CHAPTER 3

Mechanistic studies of the hydroboration reaction utilizing borane chiral Lewis base complexes for hydroboration of prochiral olefins.
The hydroboration takes place by cis-addition of $\geq B-H$ bond to carbon-carbon multiple bonds.\textsuperscript{1,2} The addition takes place from less hindered side of the multiple bond.\textsuperscript{1,2} The diborane reacts very sluggishly with olefins in the gas phase and in hydrocarbon solvents but the presence of weak Lewis bases make the reaction fast. For the hydroboration with diborane in ether solvents, a four-centre transition state (eq.1) with direction of the addition controlled by polarisation of the boron hydrogen bond, $\geq B-H$, has been proposed.

\[
\begin{align*}
H^+ & \quad \delta^+ \\
H^2C=CH & \quad \delta^- \\
\text{CH}_2 & \quad \text{CH}_3
\end{align*}
\]

However, it remains to be established whether the Lewis base moiety in the BH$_3$-Lewis base complexes is present or absent in the transition state of the $\geq B-H$ addition to olefins and differences of opinion exist.\textsuperscript{6-9} A review of the literature reports on the mechanistic studies of the hydroboration of olefins with BH$_3$-Lewis base complexes will facilitate the discussion of the present results. The kinetic and mechanistic studies on the hydroboration of olefins with dialkylborane complexes and dibromoborane complexes have been recently reviewed\textsuperscript{6} and only relevant details will be reviewed here.
The hydroboration of substituted styrenes by diborane in various solvents (e.g. diglyme, THF, diethylether) gives products with essentially no significant difference in regioselectivities. It was suggested that since the solvents do not influence the regioselectivities, they may not be intimately associated in the transition state of the $\overset{\beta}{B-H}$ addition to the olefin. The mechanism given in eq.2-4 involving free $\text{BH}_3$ monomer as intermediate was suggested.

\[
\begin{align*}
\text{B}_2\text{H}_6 + 2 0^* & \rightarrow 2 \text{BH}_30^* \\
\text{BH}_30^* & \rightarrow \text{BH}_3 + OR_2 \\
\text{BH}_3 & \rightarrow \overset{\beta}{B-H} + \overset{\beta}{C=C} 
\end{align*}
\]

It was suggested that the hydroboration is very fast in ether solvents as they provide an alternate pathway to the reactive species, the $\text{BH}_3$ monomer. Formation of $\text{BH}_3$ directly from $\text{B}_2\text{H}_6$ is highly prohibitive since the $\text{B-H}$ would lose dimerization energy of 36 Kcal/mole in the process.

The kinetic studies of hydroboration of simple olefins with $\text{BH}_3$.THF complex in solution are complicated by three successive $\overset{\beta}{B-H}$ addition reactions (eq.5-7), three redistribution equilibria (eq.8-10) and five monomer dimer equilibria (eq.11-15).

\[
\text{Alkene} + \text{BH}_3 \rightarrow \text{RBH}_2
\]
However, kinetic studies had been carried out for the hydroboration of tetramethylethylene in BH₃·THF which is known to give monoalkylborane species.¹¹
The rate of formation of thexylborane was found to be first order in both BH₃·THF and tetramethylethylene with an activation energy of 9.2 Kcal/mole and entropy of activation of -27 e.u. The hydrogen-deuterium (\( ^{1}B-H(D) \)) kinetic isotopic effect (\( k_{H}/k_{D} \)) was found to be 1.18. On the basis of these results, the reaction was considered to involve the direct reaction between a molecule of BH₃·THF and alkene with partial displacement of THF by the olefin in a very early transition state in which the molecule of THF is still rather tightly coordinated with boron atom (Scheme 1).

Scheme 1

It was noted that these studies do not provide any information regarding the possible formation of an intermediate BH₃-olefin \( \Pi \) complex for the reaction.

It has been reported that the asymmetric hydroboration of cis-1-butene-d by diisopinocampheylborane can be rationalised considering the formation of a triangular \( \Pi \) complex and that the transition state involves a relatively small perturbation from this triangular structure. It was shown that the four centred rectangular transition state proposed earlier gave incorrect prediction in this case (Fig.1,2).
The kinetic data obtained for the hydroboration of olefins with several dialkylborane complexes have been reviewed recently.\(^8\),\(^7\) The data were interpreted by considering the mechanism outlined in Scheme 2.

On the basis of these studies, a similar mechanism was proposed for the hydroboration of olefins with diborane in ether solvents (Scheme 3).
As pointed out earlier, it was suggested that since the ether solvents provide the alternate pathway (Scheme 3) for the formation of the reactive species (i.e. BH$_3$ monomer), the catalytic effect of ether solvents can be readily explained on the basis of this mechanism.$^{7-9}$

This mechanistic proposal involving free 'BH$_3$' monomer formation was questioned.$^{14}$ It was pointed out that since the complexation energy of BH$_3$ monomer with the solvent must be strong enough to overcome the dimerization energy ($2\text{BH}_3 \rightarrow \text{B}_2\text{H}_6$, -36 Kcal/mol), spontaneous dissociation of BH$_3$.THF into free BH$_3$ monomer visualized in Scheme 3, is energetically implausible.$^{14}$ On the basis of ab initio calculations for the reaction of ethylenc with $\text{H}_3\text{BH}:\text{OH}_2$ complex (a model for hydroboration in ether solvents), it was concluded that the reaction resembles an $S_2$ displacement of the solvent by the olefin and the solvent plays essentially no role in the transition state but BH$_3$ never becomes free during the reaction$^{14}$ (Scheme 4).

Scheme 4

It was contended that the vacant p-orbital of BH$_3$ must always be engaged; in B$_3$H$_9$, in the BH$_3$-solvent complex and in the hydroboration
transition state. It was also suggested that the solvent in BH$_3$-solvent complexes provides a better leaving group than the second BH$_3$ in BH$_3$ and hence the catalytic effect of ether solvents on the hydroboration of alkenes with diborane can be easily explained.

However, strong kinetic evidence for an intermediate formation in the hydroboration reaction has been presented. For example, it was observed that the addition of Lewis bases suppresses the rate of hydroboration of olefins with BH$_3$-Lewis base complexes and the second order rate constants decrease as the reaction progresses. These findings indicate that the formation of Lewis-base along with the reactive intermediate in an equilibrium step from the BH$_3$-Lewis base complex prior to $\text{BH}_3$ addition to the olefin (i.e. an $S_n^1$ like mechanism, Scheme 5). It was proposed that the intermediate is the free 'BH$_3$' monomer.

**Scheme 5**

\[
\begin{align*}
\text{BH}_3 + \text{LB} &\xrightleftharpoons[k_2]{k_1} \text{BH}_3 + \text{LB} \\
\text{BH}_3 + \text{C}==\text{C} &\xrightarrow[k_3]{k_2} \text{BH}_2 + \text{H} \\
\end{align*}
\]

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

\[
\frac{dp}{dt} = \frac{k_1 k_3 [\text{BH}_3 \text{LB}][\text{Olefin}]}{k_2 [\text{LB}] + k_3 [\text{Olefin}]} \tag{17}
\]
It was pointed out that this rate law will reduce to eq. 18 in the presence of excess LB, $k_2[LB] \gg k_3[\text{olefin}]$

$$\frac{dp}{dt} = \frac{k_1k_3[\text{BH}_3\text{LB}][\text{Olefin}]}{k_2[LB]}$$  \hspace{1cm} (18)$$

It was argued that the kinetic data obtained previously for the reaction of BH$_3$.THF with tetramethylethylene in THF can be also rationalised by this rate law (eq. 18) as the LB (i.e. THF) will be in large excess.

Although the rate retardation effect observed clearly points out a reactive intermediate formation in an equilibrium step along with the Lewis-base prior to BH$_3$ addition, it is still not clear that such an intermediate is the free 'BH$_3$' monomer. It should be pointed out that the data can be readily explained by considering the mechanism (Scheme 6) involving the formation of a Dewar type olefin -BH$_3$ \Pi complex along with the Lewis base in an equilibrium step prior to rearrangement to alkylborane.

_Scheme 6_
Steady state treatment for this mechanism will give the rate law given in eq. 19 and 20.

\[
\frac{dp}{dt} = \frac{k_1 [BH \cdot LB] [Olefin]}{k_3 + k_2 [LB]}
\]

(19)

\[
\frac{dp}{dt} = \frac{k_1 [BH \cdot LB] [Olefin]}{1 + k_2/k_3 [LB]}
\]

(20)

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

Surprisingly, the mechanism involving \( \pi \)-complex formation outlined in Scheme 6 was not considered for explaining the rate retardation effect observed by the addition of Lewis bases. However, almost all other contributors to the mechanistic studies of the hydroboration reaction considered the possibility of olefin-BH \( \pi \)-complex intermediate for the reaction.

As outlined previously, the \( \pi \)-complex intermediate was proposed to account for the stereochemical outcome in the asymmetric hydroboration of cis-1-butene-d by diisopinocampheylborane. The \( \pi \)-complex intermediate was later considered as an alternate pathway to the apparent symmetry forbidden process of the concerted B-H \( \sigma \) bond addition to the C-C \( \pi \) bond. However, it was soon pointed out that if the involvement
of vacant p-orbital on boron in BH₃ monomer or the back lobe of the BH₃-Lewis base bond are taken into account, the process will be allowed by orbital symmetry considerations. ¹¹

Fig. 3

Gas phase reaction of BH₃ monomer generated from H₃BPF₃ with ethylene was found to have an activation energy of 2±3 Kcal/mole. ²¹ A loose BH₃-olefin Π complex formation prior to hydroboration was suggested. ²¹

Theoretical studies of the hydroboration reaction involving BH₃ monomer have lead to the suggestion of a BH₃-olefin Π complex as an energy minimum with varying energy relationships to the ground state and transition state.¹⁵ It was predicted that it might be possible to isolate BH₃-acetylene Π-complex in matrices at low temperature.¹⁶

On the basis of ab initio calculations, it was pointed out that the dominant interaction in the early stages of the hydroboration reaction is between the ethylene Π-HOMO and the vacant p-orbital (LUMO) of the
BH₃ monomer leading to the formation of the π-complex. It was also reported that the interaction of the ethylene π LUMO with one of the degenerated BH₃ HOMO's is initially weak but becomes progressively more important as the reaction proceeds and eventually leads to the delivery of hydrogen from boron to carbon.

As outlined previously, on the basis of ab initio calculations for the reaction of ethylene with BH₃OH₂ (model for BH₃·THF), it was concluded that the reaction resembles an S₂like mechanism (Scheme 6). It was also suggested that the molecular orbital changes in such a reaction are analogous to those outlined above for the BH₃ monomer reaction with ethylene (Fig.5 and Fig.6) except that the initial donor-acceptor interactions between olefin HOMO and BH₃ LUMO has been replaced by the interaction with the σ MO of the BH₃·OH complex. It was also reported that the displacement of water is essentially complete before the delivery of hydrogen from BH₃ HOMO to the ethylene LUMO becomes important. However, no comment was made regarding the possibility of a BH₃-olefin π-complex formation in this case.
The \( \pi \)-complexes formed in the reaction of substituted ethylene are unsymmetrical.\(^{13}\) For example, cyanoethylene prefers to form Markovnikov \( \pi \)-complex leading to placement of boron on the internal position in the alkylborane product and propylene gives anti-Markovnikov \( \pi \)-complex leading to placement of boron on the terminal position.\(^{13}\) It was suggested that the presence of solvent molecule during \( \text{B-H} \) addition to the olefin is not necessary to account for the observed regioselectivity of hydroboration involving simple monosubstituted alkenes such as propylene with borane.\(^{13}\)

Two compilations appeared summarising the data available in 1979\(^{22}\) and in 1982.\(^{23}\)

In the compilation published in 1979,\(^{22}\) it was concluded that the reaction of \( \text{BH}_3 \cdot \text{THF} \) in solution can be considered as involving partial nucleophilic displacement of the THF by interaction of one of the \( p \)-orbitals of the \( \pi \)-electron system with the back lobe of the \( sp^3 \) orbital on boron involved in the bonding with the oxygen atom of THF. At the same time there is development of bonding between the hydrogen \( 1s \) orbital with the other \( p \)-orbital of the \( \pi \) system. This view is essentially same as that proposed for the \( S_n2 \)-like mechanism.\(^{11}\) It was also suggested that such a transition state may be preceded by \( \pi \)-complex formation and the molecule of THF must ultimately either become dissociated as the transition state proceeds beyond the point of maximum energy or it must migrate to the boron orbital vacated by the hydrogen atom.\(^{11}\)

In the 1982 compilation,\(^{23}\) it was concluded that the data available
in 1982 for hydroborations with borane in solution are more consistent with a concerted [2+2] cycloaddition involving a BH$_3$·THF complex rather than with a rate determining π-complex formation and in the gas phase, a loose π complex is probably formed early along the reaction coordinate.$^{23}$

It is interesting to note that both these compilations did not consider the possibility of dissociation of BH$_3$·THF into free BH$_3$ monomer before addition of \( \text{B-H} \) moiety to the olefin.$^{20,23}$

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

**Scheme 7**

\[
\begin{align*}
1 & \xrightarrow{1. \text{BH}_3 \cdot \text{THF}, 12 \text{h}} 2 \oplus 3 \\
& \xrightarrow{2. 100^\circ \text{C}, 0.5 \text{ to } 2 \text{h}} \\
& \xrightarrow{3. \text{H}_2\text{O}_2/\text{NaOH}} \\
1 & \xrightarrow{\geq 99\%} 2 \oplus 3 \\
& \xrightarrow{\leq 1\%} \\
2 & \xrightarrow{\geq 99\%} 2 \oplus 3 \\
& \xrightarrow{\leq 1\%} \\
& \frac{1}{100} \text{products}
\end{align*}
\]

It was demonstrated that the hydroboration-rearrangement does not take place through dissociation of the intermediate alkylborane to the 2-methyl-1-methylene cyclohexene and \( \text{H-B}^\cdot \) (Scheme 8) followed by re-hydroboration since this olefin on reaction with either BH$_3$·THF or BH$_2$, followed by oxidation gives only a 70:30 mixture of 2 and 3 (Scheme 8).$^{20}$
It was concluded that the observed stereoselectivity provides strong support for an intramolecular process, most likely involving an intermediate π-complex, which must give rearranged alkylborane faster than dissociated entities (Scheme 9).

It was observed that the stereochemical results are the same both in the presence or absence of THF, indicating that the solvent plays no critical role in the above intramolecular migration. The rearrangement results were considered in the context of the mechanism of hydroboration and it was suggested that principle of microscopic reversibility would predict a π-complex intermediate for the reverse reaction (i.e. hydroboration) but it was concluded that such an inter-
mediate must be different from that involved in the rearrangement process as the two reactions differ in conditions (temperature, possibly structure of reactants). The authors noted that this conclusion is surprising considering close similarities of the two processes. In any case, this excellent piece of work necessitates that the mechanism involving intermediate of π-complex should be also considered in the interpretation of data.

From the foregoing survey, three general mechanistic pictures can be deduced for the hydroboration of alkenes with BH₃:LB complexes.

1. **S 1-like mechanism**: Involving free 'BH₃' monomer formation in an equilibrium step (Scheme 10).

   **Scheme 10**
   \[
   \text{BH}_3\text{LB} \rightleftharpoons \text{BH}_3 + \text{LB}
   \]

   \[
   \text{CH}_2=\text{CH-R} + \text{BH}_3 \rightarrow [\text{CH}_2=\text{CH-R}] \rightarrow \text{R-CH}_2-\text{CH}_2-\text{BH}_2
   \]

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

   **Scheme 11**
   \[
   \text{CH}_2=\text{CH-R} + \text{BH}_3\text{LB} \rightarrow [\text{CH}_2=\text{CH-R}] \rightarrow \text{R-CH}_2-\text{CH}_2-\text{BH}_2
   \]

3. **Mechanism with π-complex Intermediate**: The LB may or may not be present in the transition state of the >B-H-addition (Scheme 12).
From these mechanistic pictures, it is clear that in the $S_N^1$-like mechanism, the Lewis base is absent in the transition state while the $\gamma B$-$H$ addition to C-C double bond takes place (Scheme 10). It is also clear that in the case of $S_N^2$-like mechanism (without any intermediate), the Lewis base is present in the transition state while the $\gamma B$-$H$ moiety is added to the olefin (Scheme 11). It is not understood whether the Lewis base will be present or absent in the transition state of the $\gamma B$-$H$ addition to the olefin in the mechanism with $\Pi$-complex intermediate (Scheme 12). The possibility of the Lewis base interacting with the boron while the hydrogen is delivered from boron to carbon in the $\Pi$-complex cannot be completely ruled out. However, any such interaction may not influence the stereochemical outcome very much since the $\gamma BH$ addition here is an intramolecular rearrangement.
Answer to the question whether the Lewis base is present or absent in the transition state will facilitate the understanding of the mechanism of this important and interesting reaction.

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

**Scheme 13**

\[
\text{CH}_3 X = \text{Camphor - 10 - Sulphonate}
\]

Chiral amine-borane complexes are known to give asymmetric reductions of prochiral ketones into the corresponding alcohols to the extent of 42% in the presence of $\text{F}_2\text{B:OEt}_2$. Even in the absence of $\text{F}_2\text{B:OEt}_2$, chiral $\text{N-methyl-}\alpha\text{-methylbenzylamine-BH}_3$ and $\text{N,N-dimethyl-}\alpha\text{-methylbenzylamine-BH}_3$ complexes reduce acetophenone into 1-phenylethanol with 3.5 to 5% ee. It was suggested that the observations of optical inductions in these cases are not in accord with dissociation of the amine-borane complexes followed by reduction of the ketone by BH$_3$. It occurred to us that the question whether the Lewis base is present or absent in the hydroboration transition state can be examined
by utilizing chiral Lewis base-borane complexes for hydroboration of prochiral olefins.
RESULTS AND DISCUSSION

Synthesis of Chiral Lewis base precursors

The RCOOH/NaBH₄ system hydroborates alkenes (Chapter 1). It was thought that the hydroboration of prochiral olefins with a chiral carboxylic acid/NaBH₄ system will throw some light on the nature of the hydroborating species and also on the mechanism of the reaction.

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

\[ \text{CH}_3 - \text{CH-COOH} \]

11

\[ \text{H}_3\text{CO} - \text{CH-CH}_3 \text{COOH} \]

12

\[ [\alpha]_{D}^{20} = 61.2 \text{ (C1, CHCl}_3) \]

lit. \[ [\alpha]_{D} = 65.5 \text{ (Cl, CHCl}_3) \]

28

\[ [\alpha]_{D} = -41.26 \text{ (C3.98, EtOH)} \]

\[ \text{lit.} [\alpha]_{D} = + 48.3 \text{ (C4, EtOH)} \]

29
Hydroboration of $\alpha$-pinene with $\text{CH}_3\text{COOH}/\text{NaBH}_4$ followed by oxidation with $\text{H}_2\text{O}_2/\text{NaOH}$ gave (-) cis-myrtanol (14). We have carried out the conversion of cis-myrtanol to cis-myrtanic acid (12) utilizing several oxidising reagents following related literature procedures (eg. PDC/DMF, $\text{SeO}_2$, followed by oxidation of the aldehyde by $\text{Ag}_2$, chromic acid/acetone (Jones), $\text{KmNO}_4/\text{NaOH}$, sodium bromate/HBr, $\text{KmNO}_4/\text{H}_2\text{SO}_4$ in water system). The yields were not satisfactory in all these cases. The method utilizing $\text{KmNO}_4/\text{H}_2\text{SO}_4$ in water without any solvent has been reported to give cis-myrtanic acid. Following this method, we have obtained pure cis-myrtanic acid (12) in 23% yield with $[\alpha]^\circ_D = -41.26$ (C3.98, EtOH). We have followed this method for accumulating myrtanic acid for utilization in the present studies.

Although hydroborations utilizing chiral carboxylic acid/NaBH$_4$ system will certainly throw some light on the mechanism of the hydroboration reaction, as indicated in Chapter 1, there are some ambiguities about the precise structure of the hydroborating species in this system since the initially formed $\text{RCO}O\text{BH}_3$ species disproportionates into NaBH$_4$ and NaB(OOCR)$_4$.
The amine bases form stable 1:1 complexes with BH$_3$\textsuperscript{22}. Although many amine-borane complexes hydroborate alkenes only at elevated temperatures (>100°C), some sterically hindered amine-borane complexes such as (15) and N,N-dialkylaniline derivatives (16) give rapid hydroborations.\textsuperscript{9,22}

![Image of structures](image)

Reaction with 1-octene in toluene at 75°C, $t/2 = 5$ min. Reaction with 1-octene in toluene at 25°C, $t/2 = 26$ min.

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

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

![Image of structures](image)

The synthesis of N-ethyl-N-isopropyl-$\alpha$-methylbenzyl amine was envisaged as given in Scheme 15.
Isopropylation of R(+)-α-methylbenzylamine (19) gave isopropyl-α-
methylbenzylamine (20) in 85% yield with $[\alpha]_D = 62.0$ (C 1.83, EtOH) which on acylation with acetic anhydride/pyridine gave the amide (21) in 78% yield. Reduction of the amide with LAH gave the t-amine (22A) with $D = 13.78$ (C 3.434, EtOH). BH .THF reduction of the amide gave the t-amine (223) with $[\alpha] = 5.26$ (C 4.1824, EtOH). The results indicate that at least in the case of BH .THF reduction racemization takes place during the reaction. It is also possible that LAH reduction also may give some racemization since the mechanism of reduction in both cases are similar, involving the intermediacy of iminium ions $_{42,43}$ (Scheme 16).
If the iminium ion undergoes the following equilibration, then racemization will result (eq. 21). Although mechanism of such an equilibrium is not clearly understood, it is possible that it may proceed by the removal of the benzylic proton by the hydride reagent.  

\[ \text{Ph} \text{CH}_3 \text{C}^{\text{+}} \text{NH}_2 \text{C} = \text{N} \text{-H} \text{CH}_3 \text{C} \text{=} \text{N} \text{-H} \text{CH}_3 \]  \hspace{1cm} (21)

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

Similarly, N,N-dibenzyl-α-methylbenzylamine was also prepared (Scheme 18).
The N-methyl-N-isobornylaniline (30) was prepared by following closely related literature procedures as outlined in Scheme 19.

(+)-Camphor (25) \( \alpha_D = +43.5\pm1^\circ \) supplied by Fluka, Switzerland was condensed with aniline in toluene in the presence of TiCl₄ at 125°C.
to give camphor-anil (27) in 65% yield. It is known that catalytic hydrogenation of camphor-anil (27) using Pt/C gives N-isobornylaniline (28). We have observed that the Pt/C reduction of camphor-anil (27) gives N-isobornylaniline in 82% yield and the signals corresponding to the endo isomer are not found in the $^{13}$C NMR spectrum of the product. We have tried several other methods for this conversion. Utilization of Pd-C/H$_2$ did not give any reduction. Formic acid which is known to reduce enamines derived from camphor, did not affect the conversion with the camphor-anil. However, NiCl$_2$.6H$_2$O/NaBH$_4$/CH$_3$OH system and CCl$_2$/NaBH$_4$/CH$_3$OH systems gave the desired N-isobornylaniline in 75% and 82% yield respectively. We have utilized the NiCl$_2$.6H$_2$O/NaBH$_4$.CH$_3$OH reagent system for accumulating the amine required for the present studies.

Initially we have carried out the methylation of the N-isobornylaniline (28) with the HCHO/HCO$_2$H;HCO$_2$H/H$_2$SO$_4$/NaBH$_4$ method but the yield was poor. Methylation with CH$_3$I after preparation of the amide (29) from N-isobornylaniline gave better results. The N-methyl-N-isobornylaniline (30) obtained in this way was chromatographed on a silica gel column using hexane/chloroform as eluent. The chromatographed tertiary amine was distilled under reduced pressure before utilization in the preparation of the corresponding BH$_3$ complex.

Hydroboration of prochiral olefins with BH$_3$-chiral Lewis base complexes

The hydroboration of 1-methyl-1-cyclohexene with the cis-myrtanic acid/NaBH$_4$ in THF for 24 h at room temperature followed by oxidation
with H\textsubscript{2}O\textsubscript{2}/NaOH gave the trans-2-methylcyclohexanol in 60% yield with an enantiomeric excess of 4.2% (Table 3.1). Hydroboration of 1-methyl-1-cyclohexene utilizing cis-myrtanic acid/LiBH\textsubscript{4} system followed by oxidation gave the trans-2-methylcyclohexanol in 53% yield with 4.8%ee. Both the cis-myrtanic acid/NaBH\textsubscript{4} and cis-myrtanic acid/LiBH\textsubscript{4} systems failed to hydroborate 1-phenyl-1-cyclopentene even after 72 h at room temperature. We have found that under the same conditions CH\textsubscript{3}COOH/NaBH\textsubscript{4} system does not have any problem in reacting with 1-phenyl-1-cyclopentene and 68% of trans-2-phenylcyclopentanol can be isolated after oxidation (Scheme 20). Hydroboration-oxidation of 2,3-dihydrofuran with this system gave 3-hydroxytetrahydrofuran in 68% yield with 10.2%ee.

**Scheme 20**

Hydroboration of 1-methyl-1-cyclohexene with the (\(+\))2-(6'-methoxy-2'-naphthalene)propionicacid/NaBH\textsubscript{4} system followed by oxidation gave trans-2-methyl-1-cyclohexanol in 68% yield with 2.4%ee (Table 3.1).
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<th>Olefin</th>
<th>Borane/LB</th>
<th>Reaction time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
<th>([\alpha]_D^{20}(C,\text{solvent}))</th>
<th>% ee.</th>
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<td><img src="image9.png" alt="Image" /></td>
<td>CH-COOH/NaBH₄</td>
<td>14</td>
<td><img src="image10.png" alt="Image" /></td>
<td>68</td>
<td>-1.06(C2.83,CH₃OH)</td>
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<td>7.</td>
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<td>&quot;</td>
<td>12</td>
<td><img src="image12.png" alt="Image" /></td>
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<td>D.O.</td>
<td>Substrate</td>
<td>Value</td>
<td>Solvent</td>
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<td>-1.60(C2.5,CH3OH)</td>
<td>9.2</td>
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contd.
a. The reactions were repeated several times in each case and the measured observed rotations always fell within ±0.01° which is also the accuracy limit of the polarimeter (Autopol II automatic polarimeter). In each case, the condition of the polarimeter was checked by measuring a standard solution of either camphene, \([\alpha]_{D}^{20} = +17\pm1°\) (C4,Ether) or α-Methylbenzylamine \([\alpha]_{D}^{20} = +30\pm2°\) (C10,EtOH) supplied by Fluka. The differences in the observed rotations of standard solutions in different runs also fell within ±0.01°. The polarimeter was set to zero reading using the solvent used. Same concentration of racemic compounds were also run and in all cases the reading of racemic compound fell within ±0.01°.

b. Time required for getting optimum chemical yields.

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

d. In each case the optical rotations were measured in two concentrations and the values for concentrations closer to the concentrations utilized in the literature \([\alpha]_{D}\) values are given here.

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

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

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

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

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

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

Asymmetric induction of 2.4%ee to 10.2%ee observed in the above experiments indicate that the acyloxy groups do have some influence on the hydroboration of alkenes. However, there is ambiguity about the structure of the hydroborating species here. As outlined in Chapter 1, it has been found that the mixing of RCOOH/MBH$_4$ system, does not give cleanly CH$_3$COOBH$_3$. The resulting species are MBH$_4$ and MB(OCOR)$_4$ or MBH$_4$ in equilibrium with MBH$_3$(OCOR), MBH$_2$(OCOR)$_2$, MBH(OCOR)$_3$ and MB(OCOR)$_4$. However, the fact is that the RCOOH/MBH$_4$ system is able to hydroborate alkenes. Both the chiral carboxylic acid/MBH$_4$ systems
studied here on treatment with $\text{Ph}_3\text{P}$ gave $\text{Ph}_3\text{PBH}_3$ in essentially quantitative yields. Clearly, the $\text{RCOOH/MBH}_4$ system is able to supply $'\text{BH}_3'$ moiety. It is known that among the three acyloxyborohydride species, the $\text{NaBH}_3\text{OAc}$ is the most reactive species in reductions (i.e. $\text{NaBH}_3\text{OAc} > \text{NaBH}_2\text{(OAc)}_2 > \text{NaBH}(\text{OAc})_3$) and under the conditions where the $\text{NaBH}(\text{OAc})_3$ will be the species present (neat carboxylic acid/$\text{NaBH}_4$) no hydroboration is observed. Accordingly, most probably $\text{NaBH}_3\text{OCOR}$ will be the hydrobating species in the $\text{RCOOH/NaBH}_4$ systems.

Observation of asymmetric inductions in the hydroboration/oxidation of prochiral alkenes with the above $\text{RCOOH/NaBH}_4$ systems points out that the acyloxy groups in these cases do have some influence in the transition state of the hydroboration reaction. However, since there is ambiguity about the precise structure of the reactive species in the $\text{RCOOH/NaBH}_4$ systems, we have decided to study the mechanism of hydroboration reaction further utilizing chiral amine-borane complexes for hydroboration.

The amine-borane complexes (31), (32) and (33) can be readily prepared in benzene utilizing the $\text{I}_2$/NaBH$_4$ reagent system for diborane generation as outlined in Chapter 2.

![Chemical structures](image_url)
of the amine gives 10 mmol of \( \text{Ph}_3\text{PBH}_3 \) on treatment with 15 mmols of \( \text{Ph}_3\text{F} \), confirming the formation of a 1:1 amine borane complex.

The hydroborations were carried out using 10 mmol of chiral amine borane complex in benzene (40 mL) with 10 mmol of prochiral olefins and the reactions were performed for the time indicated in Table 3.1. The reaction mixture was hydrolysed by careful addition of 3N HCl (2 mL). Oxidation of the organoborane with \( \text{H}_2\text{O}_2/\text{OH} \) was carried out after adding 40 mL of dry THF in order to facilitate the oxidation. In runs with 1-methyl-1-cyclohexene and 1-phenyl-1-cyclopentene, the alkaline reaction mixture obtained after oxidation with \( \text{H}_2\text{O}_2/\text{OH} \) was extracted with ether several times and the combined ether layer was washed with 6N HCl (3x10 mL) to recover the chiral amine. In runs with 2,3-dihydrofuran and 3,4-dihydro-pyran, since the alcohols are water soluble, the alkaline reaction mixtures obtained after oxidation were saturated with solid anhydrous \( \text{K}_2\text{CO}_3 \) and extracted several times with ether. From the combined amine-alcohol residue obtained after evaporation of solvent, the alcohol could be readily distilled out under reduced pressure. Alternatively, the alkaline reaction mixture after oxidation with \( \text{H}_2\text{O}_2/\text{OH} \) was first extracted with ether (3x30 mL) to isolate the amine and the aqueous layer was then saturated with solid \( \text{K}_2\text{CO}_3 \) and the alcohol was isolated by extraction with ether. We have found that both these procedures gave comparable results but we find the latter method is more convenient. The optical rotation of the recovered amines remained unchanged.

The alcohols obtained in the hydroboration of prochiral olefins with chiral amine borane complexes (31, 32 and 33) were distilled under
reduced pressure, further purified by eluting through a silica gel column and distilled again under reduced pressure before optical rotations were measured. The data are summarised in Table 3.1.

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

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

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

The $S_11$-like mechanism (Scheme 10) involves the dissociation of $BH_3$-Lewis base complex into free $'BH_3'$ and Lewis base followed by addition of the $\geq B-H$ bond of the free $'BH_3'$ into the olefin through a four centred transition state. The proposed mechanism implies
(Scheme 10) that the Lewis base is not bonded to boron during the actual hydroboration step and hence this mechanism cannot explain the asymmetric inductions obtained in the hydroboration of 1-methyl-1-cyclohexene and 2,3-dihydrofuran. In the case of 1-phenyl-1-cyclopentene, the observed inductions are almost negligible. However, it is doubtful that the mechanism involving free 'BH$_3$' intermediate would operate even here. For example, as mentioned previously, we have found that the cis-myrtanic acid/MBH$_4$ (M = Na or Li) system failed to react with 1-phenyl-1-cyclopentene even after 72 h at r.t. However, the CH$_3$COOH/NaBH$_4$ system does hydroborate 1-phenyl-1-cyclopentene under the same conditions. This difference in reactivity of the two RCOOH/NaBH$_4$ system cannot be explained assuming free 'BH$_3$' species as the hydroborating species.

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

However, as outlined earlier, there are strong evidences for the formation of an intermediate in the hydroboration of olefins in some cases. As pointed out in the introductory section, the intermediate may very well be a $BH_{3}^{3}$ olefin $\pi$ complex, formed in an equilibrium step from olefin and $BH_{3}^{3}.LB$ complex as given in the mechanism involving a $\pi$-complex intermediate (Scheme 12). As pointed out earlier, it is not clear whether the Lewis base will be present in the transition state while the rearrangement of the $\pi$-complex to alkylborane takes place. However, even if the Lewis base gets attached during rearrangement, its influence on the stereochemical outcome may not be very much as the $\sigma$-$B-H$ addition here is an intramolecular rearrangement. It seems likely that the asymmetric inductions will be higher only if the reaction goes through without such a $\pi$-complex intermediate, (Scheme 11 and 12). The present results can be explained by considering a spectrum of mechanisms between $S_{2}$-like mechanism without intermediate and the mechanism with a $\pi$-complex intermediate. Consideration of the interactions of the frontier orbitals of the reactants will further illustrate this point.

As outlined in the introductory section, the frontier orbital interactions in the hydroboration reaction utilizing $BH_{3}.LB$ complex are the interaction of the olefin $\pi$-HOMO with the $\sigma$ LUMO of the borane-
Lewis base bond and interaction of the olefin \( \text{LUMO} \) with the \( \pi - \text{HOMO} \) of the one of the degenerate \( \pi^* - \text{B-H} \) bonds. \(^{15} \) For enol ethers, the \( \pi - \text{HOMO} \) of the olefin will be higher in energy and will have larger coefficient in the \( \beta - \text{carbon} \) atom and hence the interaction between the \( \beta - \text{carbon} \) atom of the olefin and the \( \sigma \) LUMO of the boron-LB bond will be very much energy lowering and hence the carbon-boron bond formation will be facile (Fig. 8). In addition, the delivery of the hydrogen from boron to the \( \alpha - \text{carbon} \) atom of the enol ether will be also facile as the LUMO of enol ethers will have larger coefficient at the \( \alpha - \text{carbon} \) atom (Fig. 9). Hence, it is likely that the hydroboration of enol ethers may take place in a concerted manner without the intervention of an intermediate.

Alkyl substitution affects the IT-HOMO of the olefin in a similar way and polarizes the HOMO to lesser extent compared to enol ethers. But the coefficients of LUMO of alkyl substituted olefins at \( \alpha - \) and \( \beta - \text{carbon} \) atoms are the same (Fig. 10 and 11).\(^{58} \) Phenyl substitution on ethylene affects the TT-HOMO of the olefin in the same way with polarization to lesser extent compared to enol ethers (Fig. 12 and 13) but the
LUMO will be polarised so that the coefficient is smaller at the \( \alpha \)-carbon atom. This will make the delivery of the hydrogen from boron to \( \alpha \)-carbon atom relatively difficult and hence in the case of 1-phenyl-1-cyclopentene the reaction is likely to go through stages.

In the above discussion considering the interactions of the frontier orbitals, the steric effects of the reagents which will certainly play a major role in determining the differences in the diastereomeric
transition states in each case are ignored. However, in the case of 1-phenyl-1-cyclopentene consideration of steric effects will also lead to same conclusion. The reaction in the case of sterically hindered olefins such as 1-phenyl-1-cyclopentene with borane Lewis base complexes will lead to a highly crowded transition state if the reaction goes through a concerted $S_N^1$-like mechanism in which the Lewis base is present in the transition state. Accordingly, steric effects would also shift the mechanism away from the $S_N^1$-like mechanism involving concerted formation of carbon-boron bond and carbon-hydrogen bond.

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

CONCLUSION

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

General details:

Several of the general experimental details outlined in Chapter 1 and 2 are also applicable here. +6-methoxy-β-naphthalene-2-propionic acid, $\left[\alpha\right]_D = +65.5^\circ$ (C1, CHCl$_3$) supplied by Sigma, USA was utilized. β-pinene, $\left[\alpha\right]_N = -21^\circ$ (neat) supplied by Tokyo Kesai, Japan was used for the synthesis of (-) cis-myrtanic acid, $\left[\alpha\right]^{20}_D = -41.26^\circ$ (C3.98, EtOH). R(+)-α-methylbenzylamine, $\left[\alpha\right]^{20}_D = +30\pm 2^\circ$ (C10, EtOH) and camphor $\left[\alpha\right]^{20}_D = +43.5 \pm 1^\circ$ supplied by Fluka, Switzerland was used for the synthesis of the corresponding tertiary amines. Optical rotations were measured on a Autopol II automatic polarimeter. The hydroboration reaction was repeated several times in each case and the measured observed rotations always fell within ±0.01° which is also the accuracy limit of the polarimeter used. In each case, the condition of the polarimeter was checked by measuring a standard solution of camphene, $\left[\alpha\right]_D = +17\pm 1^\circ$ (C4, ether) or α-methylbenzylamine, $\left[\alpha\right]^{20}_D = 30\pm 2^\circ$ (C10, EtOH) supplied by Fluka. The differences in the observed rotations of standard solutions in different runs also fall within ±0.01°. The polarimeter was set to zero reading using the solvent used. Same concentration of racemic compounds were also run and in all cases the reading of racemic compounds also fall with in ±0.01°. In each case the optical rotations were measured in two concentrations and concentrations closer to the concentration utilized...
in the literature $[\alpha]_D$ values are given in the Table 3.1.

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

$$[\alpha]_{D}^{20} = \frac{\text{Observed rotation}}{1 \times c}$$

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

**Synthesis of cis-Myrtanic acid (12)**

cis-Myrtanol (14) was prepared through hydroboration of β-pinene with acetoxyborohydride followed by $\text{H}_2\text{O}_2$/NaOH oxidation as described in Chapter 1. The product, bp. 80°C/1.5 mm lit. 31 bp. 68°C/0.2 mm had an $[\alpha]_D^{25}$ value of -19.0 (C11, CHCl$_3$) corresponding to 90.5% optical purity.

The conversion of the alcohol into the acid was carried out following a literature procedure. 29 cis-Myrtanol (6.25 g, 40 mmol) was dispersed in a mixture of 95% $\text{H}_2\text{SO}_4$ (25 mL) and water (200 mL) at room temperature. Finely powdered $\text{KMnO}_4$ (11.5 g) was added in small portions with stirring as fast as purple colour was discharged. The precipitated MnO$_2$ was reduced by the addition of sodium metabisulfite and the mixture was extracted with ether (3x30 mL). The combined ether extract was washed with 2N KOH (3x30 mL), dried (MgSO$_4$) and concentrated to yield myrtanic acid (12).
It was recrystallized from acetonitrile (1.5 g, 23%, mp.109°C, lit. mp.111°C; \( [\alpha]_D^{25} = -41.26 \) (C3, 98, EtOH), corresponding to 85.4% optical purity.

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

\( ^{13}\)C NMR (25.0 MHz, CDCl\(_3\)): \( \delta \) ppm 183.6, 43.9, 43.0, 40.5, 38.9, 29.1, 27.0, 24.7, 21.7, 15.2.

**Synthesis of N,N dibenzyl-\( \alpha \)-methylbenzylamine (24)**

A mixture of \( \alpha \)-methylbenzylamine (12.1 g, 100 mmol), KOH powder (32.0 g, 500 mmol), benzyl bromide (25 mL, 250 mmol) and NaI (3.0 g, 20 mmol) was refluxed for 20 h. The contents were brought to r.t. and extracted with ether (3x50 mL). The ether layer was treated with 5N HCl (30 mL) to precipitate the amine as hydrochloride salt which was found to be insoluble in water. The amine hydrochloride was once washed with ether (30 mL) and the amine was regenerated with 5N KOH (phenolphthalein indicator). The amine was extracted into ether (3x25 mL), dried (MgSO\(_4\)) and the solvent was evaporated. The residue was recrystallized from benzene-hexane mixture to yield white crystalline \( N,N \)-dibenzyl-\( \alpha \)-methylbenzylamine (24) 24 g, 80%, mp.72°C, \( [\alpha]_D^{25} = +100.5^\circ \) (C2.54, CHCl\(_3\)).

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

\( ^{13}\)C NMR (25.0 MHz, CDCl\(_3\)): \( \delta \) ppm 143.0, 140.4, 129.3, 128.4, 128.3, 127.0, 56.3, 53.7, 13.9.
Analysis: Calculated for C$_{22}$H$_{23}$N: C, 87.7; H, 7.6; N, 4.7; Found: C, 88.0; H, 7.7; N, 5.0.

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

(a) Preparation of N-isopropyl-α-methylbenzylamine (20): A mixture of α-methylbenzylamine (6.5 g, 50 mmol), KOH powder (22.4 g, 400 mmol) and isopropyl iodide (51 g, 300 mmol) was refluxed for 14 h. The contents were brought to room temperature and extracted with ether (4x25 mL). The ether layer was washed with water (2x20 mL), brine (15 mL), dried (MgSO$_4$) and the solvent was removed. The residue was distilled under reduced pressure to yield N-isopropyl-α-methylbenzylamine (20) 6.9 g, 85%, bp. 65°C/3 mm. [α]$_D^\circ$ = +62.0° (C1.83, CH$_3$OH).

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

$^1$H NMR (100 MHz, CDCl$_3$): δ ppm 7.2 (s, 5H), 3.8 (q, 1H), 2.56 (p, 1H), 1.28 (d, 3H), 0.92 (q, 6H).

$^{13}$C NMR (25.0 MHz, CDCl$_3$): 6 ppm 146.0, 128.1, 126.5, 126.2, 54.8, 45.1, 24.5, 23.7, 21.8.

(b) Acylation of N-isopropyl-α-methylbenzylamine: An equal volume of freshly distilled acetic anhydride was added to N-isopropyl-α-methyl benzylamine (3.26 g, 20 mmol) and the residue was stirred for 14 h at r.t. 6N HCl (15 mL) was added and the mixture was extracted with ether (3x20 mL). The combined organic extract was washed with NaHCO$_3$ solution, dried (MgSO$_4$) and evaporated to yield N-acetyl-N-isopropyl-α-methyl
benzylamine (21), 3.2 g, 78%, mp. 112°C, \([\alpha]^{25}_D = +53.7°(C1.42, \text{EtOH}).\)

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

\(^1\)H NMR (100 MHz, CDCl\(_3\)): 6 ppm 7.08 (s, 5H), 4.6 (s, 1H), 2.42 (p, 1H), 1.84 (s, 3H), 1.32 (d, 3H), 1.08 (d, 3H), 0.72 (d, 3H).

\(^13\)C NMR (25.0 MHz, CDCl\(_3\)): \(\delta\) ppm 169.4 (\(-\text{N-CO-CH}\)), 140.1, 127.8, 126.8, 126.4, 54.4, 46.4, 23.4, 20.3, 19.2, 17.2.

**Reduction of N-acyl-N-isopropyl-\(\alpha\)-methylbenzylamine (21) with BH\(_3\)-THF**

The amide (21) (2.06 g, 10 mmol) was dissolved in 50 ml of dry THF and diborane generated (Chapter 2) using I\(_2\) (12.5 mmol) and NaBH\(_4\) (25 mmol) was bubbled at 0°C and stirred at r.t. for 1 h. The mixture was then refluxed for 6 h. It was brought to r.t. and 6N HCl (15 mL) was added. THF was distilled out and NaOH pellets were added to neutralize amine hydrochloride. The reaction mixture was extracted with ether (3x25 mL), dried (MgSO\(_4\)) and the solvent was evaporated. The residue was distilled under reduced pressure to isolate N-ethyl-N-isopropyl-\(\alpha\)-methyl benzylamine (22B), 1.53 g, 80%, bp. 72°C/25 mm, \([\alpha]_D = +5.26\ (C4.1824, \text{EtOH}).\)

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

\(^1\)H NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 7.28 (t, 5H), 3.84 (q, 1H), 2.92 (p, 1H), 2.48 (g, 2H), 1.3 (d, 3H), 0.92 (m, 9H).
\[ ^{13} \text{C NMR (25.0 MHz, CDCl}_3 \] : 6 ppm 146.7, 128.0, 127.5, 126.2, 58.4, 48.2, 39.0, 20.0, 19.7, 19.2, 16.9.

Reduction of N-acyl-N-isopropyl-OHmethylbenzylamine with LAH/Ether

To the amide (21) (1 g, 5 mmol) in dry ether (30 mL), LAH (6 g) was added in portion from a solid addition flask and the contents were stirred for 14 h at r.t. The mixture was cooled and ethylacetate (5 mL) was added followed by 6N NaOH (10 mL). The reaction mixture was extracted with ether (3x20 mL), washed with saturated NaCl solution and dried over anhydrous MgSO. The solvent was removed and the residue was distilled to isolate N-ethyl-N-isopropyl-Ot-methylbenzylamine (22A), 0.57 g, 75%, bp. 85°C/3.5 mm, \([\alpha]_D^{13} = +13.78 \text{ (C3.99, EtOH).}\]

The IR, H-NMR and C-NMR spectra were identical with the sample obtained by the BH$_3$.THF reduction in the previous experiment.

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

A mixture of N-isopropyl α-methylbenzylamine (20) (16.3 g, 100 mmol), NaI (3 g, 20 mmol), powdered KOH (40 g, 625 mmol) and benzyl bromide (21.3 g, 125 mmol) was refluxed for 14 h at 100°C. The mixture was cooled and extracted with ether (3x50 mL) and the combined ether extracts were treated with 5N HCl (3x10 mL). The combined aqueous extract was once again extracted with ether (15 mL) and the amine was regenerated from the amine hydrochloride solution by the addition of 5N KOH (phenolph-
thalein indicator). It was extracted with ether (3x25 mL), dried (MgSO₄) and the solvent was removed. The residue was distilled to obtain N-benzyl-N-isopropyl-α-methylbenzylamine (20.3 g, 80%, bp.124°C/1 mm Hg). The amine thus obtained was purified by column chromatography on a silica gel column (hexane/chloroform as eluent) and distilled under reduced pressure to isolate and N-benzyl-N-isopropyl-α-methylbenzylamine (23), \([\alpha]_D^{20} = 17.29^\circ (C3.932, \text{CHCl}_3)\).

IR (neat) \(\nu_{\text{max}}^1\): 3095, 3075, 1600, 1350, 1145, 690 cm⁻¹.

\(^1\)H NMR (100 MHz, CDCl₃): 6 ppm 7.4 (m,5H), 7.2 (m,5H), 3.88 (q,1H), 3.64 (d,2H), 2.96 (p,1H), 1.28 (d,3H), 0.96 (p,6H).

\(^{13}\)C NMR (25.0 MHz, CDCl₃): 6 ppm 145.9, 143.3, 128.2, 128.0, 127.7, 126.6, 126.4, 58.2, 49.4, 48.0, 20.7, 19.1, 18.7.

Analysis: Calculated for C₁₁H₁₉N: C,85.41; H,9.1; N,5.5; Found: C,85.1; H,9.0; N,5.9.

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

(a) Preparation of camphor-anil (27): To a stirred solution of camphor (20.4 g, 150 mmol) and aniline (41.85 g, 450 mmol) in dry toluene (200 mL), TiCl₄ (10 mL) was added carefully and the reaction mixture was refluxed for 14 h under nitrogen atmosphere. The mixture was brought to room temperature. TiO₂ was filtered off and washed with petroleum ether (150 mL). The combined organic layer was dried (MgSO₄) and the solvent was removed.
The residue was distilled under reduced pressure to isolate camphor-anil (22 g, 65%, bp. 110°C/0.6 mm, lit. bp. 118°C/1 mm).

IR (neat) $\nu_{\text{max}}$: 1680, 1600 cm$^{-1}$

$^1$H NMR (100 MHz, CDCl$_3$): $\delta$ ppm 7.16-6.68 (m, 5H), 2.08 (m, 1H), 1.72 (m, 6H), 1.08 (s, 3H), 0.92 (s, 3H), 0.84 (s, 3H).

$^{13}$C NMR (25.0 MHz, CDCl$_3$): 6 ppm 184.1, 152.2, 128.8, 122.7, 119.7, 53.6, 46.7, 43.4, 35.8, 31.7, 27.1, 19.2, 18.7, 10.9.

(b) Conversion of camphor-anil (27) into isobornyl aniline (28) using NiCl$_2$·6H$_2$O/NaBH$_4$ system: Camphor-anil (2.27 g, 10 mmol) and NiCl$_2$·6H$_2$O (5.7 g, 20 mmol) were taken in methanol (100 mL) and cooled to -30°C. NaBH$_4$ (3.8 g, 100 mmol) was added in portions from a solid addition flask over a period of 1 h and stirred further for 1 h at -30°C and 4 h at r.t. 3N NaOH (15 mL) was added followed by ether (100 mL) and the black precipitate was filtered off and the layers were separated. The organic layer was washed with saturated NaCl solution, dried (MgSO$_4$) and distilled to yield N-isobornyl aniline (28). 1.72 g, 75%, bp. 134°C/1 mm, lit. bp. 131°C/1 mm. $\lbrack \alpha \rbrack_D^{20} = -71.5^\circ$ (C11.6, EtOH), lit. $\lbrack \alpha \rbrack_D^{19.5} = -89.1$ (unverified).

IR (neat) $\nu_{\text{max}}$: 3350, 1685, 1600 cm$^{-1}$.

$^{13}$C NMR (25.0 MHz, CDCl$_3$): 6 ppm 148.4, 129.4, 116.8, 112.0, 61.7, 48.4, 47.3, 45.3, 40.9, 36.9, 27.6, 20.6, 12.5.
The above secondary amine on acylation with Ac$_2$O or acetyl chloride gave the corresponding amide mp.124°C, lit.mp.123°C.$^{45}$

IR (KBr) $\nu_{\text{max}}$: 1650, 1590 cm$^{-1}$.

$^{13}$C NMR (25.0 MHz, CDCl$_3$): $\delta$ ppm 172.12, 140.3, 132.1, 130.8, 128.8, 127.9, 62.9, 50.9, 45.9, 44.7, 37.8, 34.4, 26.3, 24.3, 21.2, 20.7, 11.6.

(c) Conversion of isobornyl aniline (28) into N-isobornyl-N-methyl aniline (30): To the isobornyl aniline (2.29 g, 10 mmol) in dry ether (30 mL), butyllithium (12 mmol, 12 mL) was added at 10-15°C and the mixture was stirred further for 1 h at r.t. The reaction mixture was refluxed for 2 h, cooled to 0°C. Methyl iodide (3 mL, 50 mmol) was added and the contents were stirred further for 4 h at r.t. Excess BuLi was destroyed with water-methanol (10 mL V/V) and extracted with ether (2x30 mL). The combined organic layer was washed with saturated NaCl solution, dried (MgSO$_4$) and the solvent was evaporated. The residue was distilled to isolate N-methyl-N-isobornyl aniline. The product was purified by column chromatography on a silica gel column (hexane as eluent) and distilled to yield pure amine (30), (1.82 g, 75%, bp.120°C/1.5 mm), $\left[\alpha\right]_D^{20} = -22$ (C6, EtOH).

IR (neat) $\nu_{\text{max}}$: 1590, 1480 cm$^{-1}$.

$^1$H NMR (100 MHz, CDCl$_3$): $\delta$ ppm 7.88-8.6 (m,5H), 4.4 (t,1H), 3.72 (s,3H), 2.64 (m,1H), 2.28 (m,6H), 2.0 (s,3H), 1.88 (s,6H).
Hydroboration of 1-Methyl-1-cyclohexene with NaBH₄/2-(6'-methoxy-2'-naphthalene) propionic acid (11) system

To a stirred suspension of NaBH₄ (0.8 g, 20 mmol) in dry THF (40 mL) the carboxylic acid (11) (4.6 g, 20 mmol) in THF (20 mL) was slowly added at 0°C under nitrogen atmosphere. The mixture was stirred at r.t. for 1 h and 1-methyl-1-cyclohexene (1.92 g, 20 mmol) was added. The contents were stirred for 14 h at r.t. The excess hydride was destroyed by adding water (2 mL) and the organoborane was oxidised with H₂O₂ (16%, 25 mL) and 3N NaOH (20 mL). The organic layer was separated and the aqueous layer was extracted with ether (2x30 mL). The combined organic extract was washed with brine, dried (MgSO₄) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methylcyclohexanol. The product was further purified by distillation under reduced pressure. Yield: 1.52 g, 68%, bp. 65°C/10 mm, lit.¹⁰, bp. 166°C/760 mm, [α]D²⁰ = -1.06 (C2.83, CH₃OH) [α]D²⁰ = +43.1 (C1, MeOH) (maximum reported value).

IR (neat) Vmax : 3500-3200, 1440, 1050, 900, 790 cm⁻¹.

¹³C NMR (25.0 MHz, CDCl₃) : 6 ppm 153.5, 128.7, 120.1, 114.0, 68.2, 50.4, 46.8, 44.8, 40.4, 37.2, 35.9, 27.3, 21.3, 20.4, 13.5.
Hydroboration of 2,3-dihydrofuran with NaBH₄/2-(6'-methoxy 2'-naphthalene)-propionic acid system

The acyloxyborohydride species was prepared at 0°C by addition of carboxylic acid CH₆(4.6 g, 20 mmol) in THF (20 mL) to a stirred suspension of NaBH₄ (0.8 g, 20 mmol) in dry THF (40 mL). The reaction mixture was stirred at r.t. for 1 h. 2,3-Dihydrofuran (1.4 g, 20 mmol) was added and the contents were further stirred for 12 h at r.t. The excess hydride was destroyed with water (1 mL) and oxidation was carried out with H₂O₂/NaOH. The reaction mixture was adjusted to pH 5, with 6N HCl and extracted with ether (3x30 mL). The organic extract was washed with water (2x10 mL) and the combined aqueous layer was neutralized to pH 8 with 5N NaOH. From the organic layer carboxylic acid was recovered. The aqueous layer was saturated with anhydrous K₂CO₃ (~40-50 gms) and extracted with ether (3x40 mL). It was dried over anhydrous MgSO₄, the solvent was evaporated and the residue was chromatographed on a silica gel column (hexane/ether as eluent) to isolate 3-hydroxytetrahydrofuran. The chromatographed alcohol was distilled under reduced pressure to afford pure 3-hydroxy tetrahydrofuran, yield, 1.23 g, 70%, bp.70°C/10 mm, lit. bp.80°C/15 mm, [α]D = -1.6 (C2.5, CH₃OH), lit. [α]D = -17.3 (C2.4, CH₃OH) (maximum reported value).

IR (neat) ν_max: 3450, 2940, 2878, 1441, 1272, 1120, 1065 cm⁻¹.

¹H NMR (100 MHz, CDCl₃): 6 ppm 4.3 (m,1H), 4.0 (m,2H), 3.75 (d,2H), 1.92 (m,2H).

¹³C NMR (25.0 MHz, CDCl₃): 6 ppm 75.3, 71.3, 66.8, 55.3.
Hydroboration of 1-methyl-1-cyclohexene with cis-myrtanic acid/NaBH₄ system

To a stirred suspension of NaBH₄ (0.4 g, 10 mmol) in THF (35 mL) myrtanic acid (12) (1.6 g, 10 mmol) in THF (10 mL) was slowly added at 0°C under nitrogen atmosphere. The mixture was stirred for 1 h at r.t. and 1-methyl-1-cyclohexane (0.96 g, 10 mmol) was added. The contents were stirred for 24 h at r.t. The excess hydride was destroyed by addition of water (2 mL) and it was oxidised with H₂O₂/NaOH. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extract was washed with brine, dried (MgSO₄) and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methyl cyclohexanol (0.68, 60%). It was further purified by distillation under reduced pressure, bp. 78°C/20 mm, lit.⁶⁰, bp. 166°C/760 mm, [α]²⁰_D = +1.819 (C₂H₄, CH₃OH), lit.⁵² [α]⁵²_D = +43.1 (C₂H₃OH) (maximum reported value).

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

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

Flydroboration of 1-methyl cyclohexene with Li BH₄/cis-myrtanic acid system

Lithiumborohydride was prepared in situ in THF following a reported
procedure by refluxing a mixture of lithium bromide (1.1 g, 11 mmol) and \( \text{NaBH}_4 \) (0.440 g, 11 mmol) in THF for 16 h in nitrogen atmosphere. cis-Myrtanic acid (12) (1.6 g, 10 mmol) in THF (10 mL) was carefully added at 0°C and stirred further for 1 h at r.t. 1-Methyl-1-cyclohexene (0.96 g, 10 mmol) was added and the mixture was stirred for 24 h at r.t. The excess hydride was destroyed with water (1.5 mL) and the organoborane was oxidised with \( \text{H}_2\text{O}_2/\text{NaOH} \). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with brine, dried (\( \text{MgSO}_4 \)) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methylcyclohexanol (0.6 g, 53%). The product was further purified by distillation under reduced pressure, bp.64°C/10 mm, lit. 60 bp.166°C/60 mm, \( [\alpha]_D^{20} = +2.08 (\text{C}_2.4, \text{CH}_3\text{OH}) \), lit. 52 \( [\alpha]_D^{20} = 43.1 (\text{C}_1, \text{CH}_3\text{OH}) \). The spectral data were identical with the data reported previously.

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

**Hydroboration of 2,3-dihydrofuran with cis-myrtanic acid/NaBH\(_4\) system**

To a stirred suspension of \( \text{NaBH}_4 \) (0.8 g, 20 mmol) in dry THF (40 mL), myrtanic acid (3.36 g, 20 mmol) was slowly added at 0°C under nitrogen atmosphere and the mixture was stirred for 1 h at r.t. 2,3-Dihydrofuran (1.4 g, 20 mmol) was added and the mixture was stirred further for 12 h. The excess hydride was destroyed by careful addition of water.
(1 mL) and the organoborane was oxidised with \( \text{H}_2\text{O}_2/\text{NaOH} \). It was acidified to pH 5 with 6N HCl and extracted with ether (3x30 mL). The ether extract was washed with water (2x10 mL) and the combined aqueous layer was neutralized to pH 8 with 5N NaOH and saturated with anhydrous \( \text{K}_2\text{CO}_3 \) (50 g). It was extracted with ether (3x40 mL), dried (\( \text{MgSO}_4 \)) and the solvent was evaporated. The residue was chromatographed on a silica gel column (hexane/ether as eluent) and the product was distilled under reduced pressure to isolate pure 3-hydroxytetrahydrofuran, yield: 1.18 g, 68%, bp.70°C/10 mm, lit. pp.80°C/15 mm, \([\alpha]_D^{25} = -1.762 (\text{C}2.832, \text{CH}_3\text{OH})\), lit. \([\alpha]_D^{54} = -17.3 (\text{C}2.4, \text{MeOH})\).

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

**Reaction of NaBH\(_4\) (10 mmol)/cis-myrtnic acid (10 mmol) with \( \text{Ph}_3\text{P} \)**

To a freshly prepared suspension of NaBH\(_4\) (2.5 mmol) and myrtnic acid (2.5 mmol) in THF (25 mL) \( \text{Ph}_3\text{P} \) (3.5 mmol) in THF (5 mL) was added and the mixture was stirred for 24 h at r.t. To the reaction mixture water (5 mL) was added. Work up (Chapter 1) and chromatography of the residue over a silica gel column (hexane/chloroform as eluent) gave 0.65 g (95%) of triphenylphosphineborane. The spectral data of this product were identical to the data reported in Chapter 1. Mp.186°C, lit. mp.189°C.
Hydroboration of 1-methyl-1-cyclohexene with borane-N,N-dibenzyl-α-methylbenzylamine complex (33)

Diborane (12.5 mmol) generated using I$_2$ (12.5 mmol) and NaBH$_4$ in diglyme (25 mmol) was bubbled through N,N-dibenzyl α-methylbenzylamine (3.07 g, 10 mmol) in dry benzene (40 mL) at 5 to 10°C. The amine borane slurry was brought to r.t. and flushed with dry nitrogen to remove traces of diborane gas above the benzene solution. 1-Methyl-1-cyclohexene (0.96 g, 10 mmol) was injected and the mixture was stirred at r.t. for 24 h. The contents were brought to 0°C and ethanol (2 mL) and THF (35 mL) were added. The mixture was oxidised with $\text{H}_2\text{O}_2$ (16%, 20 mL) and 3N NaOH (10 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with 3N HCl (3x10 mL) to separate the amine. The organic extract was washed with NaHCO$_3$ (10%) solution, brine solution, dried (MgSO$_4$) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate pure trans-2-methylcyclohexanol. The product was distilled under reduced pressure 0.62 g, 55%/ bp.70°C/10 mm, lit. 60° bp.166°C/760 mm and optical rotation was measured, $[\alpha]_D^{25} = +1.08$(C3.7, CH$_3$OH), lit.$[\alpha]_D^{25} = 43.1$(C1, CH$_3$OH).52 The spectral data were identical to the data for the sample obtained previously.

Hydroboration of 2,3-dihydrofuran with borane-N,N-dibenzyl-α-methylbenzylamine complex (33)

Amine borane (20 mmol) in benzene was prepared as described above and 2,3-dihydrofuran (1.4 g, 20 mmol) was injected. It was stirred at
r.t. for 12 h, cooled to 0°C and ethanol (2 mL) and THF (35 mL) were added. The organoborane was oxidised with \( \text{H}_2\text{O}_2 \) (16%, 25 mL) and 3N NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with water (2x10 mL) and the combined aqueous layer was saturated with anhydrous \( \text{K}_2\text{CO}_3 \) and extracted with ether (3x40 mL). It was dried (\( \text{MgSO}_4 \)) and the solvent was removed. The residue was chromatographed on a silica gel column (hexane/ether as eluent) to isolate pure 3-hydroxy tetrahydrofuran. The alcohol was distilled under reduced pressure and optical rotation was measured. Yield, 1.18 g, 67%, bp. 68°C/15 mm), \([\alpha]_D^{20} = -1.6(\text{C}2.5, \text{CH}_3\text{OH})\), lit. \([\alpha]_D^{20} = -17.3(\text{C}2.4, \text{CH}_3\text{OH})\). The spectral data were identical to the data of the sample obtained previously with other borane Lewis base systems.

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

Diborane (12.5 mmol), generated using \( \text{I}_2 \) (12.5 mmol) and \( \text{NaBH}_4 \) (25 mmol) system was bubbled through N-benzyl-N-isopropyl-α-methylbenzylamine (2.53 g, 10 mmol) in dry benzene (40 mL) at 5-10°C. The mixture was stirred for 30 minutes at r.t. and diborane gas (if any) present above the solution was driven off by a stream of dry nitrogen and 1-methyl-1-cyclohexene (0.96 g, 10 mmol) was added. The mixture was stirred at r.t. for 24 h. The contents were brought to 0°C and 2N HCl (1.5 mL) was carefully added and stirred for 30 minutes at r.t. 3N NaOH (10 mL) and THF (35 mL) were added and the organoborane was oxidised with \( \text{H}_2\text{O}_2 \) (16%, 25 mL). The aqueous and organic layers were separated and the...
aqueous layer was extracted with ether (3x25 mL). The combined organic layer was treated with 6N HCl (3x10 mL) and the amine was regenerated from the aqueous layer after neutralization with 5N NaOH (phenolphthalein indicator). The ether layer was washed with saturated aqueous NaHCO$_3$ (10 mL) solution, brine solution (10 mL), dried (MgSO$_4$) and the solvent was removed. The residue was chromatographed on a silica gel column using hexane/chloroform as eluent to isolate trans-2-methylcyclohexanol. The alcohol was purified further by distillation under reduced pressure yield. 0.7 g, 62%, bp.68°C/15 mm, lit. 60, bp.166°C/760 mm, [α]$^2_D$ = -1.5 (C3.33, CH$_3$OH), lit. 52 [α]$^2_D$ = +43.1(C1, CH$_3$ OH). The spectral data were identical to the data for the sample obtained previously.

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

Diborane prepared using I$_2$ (12.5 mmol) and NaBH$_4$ (25 mmol) in diglyme was passed through the amine (2.53 g, 10 mmol) in dry benzene at 5-10°C. The contents were flushed with dry nitrogen. 1-Phenyl-1-cyclopentene (1.44 g, 10 mmol) was injected and the contents were stirred at r.t. for 48 h. The mixture was cooled to 0°C and 2N HCl (2 mL) was carefully added and stirred at r.t. for 30 minutes. 3N NaOH (15 mL) THF (35 mL) were added and the organoborane was oxidised with H$_2$O$_2$ (16%, 25 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic layer was treated with 6N HCl (3x10 mL) and the amine was recovered from amine hydrochloride. The ether layer was washed with saturated aqueous sodium-bicarbonate (10 mL), brine (15 mL) and dried over anhydrous MgSO$_4$. The
solvent was removed and the residue was chromatographed on a silica gel column (hexane/chloroform as eluent) to isolate trans-2-phenylcyclopentanol. The alcohol was purified further by distillation under reduced pressure. Yield. 0.97 g, 60%, bp.87°C/1 mm; lit. bp.129-131°/6 mm, \([\alpha]_D^{20} = -0.84(C8.33, \cdot \text{EtOH})\), lit. \([\alpha]_D^{20} = + 71.1(C11.9, \text{EtOH})\) (maximum reported value).

\(\text{C NMR (25.0 MHz, CDCl}_3\): 6 ppm 144.1, 128.7, 127.8, 126.5, 80.3, 54.4, 34.3, 33.2, 32.1.}

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

Borane-N-benzyl-N-isopropyl-α-methylbenzylamine complex (20 mmol) was prepared as given in the above experiment. 2,3-Dihydrofuran (1.4 g, 20 mmol) was added and the mixture was stirred at r.t. for 12 h. Water (1 ml) and 2N HCl (1 mL) were added followed by the addition of 3N NaOH (10 mL) and THF (35 mL). Oxidation was carried out using \(\text{H}_2\text{O}_2\) (16%, 20 mL). As the 3-hydroxytetrahydrofuran is highly soluble in water, the workup was carried out after saturation of the contents with anhydrous \(\text{K}_2\text{CO}_3\). The contents were extracted with ether (4x30 mL). The combined organic extract was dried (MgSO\(_4\)) and the solvent was removed. The alcohol was distilled out under reduced pressure leaving the amine residue. The distilled alcohol was chromatographed on a silica gel column using hexane/ether as eluent to isolate pure 3-hydroxytetrahydrofuran. The chromatographed alcohol was distilled once again under reduced pressure to isolate pure 3-hydroxytetrahydrofuran, yield: 1.2 g, 69%, bp.70°C/8 mm,
The spectral data were identical with the data of the sample obtained previously with other borane-Lewis base systems.

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

Diborane generated using $\text{I}_2$ (12.5 mmol) and $\text{NaBH}_4$ (25 mmol) was bubbled through $\text{N-methyl-N-isoborHylaniline}$ (2.43 g, 10 mmol) in dry benzene (40 mL) at 5-10°C. The diborane gas (if any) present above the benzene solution was driven off by a stream of dry nitrogen. 1-Methyl-1-cyclohexene (0.96 g, 10 mmol) was added and the mixture was stirred for 24 h at r.t. Excess hydride was decomposed by addition of water (1 mL) and 2N HCl (2 mL). The mixture was further stirred for 30 minutes at r.t. 3N NaOH (10 mL) and THF (30 mL) were added and the organoborane was oxidised with $\text{H}_2\text{O}_2$ (16%, 20 mL). The organic layer was separated and the aqueous layer was extracted with ether (3x25 mL). The combined organic extract was washed with 5N HCl (3x10 mL) to separate the amine as its hydrochloride salt from which the amine was regenerated using 3N NaOH (phenolphthalein indicator). The ether extract was washed with saturated NaHCO$_3$ (15 mL), brine (15 mL) and dried over anhydrous MgSO$_4$. The solvent was removed and the residue was chromatographed on a silica gel column (hexane/chloroform as eluent) to isolate trans-2-methylcyclohexanol. The alcohol was distilled under reduced pressure to isolate pure trans-2-methylcyclohexanol, yield: 0.8 g, 70%, bp.65°C/10 mm, lit.$^6$ bp.166°C/760 mm, $[\alpha]_D^2 = -1.66(C3, \text{CH OH})$, lit.$-[\alpha]_D^2 = +43.1^\circ(C1,\text{CH OH})$. The spectral data were identical to the data of the sample obtained previously in reactions with other BH -Lewis base complexes.
Hydroboration of 1-phenyl-1-cyclopentene using borane-N-isobornyl-N-methyl aniline complex (31)

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

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

Diborane generated using I$_2$ (25 mmol) and NaBH$_4$ (50 mmol) was bubbled through N-isobornyl-N-methylaniline (4.86 g, 20 mmol) in dry benzene (40 mL) at 5–10°C. The diborane gas (if any) present above the benzene solution was driven off by a stream of dry nitrogen. 2,3-Dihydrofuran (1.4 g, 20 mmol) was added and the mixture was stirred for 4 h at r.t. 2N HCl (2 mL) was carefully added and the contents were stirred for 30 min at r.t. 3N NaOH (15 mL) and THF (35 mL) were added and oxidation was carried out using H$_2$O$_2$ (16%, 20 mL). The contents were extracted with ether (3x25 mL) and the combined ether extract was washed with
water (10 mL) and the combined aqueous layer was saturated with anhydrous K₂CO₃ (50-60 g). The contents were extracted with ether (3x40 mL), dried (MgSO₄) and the solvent was removed. The alcohol was distilled under reduced pressure and passed through a silica gel column (hexane/ether eluent) to isolate pure 3-hydroxytetrahydrofuran. The chromatographed alcohol was again distilled under reduced pressure to isolate pure alcohol.

Yield: 1.3 g, 76%, bp.70°C/10 mm, [α]D²⁰ = -3.3 (C3, MeOH), lit. bp.80°C/15 mm, [α]D²⁰ = -17.3 (C2.4, CH₃OH). The spectral data were identical to the data obtained previously in reactions with other borane-Lewis base complexes.

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

The amine borane complex (20 mmol) was prepared following the procedure outlined in the previous experiment. 3,4-Dihydro-2H-pyran (1.68 g, 20 mmol) was added and the reaction mixture was stirred for 4 h at r.t. The oxidation and workup were carried as in the above experiment and the alcohol isolated was distilled under reduced pressure, chromatographed on a silica gel column (hexane/ether eluent) and again distilled under reduced pressure to isolate pure 3-hydroxytetrahydropyran.

Yield: 1.4 g, 68%, bp.70°C/8 mm Hg, [α]D²⁰ = -1.24 (C4, MeOH), lit. [α] = -11.8 (neat) (maximum reported value).

IR (neat) νmax: 3380, 2930, 2840, 1441, 1048 cm⁻¹.

**¹H NMR (100 MHz, CDCl₃):** 63.25-3.9 (m, 5H), 3.1 (s, 1H), 1.65-2.15 (m, 4H).

**¹³C NMR (25.0 MHz, CDCl₃):** 6 ppm 72.9, 67.9, 65.7, 31.5, 23.3.
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