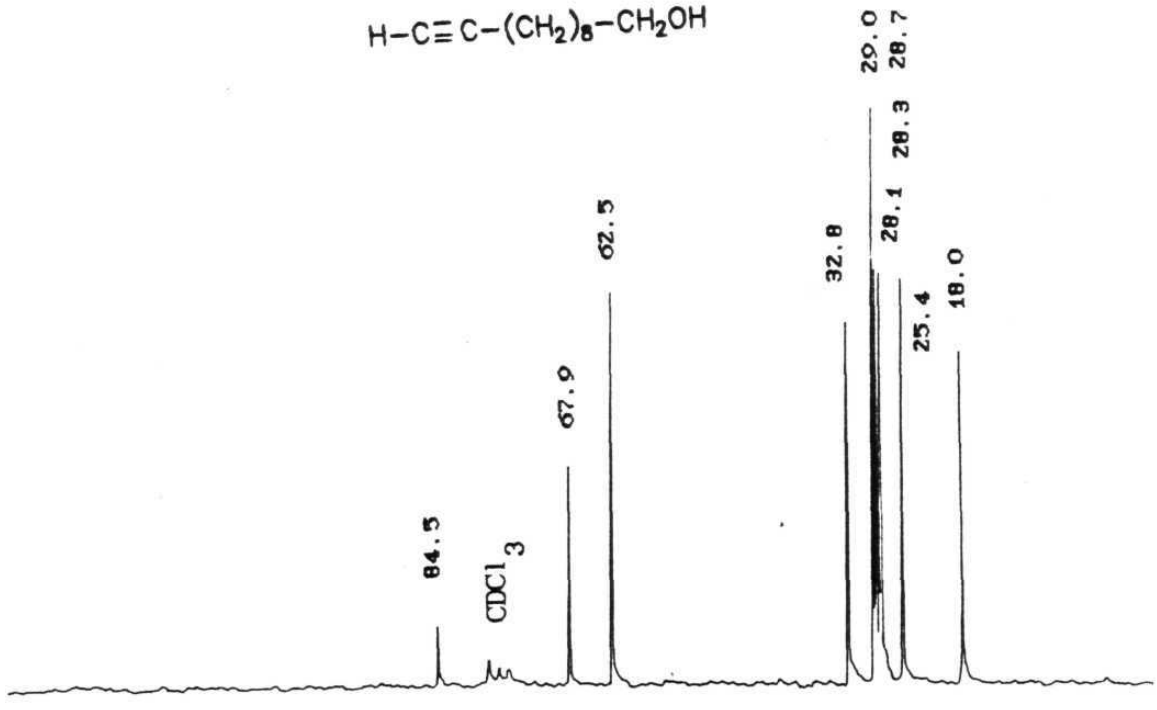
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 9



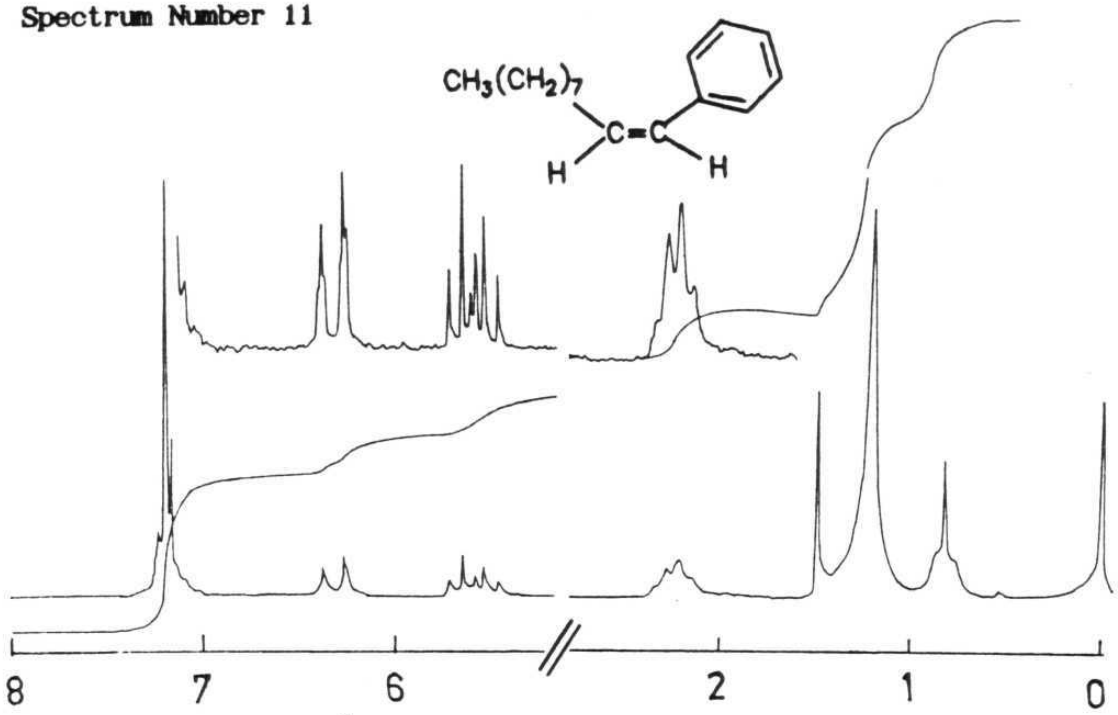
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 10



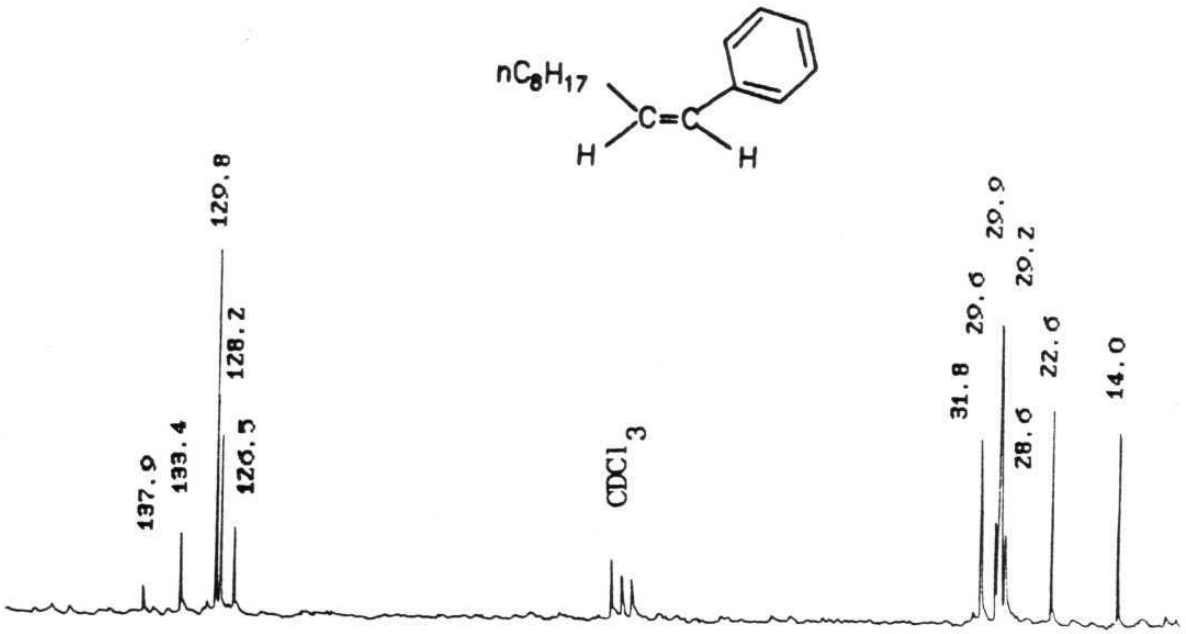
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 11



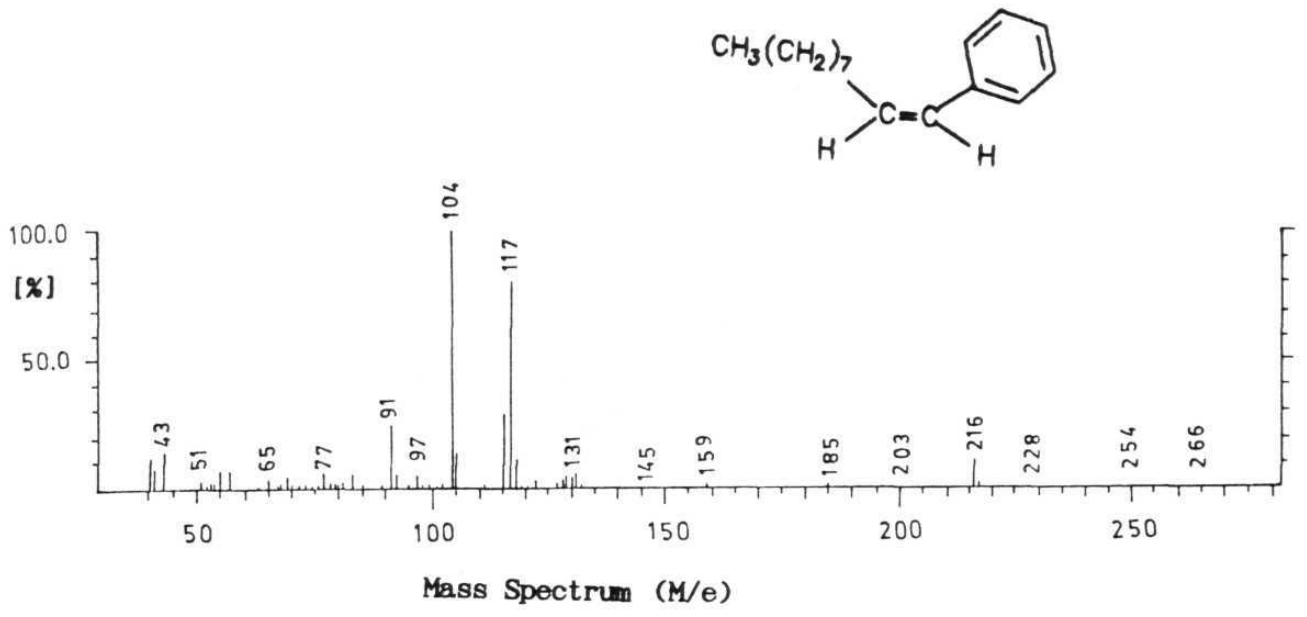
^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

Spectrum Number 12



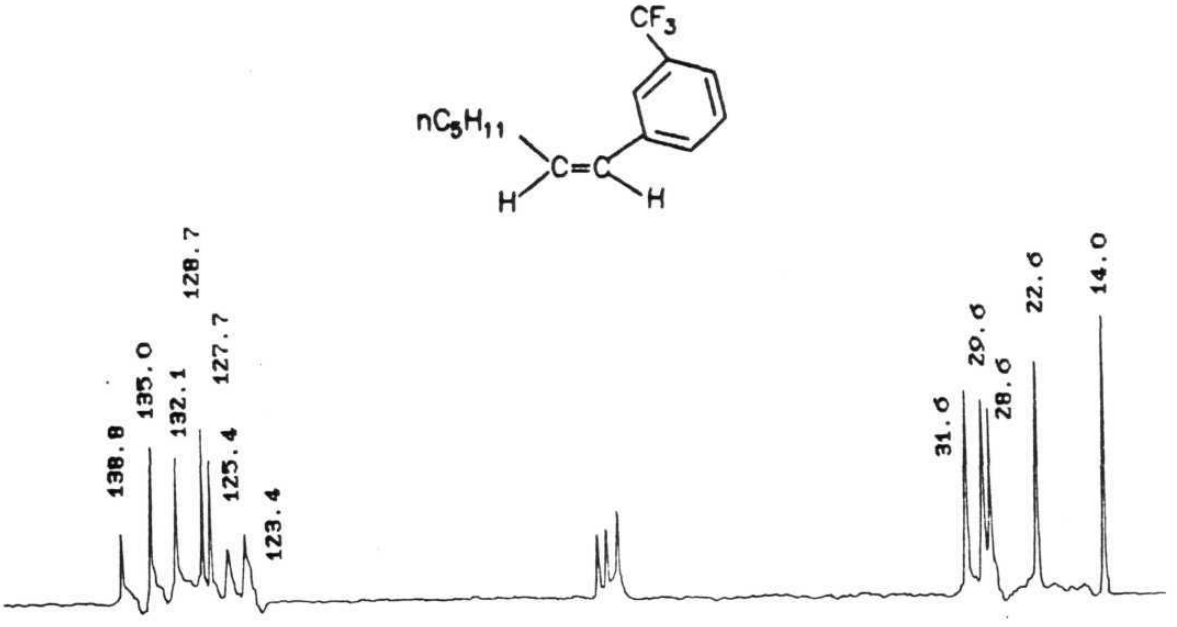
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 13



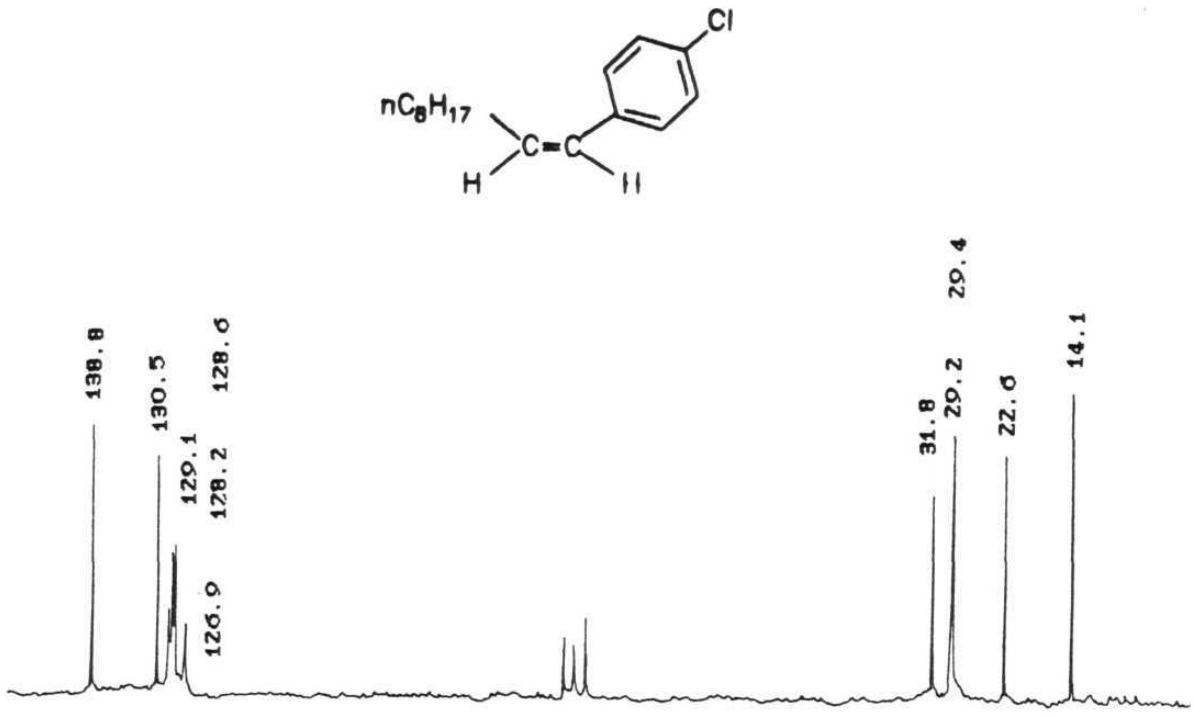
Mass Spectrum (M/e)

Spectrum Number 14



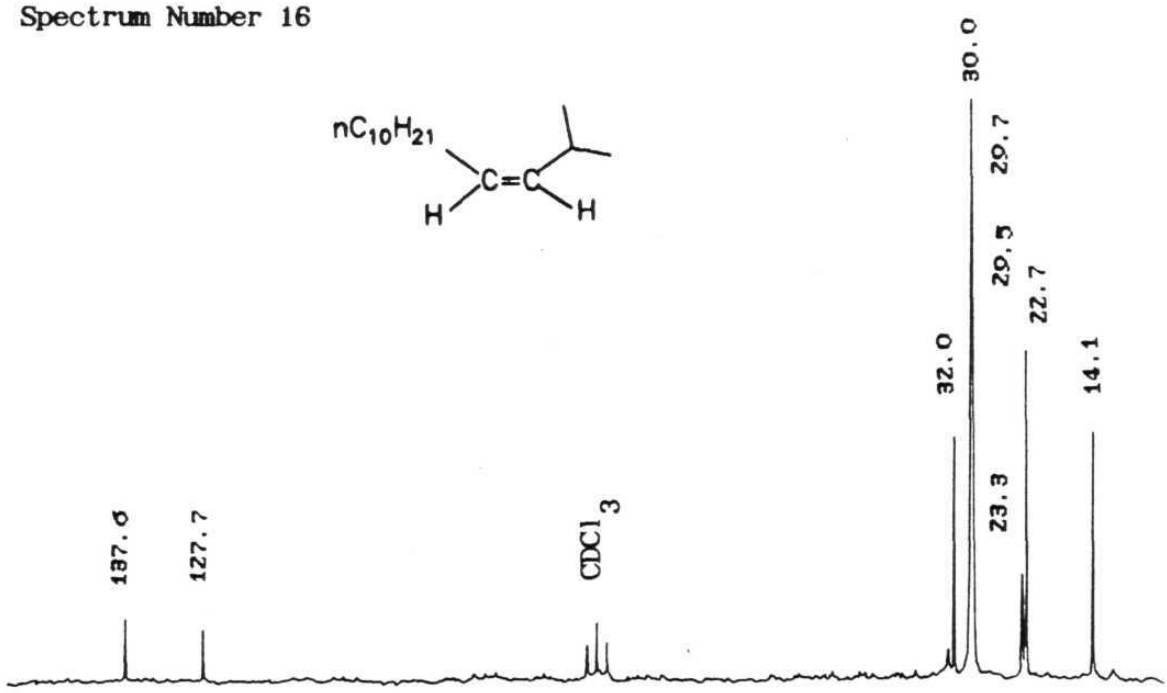
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 15



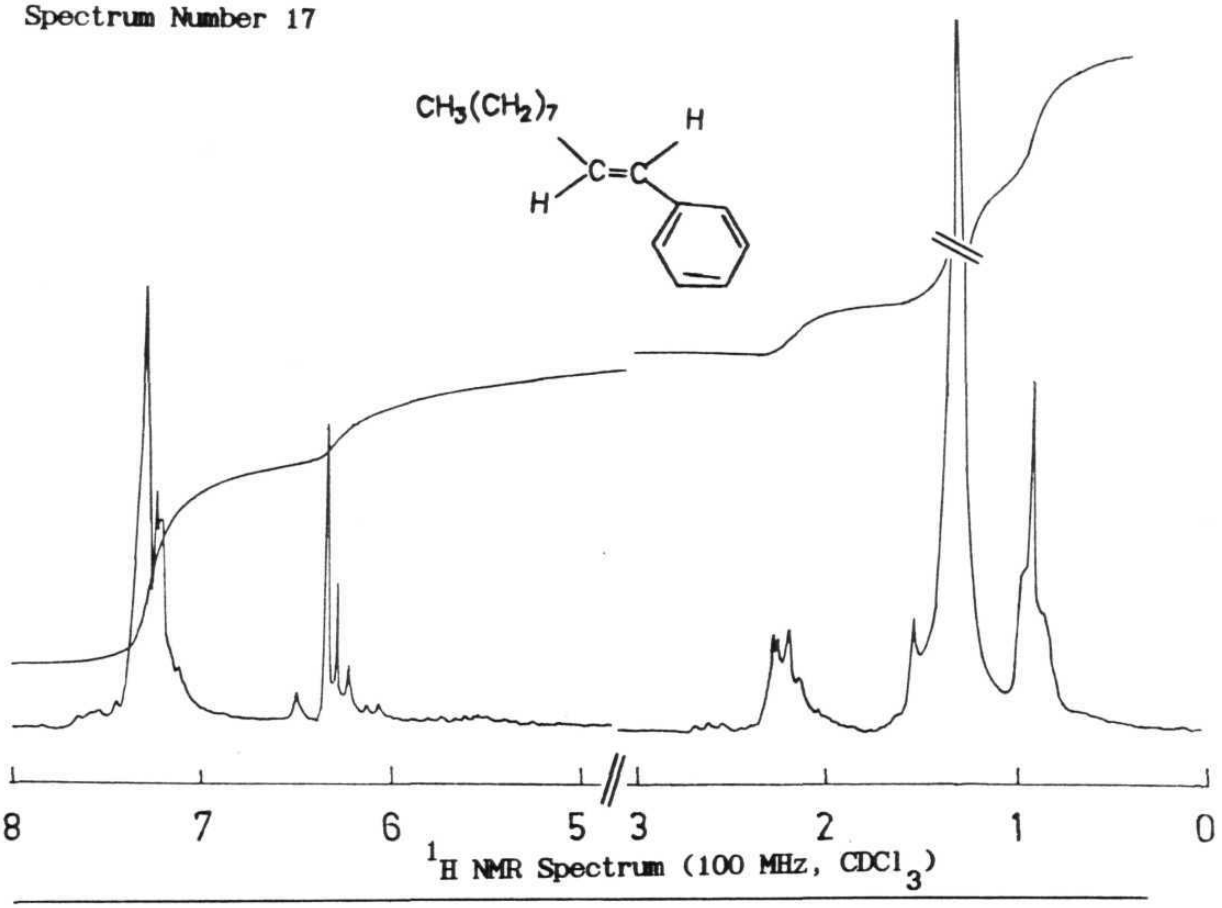
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum Number 16



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

Spectrum Number 17



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

VITAE

Y. Suseela was born on 9th June 1964 in Nidadavolu, Andhra Pradesh. Following her earlier education at Kendriya Vidyalaya, Tirumalagiri (10+2) she joined the St. Francis College, Hyderabad and obtained her B.Sc. from the Osmania University in 1984. Later she joined the University of Hyderabad and received her M.Sc. and M.Phil. degrees from the School of Chemistry in 1986 and 1987 respectively. Later she joined Ph.D. programme in the same school in 1987. She was awarded the Junior and Senior Research Fellowships by the CSIR on the basis of CSIR National Level Test.

List of Publications:

1. Catalytic Effect of a BH_3:N,N-Diethylaniline Complex in the Formation of Alkenyl Catecholboranes from Alk-1-ynes and Catecholborane.

   Y. Suseela, A.S. Bhanu Prasad and M. Periasamy,

   J. Chem. Soc., Chem. Commun., 1990, 446.

2. Reduction of Carboxylic Acids into Alcohols Using $NaBH_4$ in the Presence of Catechol and/or CF_3COOH.

   Y. Suseela and M. Periasamy,

   Tetrahedron., 1992, **48**, 371.

3. Convenient Method for the Preparation of Catecholborane and Promotion of the Formation of Alkenyl Catecholborane Using BH_3 Complex.

Y. Suseela and M. Periasamy,

J. Organomet. Chem., 1993, 0000.

4. Hydroboration of Olefins Using $NaBH_4$ in the Presence of Catechol and/or CF_3COOH.

Y. Suseela and M. Periasamy,

to be submitted for publication.

5. A Simple and Convenient Method for the Syntheses of Cis-Olefins Utilizing Alkenyl Catecholboranes and Alkyl and Aryl Grignard Reagents.

Y. Suseela and M. Periasamy,

to be submitted for publication.