Hydroboration-oxidation of styrene, 2,3 dihydrofuran and quadricyclene dimethylester promoted by Wilkinson's catalyst

Pingyun Feng

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HYDROBORATION-OXIDATION OF STYRENE, 2,3-DIHYDROFURAN
AND QUADRICYCLENE DIMETHYLESTER PROMOTED
BY WILKINSON’S CATALYST

PINGYUN FENG

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THESIS
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REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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Hydroboration-oxidation of Styrene, 2,3-Dihydrofuran and Quadracyclene

Dimethylester Promoted by Wilkinson's Catalyst

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Date: Nov. 25, 1991

Pingyun Feng
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Introduction

The remarkable facile addition of diborane in ether solvents to olefins\(^1\), dienes\(^2\) and acetylenes\(^3\) at room temperature was discovered in 1956 by Herbert C. Brown.\(^4\) The reaction, hydroboration, makes readily available a wide variety of organoboranes which are proving to be exceedingly useful in organic synthesis. A wide variety of olefins, amines, ketones and particularly, alcohols of desired structure and stereochemistry have been prepared by the hydroboration - oxidation sequence.\(^5\)

Preliminary observations indicated that the addition to an unsymmetrical olefin proceeds to place the boron atom on the less substituted of the two carbon atoms forming the double bond\(^6\). Since the organoborane is readily converted to the corresponding alcohol by oxidation with alkaline hydrogen peroxide, hydroboration provides a simple convenient synthetic route for the anti-Markovinikoff hydration of olefins.

Recently, several groups (RIT, Harvard, Rice, Germany) have applied transition metal catalysis to hydroboration resulting in rate enhancements for less reactive borane reagents as well as complementary or improved regio- and stereochemistry. The possibility has been raised that transition metal catalysis might significantly extend the utility of the hydroboration reaction.\(^7\)

---

4 Purdue University, *Nobel Prize Laureate* 1979.
Borane, BH₃, is an avid electron pair acceptor because only a sextet of valence electrons is present at boron in the monomeric molecule. The pure neat material exists as a dimer. Diborane can be generated in situ from sodium borohydride and boron trifluoride. In aprotic solvents which act as electron pair donors such as ethers, tertiary amines, and sulfides, tetrahydrofuran, we have known that diborane forms stable Lewis acid-Lewis base complexes.

\[ \text{B}_2\text{H}_6 \rightarrow 2\text{BH}_3 \]

Solutions of BH₃·THF complex in tetrahydrofuran are commercially available. An alternative commercially available borane reagent is the borane-dimethyl sulfide complex. Both hydroboration reagents BH₃·THF and BH₃·SMe₂ react rapidly with unsaturated carbon-carbon bonds and do not require metal or other catalysis.

**Mechanism of Hydroboration-Oxidation**

Hydroboration is not only stereospecific (syn addition) but also regioselective; steric and electronic factors control the regioselectivity: the boron atom binds to the less hindered (less substituted) carbon, and the hydrogen atom binds to the more substituted carbon.

Because the \( \pi \) bond in a carbon-carbon double bond is electron rich and borane is electron poor, it is reasonable to formulate an initial Lewis acid-base complex, requiring the participation of the empty \( p \) orbital on BH₃, as in the borane-

---

ether complex. Subsequently, one of the hydrogens is transferred by means of a four
centered transition state to one of the alkene carbons. All three B-H bonds are reactive
in the same way and therefore trialkylboranes are formed. Then the trialkylboranes are
oxidized with basic aqueous hydrogen peroxide; the highly nucleophilic and electron-
rich hydroperoxide ion attacks the electron-poor boron atom. The resulting
intermediate undergoes a rearrangement in which an alkyl group migrates with its
electron pair keeping the same configuration to the neighboring oxygen, displacing a
hydroxide group in this process. Although the hydroxide ion is usually a poor leaving
group, the reactive O-O bond and the simple intermolecular nature of this reaction
allows it to leave. The initial product R₂BOR undergoes further similar oxidations to a
trialkyl borate (RO)₃B which is hydrolyzed by the basic aqueous medium to the alcohol
(ROH) and sodium borate.⁹.

This mechanism is shown below:

![Mechanism Diagram]

---

In addition to borane reagent, there are other hydroboration reagents which are available such as disiamylborane, 9 - BBN, catecholborane, and chloroborane. One of the more interesting is catecholborane (1,3,2-benziodioxaborole).

**Catecholborane**

Catecholborane (CB) is readily available from the reaction of catechol with borane complex in THF\textsuperscript{10}:

In catecholborane, the boron atom is part of a planar five-membered ring. It has unique structural features and is only a mild hydroboration agent due to competing electron donation from the adjacent oxygen in the five-membered ring. It is a much weaker Lewis acid than the borane complex. Hydroboration with catecholborane is usually very slow at room temperature, while at high temperature the hydroboration proceeds at much more satisfactory rate. It hydroborates olefins at 100°C.\textsuperscript{11} It reacts with acetylenes at 70°C.\textsuperscript{12}

Several groups have now applied transition-metal catalysis to hydroboration resulting in rate enhancement for less reactive boron reagents, such as


catecholborane\textsuperscript{13}. For example, without a catalyst, two above reactions require temperature of 100°C and 70°C respectively; however, they can occur without difficulty at room temperature in the presence of a catalyst. Mannig and Noth have found that it is possible to activate the carbon-carbon double bonds of olefins so strongly that they are preferentially hydroborated even in the presence of the much more reactive keto group.\textsuperscript{14} For example, without a catalyst, 5-hexen-2-one reacts with catecholborane (1) rapidly and quantitatively give 2-(1-methyl-4-pentyloxy)-1,3,2-benzodioxaborole (2), whereas in the presence of Wilkinson’s catalyst, RhCl(PPh\textsubscript{3})\textsubscript{3}, the ketone (3) is preferentially formed:

![Reaction Diagram]

In addition to Wilkinson's catalyst, the complexes [RhCl(CO){P(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}}\textsubscript{2}], [RhCl(CO){As(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}}\textsubscript{2}], and [RhCl(cod)]\textsubscript{2} (cod = 1,5-cyclooctadiene) are also suitable as catalysts for hydroboration with CB, but complexes of platium, palladium, iridium, and cobalt exhibit no or only minor catalytic effects.\textsuperscript{14} We use Wilkinson's catalyst in our experiments, the reagent that is convenient because it is stable in air and yet exhibits high reactivity.

\textsuperscript{13} Ruffing, C. J. \textit{Aldrichimica Acta}, 1989, 22, 80.
Like the keto group, other function groups such as hydroxy-, cyano-, nitro-, chloro-, azo-, ether, ester, and carboxylic acid groups are also not effected by Wilkinson’s catalyst under these conditions.

**Wilkinson’s Catalyst**

Two independent reports\(^\text{15}\) appeared in 1965 that the complex chlorotris(triphenylphosphine)rhodium(1), \(\text{RhCl(PPh}_3\text{)}_3\), in organic solvents is an active catalyst for reduction of alkynes and alkenes at ambient temperature and atmospheric pressure. This compound has subsequently become known as Wilkinson’s catalyst. Its X-ray structure\(^\text{16}\) is shown below (Fig. 1).

---

Figure 1. X-ray structure of Wilkinson's catalyst:

In this structure, RhCl(PPh₃)₃ has 16 electrons in Rh valence shell, the dimer or the 5-co-ordinate complex of RhCl(PPh₃)₄ does not form during preparation due to the excess of triphenylphosphine in the solution and the steric factor (large phenyl groups). Actually, the dimer can be readily converted to RhCl(PPh₃)₃ by heating with a 10 molar excess of triphenylphosphine in ethanol.¹⁷

The tristriphenylphosphine halide dissociates in solution as shown:

\[
\text{RhCl(PPh₃)₃} \xrightarrow{\text{Ethanol}} \text{RhCl(PPh₃)₂ + PPh₃}
\]

The essential point is that RhCl(PPh₃)₂ has vacant coordination sites which can be occupied either by weakly bound solvent molecules or by other ligand atoms. The existence of vacant sites is essential to the catalytic activity of RhCl(PPh₃)₂ as we shall see below from the mechanism.¹⁸

**Mechanism of Hydrogenation with Wilkinson's Catalyst**

The mechanism of hydrogenation includes three major steps: oxidative-addition, insertion, and reductive-elimination.

**Figure 2 : Mechanism of Hydrogenation with Wilkinson's Catalyst**

The mechanism of hydroboration promoted by Wilkinson's catalyst is not yet completely understood. A mechanism similar to hydrogenation has been suggested. We will discuss this in more detail in Results and Discussion section.

**Hydroboration - Oxidation of Styrene**

The hydroboration of simple terminal alkenes such as 1-butene, 1-pentene and 1-hexene with diborane in THF proceeds in a highly regioselective manner to give predominant addition of the boron atom to the terminal carbon atom (\( \sim 93 - 94\% \)). Only a minor amount of addition to give the secondary alkyl boron product is observed (\( \sim 6 - 7\% \))\(^{19}\). These results correspond to a predomination of anti-Markovnikov

---

\(^{19}\) Brown, H. C. and Zweifel, G. *J. Org. Chem.*, 1960, 82, 4708
addition. The hydroboration of terminal alkenes with an alkyl substituent at the 2-position, such as isobutylene, proceeds to give almost exclusively (99%) the terminal hydroboration products. On the other hand, the hydroboration of another terminal alkene, styrene, results in only 81% of the boron atom entering the terminal position, reflecting the significant non-steric directive influence of the phenyl substituent.

It became of interest to investigate such directive effects in the hydroboration of alkenes with catecholborane. In 1975 H. C. Brown and S. K. Gupta investigated such directive effects in the hydroboration of styrene with catecholborane at 100°C. The results indicated that catecholborane is more selective than borane in placing the boron atom preferentially at the less hindered carbon atom. For example, they used 1-decene, 1-diisobutylene, norbornene and styrene for their experiments. After the standard hydroboration with catecholborane (10% excess) at 100°C, the product organoborane was then oxidized with alkaline hydrogen peroxide. The following results were obtained:

CH₃(CH₂)₇CH=CH₂

CH₃(CH₂)₇CH=C(CH₃)₂

2% 98%

CH₃CH=C(CH₃)₂

CH₃CH=C(CH₃)₂

1% 99%

The above results indicate that catacholborane is somewhat more selective than borane in placing the borane in less hindered carbon atom. Even the directive effect of the styrene changed from 80% with borane to 92% with catacholborane.

It was of greater interest to investigate hydroboration of styrene and other alkenes with Wilkinson's catalyst. Some very interesting results have been obtained and we will discuss them in more detail below.

Hydroboration of Heterocyclic Olefins

Heterocyclic derivatives introduce some major differences in hydroboration-organoborane reactions. First, the heterocyclic atom plays a major role in controlling the direction of hydroboration of double (and triple) bonds. Secondly, the presence of a boron atom $\beta$- to the heteroatom can result in facile ring opening. For example:

---

Ring opening can be thought of as a elimination from the intermediate in the reaction below. The extent of elimination depends upon a number of factors, such as leaving group (X), temperature and solvent.23

If X is a good leaving group, such as Cl, or OAc, the elimination occurs rapidly.24,25,26 Elimination is minimized for poor leaving groups, such as OR and OAr. It was observed that such hydroboration can proceed with a remarkable

\[ \text{RCH} = \text{CHX} + \text{B-H} \rightarrow \text{RCHCH}_2\text{X} \rightarrow \text{RCH} = \text{CH}_2 + \text{B} - \text{X} \]

---

regioselectivity, placing essentially all of the boron atom at the β-position\textsuperscript{27,28}. For example, 1-ethoxy-2-methyl-1-propene yields 88% 1-ethoxy-2-methyl 2-propanol upon hydroboration-oxidation, indicating the preference of the boron atom for a β-carbon atom even though it is tertiary.\textsuperscript{29}

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\beta \quad \text{CH}_3\text{C} &= \text{CHOCH}_2\text{C}_2\text{H}_5 & \text{CH}_3 \quad \text{NaOH, } \text{H}_2\text{O}_2 \\
\alpha & \quad \beta \\
\text{CH}_3 & \quad \text{CH}_3\text{C} & \quad \text{CHOCH}_2\text{C}_2\text{H}_5 \\
\text{B} & \quad \text{B} \quad \text{OH} \\
\text{CH}_3\text{CCH}_2\text{OC}_2\text{H}_5 & \quad \text{CH}_3\text{CCH}_2\text{OC}_2\text{H}_5
\end{align*}
\]

Although there have been individual reports on the hydroboration of heterocyclic olefins containing oxygen,\textsuperscript{30} sulfur,\textsuperscript{31} and nitrogen\textsuperscript{32,33}, clear understanding of the optimum conditions required for clean and efficient hydroboration of heterocyclic olefins is still lacking.

\textsuperscript{27} Pasto, D. J. and Cumbo, C. C., \textit{J. Am. Chem. Soc.} 1964, 86, 4343.
So it became of interest for us to study the hydroboration of heterocyclic olefins and hydroboration of heterocyclic olefins promoted by Wilkinson's catalyst. We chose 2,3-dihydrofuran for our study.

**Hydroboration of a Cyclopropane Ring in the Quadricyclene System**

Many chemical reactions of quadricyclene system have been studied.\(^{34,35,36}\) Hydroboration-oxidation of the cyclopropane ring of this system is a very new area. The cleavage of cyclopropane in norcarane by neat diborane has been reported by Rickborn and Wood.\(^{37}\) The reaction is quite regioselective and the products were those involving boron addition to the least-substituted carbon, and hydrogen to the most-substituted carbon (Markovnikov addition). Some examples are given here.


This reaction is a highly regioselctive cleavage process with only 5% of cyclohexanol formed due to the cleavage of the internal bond.

We plan to use quadricyclene dimethyl ester for our study. Some chemical properties of this system have been studied. Early work clearly describes the
propensity for C5 - C6 or C1 - C7 (shown in compound 4) bond cleavage in this system.\textsuperscript{38}

For example, addition of bromine to this system has been reported to give (6) and (5),

\textsuperscript{38} Cristol, J., Harrington, J. K., Morrill, T. C. and greenwald, B. E., \textit{J. Org. Chem.}, 1971, 36, 2773
The C-3 carboxylic group was shown to be endo by the ready formation of lactone (6). Structure (5) with exo- Br at the secondary halide position appeared to be reasonable, as it permitted the formation of (6) by a stereochemically expected inversion process.39

Other examples such as addition of benzenesulfonyl chloride to quadricyclene dicarboxylic acid and dimethyl ester also revealed the C5-C6 (C1 - C7) bond cleavage propensity in this system.40

Experimental

Nuclear magnetic resonance spectra were obtained using either a Bruker FT-NMR spectrometer (200 MHz); or a G. E. QE (300 MHz). Tetramethylsilane (TMS) was used as a reference standard, and all chemical shifts were recorded in δ units (ppm) related to TMS (δ = 0.00 ppm). Multiplicity notations are: s, singlet; d, doublet; t, triplet.

The GC Mass Spectrometric Analyses were performed on a Hewlett Packard 5995 GC/MS with a Supeleco fused silica capillary SPB-1 non-polar column (30 m, 0.32 mm ID, 1.0 mm df). Helium was used as the carrier gas.

Capillary Gas Chromatography spectra was performed on a Hewlett Packard 5890A with a 50m x 0.32mm x 0.25 μm HP-1 (cross linked methyl silicone gum) non-polar column. Helium was used as the carrier gas. Flame ionization detector was used.

Melting points were determined using a Mel-Temp® apparatus from Lab Specialties Incorporation, and required no correction as per calibration by benzoic acid.

Photochemical reactions were carried out using a 1-liter Pyrex® photochemical reaction vessel and a 450-Watt high pressure mercury vapor lamp (Englehard Hanovia, Inc.) was placed in a quartz immersion well. The quartz immersion well was placed in
the reaction jacket. The diagram of the 1-liter Pyrex® photochemical reaction vessel was shown in Figure 3.

Dry nitrogen was prepared by passing reagent grade nitrogen from Linde Air Products through Fieser's reagent (see experiment 3) followed by passage through concentrated sulfuric acid and anhydrous potassium hydroxide.

Chemicals and solvents were purchased from Aldrich Chemical Co., Sigma Chemical Co., Fisher, and Baker.
Hydroboration-oxidation of Styrene

All glassware was predried in an oven at 150°C overnight, assembled hot, and allowed to cool under a stream of dry, deoxygenated nitrogen. The nitrogen gas was purified by Fieser's solution, NaOH, and H₂SO₄.

A dry three-necked 250 ml flask was equipped with a magnetic stirring bar, a condenser, and a pressure-equalizing dropping funnel. After cooling down to room temperature under a stream of nitrogen, the flask was charged with 2.08 g (20 mmol) of styrene by removing the condenser and adding the styrene as quickly as possible under a blanket of nitrogen. The system was then refilled with nitrogen for several minutes, and 20 ml (20 mmol) of BH₃-THF (1.0 M THF solution) was added to the dropping funnel with a syringe. Hydroboration was achieved by the slow dropwise addition of the BH₃-THF solution to the flask. Following the addition, the colorless reaction mixture was stirred at the room temperature for 1 hour. The reaction mixture was then cooled in an ice bath and 10 ml of a 30% H₂O₂ solution and 10 ml of 3M NaOH solution was added to the reaction flask. Care was taken to maintain the solution slightly alkaline (pH ~8). The reaction was stirred for 3 hours and the reaction temperature was allowed to reach room temperature.
Then anhydrous ethyl ether (3 x 20) ml was used to extract the alcohol products. The combined ether extracts were washed with a 20 ml of saturated sodium bicarbonate solution and then 2x20 ml of distilled water; the ether layer was subsequently separated and dried over anhydrous magnesium sulfate.

The product mixture was analyzed by GC/MS spectrometry and compared with authentic sample from Aldrich.

Mass spectrum of C₆H₅CHOHCH₃ (9) : m/z 79 (100%), m/z 107 (84%), m/z 122 (28%), m/z 43 (42%), m/z 51 (30%), m/z 27 (11%). Retention time as shown on GC/MS spectra was: 1.674 min.

Mass spectrum of C₆H₅CH₂CH₂OH (8) : m/z 91 (100%), m/z 122 (28%), m/z 65 (25%), m/z 31 (10%). Retention time as shown on GC/MS spectra was: 1.782 min.

\[
\begin{align*}
\text{C₆H₅=CH} & \xrightarrow{\text{1.BH₃-THF, RT, 1h}} \text{C₆H₅-CH₂-CH₂OH} & \text{80.7}\% \\
\text{C₆H₅=CH} & \xrightarrow{\text{2.H₂O₂, NaOH}} \text{C₆H₅-CH₃} & \text{19.3}\%
\end{align*}
\]

The total yield for this reaction was 78.9%. The yield was determined by weight after evaporating solvent and multiplying by the GC percentage of products (8) and (9); GC identification was done by using authentic (Aldrich) samples of (8) and (9).
2. Preparation of Dry, Deoxygenated Nitrogen

Bottled nitrogen was bubbled through a series of traps. The first one contained Fieser’s solution\textsuperscript{44} for the adsorption of oxygen. The second one was empty to prevent crossover. The third and fourth traps contained, respectively, concentrated sulfuric acid and sodium hydroxide pellets. Those last two traps were for removal of water vapor.

3. Preparation of Fieser’s Solution\textsuperscript{44}

The solution was prepared by dissolving 20 g of potassium hydroxide in 100 ml of water and adding 2 g of sodium anthraquinone - β - sulfonate and 15 g of sodium hyposulfite (Na₂S₂O₄) to the warm solution. The mixture was stirred until a clear, blood-red solution results and this red solution was allowed to cool to room temperature. Traces of oxygen in the nitrogen were removed by passage of the gas through a trap containing this solution.

The above procedure was applied to all of our hydroboration-oxidation reactions.

4. Hydroboration-oxidation of Styrene using BH₃-THF with Wilkinson’s Catalyst

All the set-up, nitrogen, and glassware went through the same procedures as described in experiment 1.

A dry three-necked 250 ml flask was charged with 2.08 g (20 mmol) styrene. The system was then flushed with nitrogen for several minutes, and 0.04 g (~0.2% mol) Wilkinson’s catalyst was added to this reaction flask. Following that addition, 20 ml (20 mmol) BH₃-THF (1.0 M THF solution) was added to the dropping funnel with a syringe, then added dropwise to the reaction flask. The reaction mixture was stirred at the room temperature for 1 hour, cooled in an ice bath, and then 10 ml of a 30% H₂O₂ solution and 10 ml of 3M NaOH were added to the reaction mixture. Care was taken to keep the solution slightly alkaline. The reaction mixture was stirred for 3 hours and the resulting product was allowed to reach room temperature.

Extraction of the alcohol products was carried out with 3 x 20 ml of anhydrous ethyl ether. The combined ether extracts were washed with 20 ml of saturated sodium bicarbonate solution and 2 x 20 ml of distilled water. Then the ether layer was separated and dried over anhydrous magnesium sulfate.

The product mixture was analyzed by GC/MS spectrometry. Mass spectra of C₆H₅CHOHCH₃ and C₆H₅CH₂CH₂OH were same as the previous experiment. The retention times as shown on GC/MS spectra were 1.770 min for (9) and 1.902 min for (8). The mass spectra were compared with those from authentic samples from Ardrich company.
The total yield of alcohol for this reaction was 67.1%. The yield was determined by total weight of product after evaporating solvent and multiplication by the GC percentage of products (8) and (9) in the total product mixture.
5. Hydroboration-oxidation of Styrene with Catecholborane

Nitrogen and glasswares was subjected to the same procedure as described in experiment 1.

A dry three-necked 250 ml flask was equipped with magnetic stirred bar and a condenser. After cooling the system to room temperature under a nitrogen stream, 5 ml of the fresh dry THF was added to the reaction flask, the system was then flushed again with nitrogen for several minutes, and finally the flask was charged with 2.08 g (20 mmol) styrene and 2.40 g (20 mmol) of catechoborane as quickly as possible under a blanket of nitrogen. The reaction mixture was stirred at room temperature for 1 hour, cooled in an ice bath, and to this was added dropwise 10 ml of a 30% H₂O₂ solution and 10 ml of 3M NaOH solution. Care was taken to maintain the solution at a slightly alkaline pH (~ 8 ). The reaction mixture was stirred for 3 hours and the reaction mixture was allowed to reach room temperature.

Anhydrous ethyl ether (3 x 20 ml) was used to extract the alcohol products. The combined ether extracts were washed with 2 x 20 ml of saturated sodium bicarbonate solution, and 20 ml of distilled water, and then the ether layer was separated and dried over anhydrous magnesium sulfate.

The product mixture was analyzed by GC/MS spectrometry. Mass spectra of C₆H₅CHOHCH₃ and C₆H₅CH₂CH₂OH were same as the previous experiment. The retention times (GC/MS) were 1.982 min and 2.437 min respectively. And the Mass spectra were compared with authentic sample from Aldrich company.
Only 3.8% of the styrene was consumed. This result was measured by GC.
6. Hydroboration-oxidation of Styrene using Catechoborane with Wilkinson’s Catalyst

The setup, nitrogen, and all glassware went through the same procedures as described in experiment 1.

The 250 ml flask was charged with 5 ml of fresh THF and 2.08 g (20 mmol) styrene was added under a stream of nitrogen, then 2.40 g (20 mmol) of catecholborane and 0.04 g (~0.2% mol) Wilkinson’s catalyst was added to the reaction flask. The reaction mixture was stirred at the room temperature for 1 hour, cooled in an ice bath, and then 10 ml of a 30% H₂O₂ solution followed by 10 ml of 3M NaOH were added to the flask. The reaction mixture was stirred for 3 hours with cooling and the reagents was allowed to reach room temperature.

Anhydrous ethyl ether 3 x 20 ml was used to extract the alcohol products. The combined ether extracts were washed with 20 ml of saturated sodium bicarbonate solution and then 2 x 20 ml of distilled water; the ether layer was separated and dried over anhydrous magnesium sulfate. The product mixture was analyzed by GC/MS spectrometry. Mass spectra of C₆H₅CHOHCH₃ and C₆H₅CH₂CH₂OH were same as the previous experiment. The GC/MS retention times were respectively, 1.864 min and 2.026 min.

The product mixture was also analyzed by gas chromatography (HP 5890A).

The retention times for authentic samples of C₆H₅CHOHCH₃ (9) and C₆H₅CH₂CH₂OH (8) (Aldrich company) were 4.787 min and 5.084 min. The retention times for the reaction product mixture were respectively, 4.779 min and 5.078 min, clearly in good agreement with the authentic samples.
The total yield of this reaction was 71.5%. The yield was determined by the same method as in experiment 1.
If the reaction time was reduced to half an hour different results were obtained.

\[
\begin{align*}
\text{C_6H_5CH=CH}_2 & + \text{B(OH)}_2 \xrightarrow{\text{RT, 0.5 h}} \text{Wilkinson's Cata.} \\
& \text{NaOH, H}_2\text{O}_2 \\
& \begin{array}{c}
\text{C_6H_5CH(OH)CH}_3 \\
\text{C_6H_5CH(OH)CH}_2\text{OH}
\end{array} \\
& \begin{array}{r}
3.1\% \\
96.9\%
\end{array}
\end{align*}
\]

The product mixture was again analyzed by gas chromatography (HP 5890A). The retention times for standard samples of C₆H₅CHOHCH₃ and C₆H₅CH₂CH₂OH (from Ardrich company) were 4.787 min and 5.084 min. The retention times for reaction product mixture were respectively, 4.776 min and 5.075 min. The yield of this reaction was 59.1%. The work up and yield determination were same as in previous experiment.
**Hydroboration-oxidation of 2,3-Dihydrofuran**

**Hydroboration-oxidation of 2, 3-Dihydrofuran with BH₃-THF**

All the glassware was predried in an oven at 150°C for 24 hours, assembled hot, and allowed to cool under a stream of nitrogen (purified by Fieser’s solution, NaOH, H₂SO₄).

A 250 ml flask was equipped with a magnetic stirring bar, a reflux condenser, and pressure-equalizing dropping funnel. After cooling to room temperature under a nitrogen stream, the reaction flask was charged with 10.5 g (150 mmol) or 3.5 g (50 mmol) of 2,3-dihydrofuran by removing the condenser and adding the 2,3-dihydrofuran as quickly as possible under a blanket of nitrogen; the system was then flushed again with nitrogen for several minutes, then 50 ml (50 mmol) of BH₃-THF complex (1.0 M THF solution) was added to the dropping funnel with a syringe.

Hydroboration was achieved by the slow dropwise addition of the BH₃-THF solution to the flask. Following addition, the clear, colorless reaction mixture was stirred at room temperature for 2 hours to complete the reaction. At this point 50 ml of 3M aqueous sodium hydroxide was added to the reaction mixture. Then 25 ml of 30% aqueous hydrogen peroxide was introduced into the dropping funnel and added dropwise to the stirred reaction mixture at a rate such that the temperature of the reaction mixture did not exceed approximately 50°C. The reaction mixture was stirred at room temperature overnight.

Anhydrous ethyl ether (3 x 50 ml) was used to extract the products, and the combined ether extracts were dried over anhydrous MgSO₄. The ether was evaporated...
resulting in 10.51 g of crude product. GC/MS spectroscopy results are shown in tables 1 and 2 below.

\[
\text{BH}_3 \text{THF} \quad \xrightarrow{\text{H}_2\text{O}_2, \text{NaOH}} \quad \text{OH} \\
\text{OH} \\
\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH} \quad + \quad \text{HOCH}_2\text{CH}_2\text{CHCH}_3 \\
(10) \quad (11) \quad (12) \quad (13)
\]

**Table 1: Hydroboration-oxidation of 2,3-dihydrofuran**

<table>
<thead>
<tr>
<th>ratio of reactants 3:1</th>
<th>% 10</th>
<th>% 11</th>
<th>% 12 &amp; 13</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncatalyzed</td>
<td>73.4</td>
<td>22.3</td>
<td>4.4</td>
<td>38.4</td>
</tr>
<tr>
<td>catalyzed</td>
<td>81.5</td>
<td>7.6</td>
<td>10.9</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Note: In Table 1, the ratio of 2,3-dihydrofuran to BH\textsubscript{3}-THF is 3:1, and “catalyzed” means Wilkinson’s catalyst was used in the reaction.
Table 2: Hydroboration-oxidation of 2,3-dihydrofuran

<table>
<thead>
<tr>
<th>ratio of reactants 1:1</th>
<th>% 10</th>
<th>% 11</th>
<th>% 12 &amp; 13</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncatalyzed</td>
<td>55.0</td>
<td>41.8</td>
<td>3.7</td>
<td>66.1</td>
</tr>
<tr>
<td>catalyzed</td>
<td>50.0</td>
<td>47.2</td>
<td>2.8</td>
<td>50.2</td>
</tr>
</tbody>
</table>

Note: In Table 2, the ratio of 2,3-dihydrofuran to BH$_3$-THF is 1:1, and “catalyzed” means Wilkinson’s catalyst was used in the reaction.
Preparation of Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,3-Dicarboxylate

\[
\begin{align*}
\text{COOC}_2H_5 & \quad \xrightarrow{178^\circ C} \quad 2 \\
\text{CH}_2C_1_2 \\n\text{COOC}_2H_5 \\
\text{C} & \quad \xrightarrow{\text{CH}_2C_1_2} \quad \text{COOC}_2H_5
\end{align*}
\]

A fractional distillation apparatus was set up in the hood with a 200 ml round bottomed flask, to which was added 40.0 g (0.30 mol) of dicyclopentadiene. A 400 ml receiving flask was attached and in this was placed 77 g (0.54 mol) of dimethyl acetylenedicarboxylate dissolved in 250 ml CH\textsubscript{2}Cl\textsubscript{2}. The dicyclopentadiene was slowly heated to avoid the distillation of the dimer. And cyclopentadiene (b.p.45-47\textdegreeC) was distilled into the receiving flask in a dropwise fashion. The reaction mixture was allowed to stand overnight at room temperature.
Upon evaporating the solvent (rotary evaporator), 113.00 g of pale yellow oil (in quantitative yield and identified $^1$H NMR to be dimethylbicyclo[2,2,1]-hepta-2,5-diene-2,3-dicarboxylate) was obtained.

$^1$H NMR data: Solvent acetone-d$_6$

![Chemical structure diagram](image)

δ 2.1 → H → δ 2.2

δ 6.9 → H → δ 3.85

δ 3.7
Preparation of dimethyl tetra-cycl[2.2.1.0^2.6.0^3.5]^heptane-2,3-dicarboxylate

Freshly prepared norbornadiene dimethylester (14) weighing 100 g (0.48 mol) was dissolved in 1000 ml ethyl ether. The solution was placed in a 1-liter Pyrex® photochemical reaction vessel (see Figure 3) and stirred with a magnetic stir bar. Then this solution was irradiated using the 450 Watt Hanovia® high pressure mercury vapor lamp. The lamp was located in a quartz immersion well. The quartz immersion well was placed in the 1-liter Pyrex® photochemical reaction vessel and cooled with water flowing around the jacket surrounding the lamp. The reaction vessel was equipped with a reflux condenser. The whole photochemical reaction vessel was covered with aluminum foil, and a N2 atmosphere was maintained during the entire reaction. The reaction mixture was irradiated for 4.5 hours. Then evaporation of the solvent gave a

pale yellow oil. The $^1$H NMR spectrum indicated that unreacted starting material as the only significant product. No successful results were obtained, even if the reaction time was increased from 4.5 hours to 8 hours, 24 hours, 48 hours or 72 hours. The amount of norbornadiene-dimethylester (14) was decreased from 100 g (0.48 mol) to 50 g (0.24 mol) and dissolved in 1000 ml ethyl ether and irradiated again for each of 8 hours, 24 hours and 48 hours. The $^1$H NMR spectrum again indicated only unreacted starting material.
Figure 3.: 1-liter Pyrex® photochemical reaction apparatus:46

Preparation of Bicyclo[2.2.1]hepta-2,5-Dicarboxylic Acid

Freshly prepared cyclopentadiene (~ 50 ml) was slowly added to 50.0 g (0.44 mol) of acetylene dicarboxylic acid which had been dissolved in 200 ml of anhydrous ether and cooled in an ice bath. The solution was vigorously stirred for four hours and the ice bath was allowed to reach the room temperature. The solution was then heated for ten minutes on a steam bath and then cooled in an ice bath. After 30 minutes of stirring, a precipitate formed, and the mixture was stirred for another hour. The solid was collected by filtration and more precipitate was obtained by evaporation of about one half of the ether layer. The combined solids were then dissolved in hot water, treated with charcoal, filtered, and allowed to crystallize (in refrigerator) overnight. After filtration, the resulting solid was dried in a desiccator for 3 days. In this way 47.30 g (59.7 %) of norbornadiene dicarboxylic acid (16) was obtained of melting point: 165 - 167°C

H¹N.M.R data: Solvent, acetone - d₆
Preparation of tetracyclo[2.2.1.0^2.6.0^3.5]heptane-2,3-Dicarboxylic Acid

(16) \[ \text{COOH} \quad \text{COOH} \quad \text{hv} \quad \text{COOH} \quad \text{COOH} \] (17)

The same 1-liter Pyrex® photochemical reaction vessel was used in this experiment. First 45.52 g of dried norbornadiene dicarboxylic acid was dissolved in 1000 ml ethyl ether. The solution was irradiated for 10 hours using the 450 Watt Hanovia® high pressure mercury vapor lamp, while being stirred under an N₂ atmosphere. Evaporation of the solvent gave a light yellow precipitate. The precipitate was recrystallized from anhydrous acetone. At the end of this period, 35.69 g (78.41%) of quadricyclene dicarboxylic acid (17) was obtained.

The product gave the characteristic complex melting behavior (similar to that recorded\(^{49}\)); at 235°C it began to melt, at 240°C it began to foam and turned brown, at 255°C it stopped foaming and a brown powder was left which did not melt until 280°C.

\(^1\)H NMR. data: Solvent DMSO - d₆,

\[ m - \delta 1.9 \text{ to } \delta 2.8 \text{ integrates for } 8H \]

Hydroboration-oxidation of Quadricyclene Dicarboxylic Acid with BH₃-THF Promoted by Wilkinson's Catalyst

The setup, nitrogen, and all glassware went through the same procedures as described in experiment 1.

The 250 ml flask was charged with 20 ml of methanol and 1.80 g (10 mmol) quadricyclene dicarboxylic acid was added under a stream of nitrogen, then 15 ml (15 mmol) of BH₃-THF and 0.02 g (~0.2% mol) Wilkinson’s catalyst was added to the reaction flask. The reaction mixture was stirred at the room temperature for 24 hour, cooled in an ice bath, and then 10 ml of 95% ethanol and 10 ml of a 30% H₂O₂ solution followed by 10 ml of 3M NaOH were added to the flask. The reaction mixture was stirred for 24 hours with cooling and the reagents was allowed to reach room temperature.

At the end of this experiment, a light yellow precipitate (0.56 g) was obtained. This precipitate did not dissolve in THF, methanol, and DMSO and thus could not be analyzed.
Results and Discussion

Hydroboration of Styrene with BH$_3$·THF

As already mentioned in the introduction, unlike other terminal olefins such as 1-butene, and 1-pentene, hydroboration of styrene with sodium borohydride and boron trifluoride etherate in diglyme gave only 80% addition of the boron to the terminal carbon position, and 20% to the secondary carbon$^{50}$. Similar results have been observed in our lab when we used BH$_3$·THF as a hydroboration reagent instead of sodium borohydride and boron trifluoride etherate (B$_2$H$_6$). Our results were 80.7% addition of the boron to the terminal position and 19.3% to the secondary carbon. Thus electronic effects play an important role in influencing the direction of addition of the boron-hydrogen moiety to the carbon-carbon double bond.

All available evidence indicates that the addition of the boron-hydrogen moiety to olefins involves a four-centered transition state$^{51}$. The boron-hydrogen bond in hydroboration agent is presumably polarized, with the hydrogen having some hydridic character. In styrene, as a result of conjugation, the required unshared pair of electrons can be brought to the terminal carbon atom by means of the polarization shown in structure 18$^{52}$.

As a result, electronic shifts can be applied to explain the preferred addition of the boron atom to the terminal position. Steric effects also contribute to this anti-Markovnikov addition.

It is known that the phenyl group can also stabilize a negative charge in the $\alpha$-position, and thus electrons can also be brought to the $\alpha$-carbon atom by means of the polarization shown in structure (19). This is the reason for the enhanced addition of boron atom at $\alpha$-carbon position.

This mechanism would place the boron at the $\alpha$-position. The transition state would be stabilized by an electron-withdrawing substituent, such as $p$-chloro-, and made less stable by an electron supplying substituent, such as $p$-methoxy- group. The first (18) of these two polarizations is apparently more important and this is why the reaction gives more addition of the boron to the terminal position.
Hydroboration of Styrene with Catecholborane

The hydroboration of styrene using catecholborane at room temperature over 1 hour gave 73.7% addition of the boron to the terminal position and 26.3% addition of the boron to the secondary carbon. Only 3.8% of styrene was consumed. Thus anti-Markovnikov addition still dominates the addition. These results are reasonable because, as mentioned in the introduction section, electron donation from the adjacent oxygen makes catecholborane a much weaker Lewis acid. This means that catecholborane is a much weaker hydroboration agent than borane agent. As a result, the hydroboration with catecholborane is very slow at room temperature.

Hydroboration of Styrene promoted by
Wilkinson's Catalyst

Mannig and Noth first reported Wilkinson's reagent catalyzed hydroboration and thus a new facet of hydroboration was revealed. We have used the Wilkinson's catalyst to promote hydroboration of styrene using catecholborane and BH3·THF. Our results showed predominant Markovnikov selectivity with catecholborane and increased Markovnikov selectivity with BH3·THF in the presence of Wilkinson's catalyst. In the absence of Wilkinson's catalyst, however both reagents afforded the anti-Markovnikov predominant products. The results are summarized in Table 3.

Table 3  Hydroboration of Styrene promoted with Wilkinson’s Catalyst

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Catalyst</th>
<th>% Anti-M&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% M&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% Yield</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB&lt;sup&gt;c&lt;/sup&gt;</td>
<td>No</td>
<td>73.7 %</td>
<td>26.3%</td>
<td>3.8%</td>
<td>1 h</td>
</tr>
<tr>
<td>CB</td>
<td>Yes&lt;sup&gt;d&lt;/sup&gt;</td>
<td>14.2%</td>
<td>85.8%</td>
<td>71.5%</td>
<td>1 h</td>
</tr>
<tr>
<td>CB</td>
<td>Yes</td>
<td>3.1%</td>
<td>96.9%</td>
<td>59.1%</td>
<td>0.5 h</td>
</tr>
<tr>
<td>BH&lt;sub&gt;3&lt;/sub&gt;⋅THF</td>
<td>No</td>
<td>80.7%</td>
<td>19.3%</td>
<td>78.9%</td>
<td>1 h</td>
</tr>
<tr>
<td>BH&lt;sub&gt;3&lt;/sub&gt;⋅THF</td>
<td>Yes</td>
<td>65.9%</td>
<td>34.1%</td>
<td>67.1%</td>
<td>1 h</td>
</tr>
</tbody>
</table>

a. % of Anti-Markovnikov product (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>OH)

b. % of Markovnikov product (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OHCH<sub>3</sub>)

c. CB means catecholborane

d. 0.2% mol of Wilkinson’s catalyst was used.

In Hayashi’s paper<sup>54</sup>, they claimed that high regioselectivity (Markovnikov addition) was only observed with rhodium complexes that have tertiary phosphine ligands and a positive charge on the rhodium atom. For example, they found that the hydroboration reaction of styrene with catecholborane in THF at 25<sup>o</sup>C for 30 mins in the presence of 1% mol of rhodium catalyst prepared in situ by mixing [Rh(COD)₂]<sub>2</sub>BF₄ and 1,4-bis(diphenylphosphino)butane (dppb) followed by oxidation gave 99%

of α-phenylethanol regiospecifically (C₆H₅CHOHCH₃ / C₆H₅CH₂CH₂OH ~ 99/ 1). In this case, Markovnikov addition product was the major product. But when Wilkinson's catalyst was used, the anti-Markovnikov product was the major product. According to their results, hydroboration of styrene with catecholborane in the presence of 1 mol % of Wilkinson's catalyst gave the following ratio: C₆H₅CHOHCH₃ / C₆H₅CH₂CH₂OH = 10 / 90. The yield was 79%.

David A. Evans' research group⁵⁵ have studied the hydroboration of styrene with deuteriocatecholborane promoted by Wilkinson's catalyst. They observed that the reaction of excess olefin with deuteriocatecholborane under standard conditions afforded only one deuterium-containing product, 1-phenyl-α-deuterioethanol (100%, C₆H₅CHOHCH₂D).

Our reactions and observations were more similar to Evans' observations. Hydroboration of styrene with catecholborane in the presence of 0.2 mol % of Wilkinson's catalyst at room temperature for half an hour provided 96% of α-phenyl ethanol Markovnikov product. Also from our results, it seems that in the presence of Wilkinson's catalyst with less reaction time, more Markovnikov product ( C₆H₅CHOHCH₃ ) was formed. Hydroboration of styrene with catecholborane for one hour gave 85.8% of Markovnikov product, whereas hydroboration of styrene with catecholborane for half an hour gave 96.9% of Markovnikov product. Even though the mechanism of hydroboration of styrene with catecholborane without Wilkinson's catalyst offered the anti-Markovnikov product as major product, this process (without Wilkinson's catalyst) is much slower than the catalytic process (with Wilkinson's reagent), and the result of these two competing processes was largely Markovnikov addition product.

We also hydroborated styrene with BH$_3$·THF in the presence of Wilkinson's catalyst. Compared to catecholborane, BH$_3$·THF is a much stronger hydroboration reagent. Our results indicated that without Wilkinson's catalyst, borane ( BH$_3$·THF ) reagent can hydroborate styrene rapidly and provide mainly anti-Markovnikov addition product. When we applied Wilkinson's catalyst to the hydroboration of styrene with BH$_3$·THF, we found that more Markovnikov addition product was obtained. It should be noted that unlike the hydroboration with catecholborane, the hydroboration using BH$_3$·THF gave anti-Markovnikov addition as major product both with and without Wilkinson's catalyst.

The effect of using Wilkinson's catalyst was an increased percentage of Markovnikov addition. These facts suggested that hydroboration of styrene controlled by the catalytic mechanism provides Markovnikov addition product, whereas conventional hydroboration mechanism (without Wilkinson's catalyst) provides anti-Markovnikov addition product.

The difference between using BH$_3$·THF and catecholborane can be explained by the hydroboration rate. Since BH$_3$·THF is a much more reactive agent than catecholborane, the rate of hydroboration of styrene using BH$_3$·THF through the conventional mechanism (without Wilkinson's catalyst) is apparently faster than the rate by the catalytic mechanism. This is why the anti-Markovnikov addition products were major products even when Wilkinson's catalyst was used. However, the catalyzed process was fast enough to cause an increased percentage of Markovnikov addition product to be obtained. On the other hand, the hydroboration using catecholborane without Wilkinson's catalyst is very slow as demonstrated by only a 3.8% conversion of styrene. Thus when Wilkinson's catalyst was used, the catalytic process heavily dominated the hydroboration reaction and gave Markovnikov addition product as major
product. The very slow hydroboration process through the conventional hydroboration mechanism may still be present and this could give mainly anti-Markovnikov product. The percentage of anti-Markovnikov product increased with reaction time as shown in Table 3. This suggests that the rate of the non-catalytic process becomes more significant compared to the catalytic process as the reaction proceeds. For better understanding, let us look the proposed mechanism of the hydroboration catalyzed by Wilkinson’s catalyst.

**Mechanism of Rhodium Catalyzed Hydroboration of Olefins**

Mannig and Noth\textsuperscript{56} have suggested a mechanism for catalyzed hydroboration of olefins, which is analogous to that proposed for the much more thoroughly investigated rhodium - catalyzed hydrometalation reactions such as hydrogenation, hydrosilation and hydroformylation\textsuperscript{57}. The mechanism is illustrated as in Figure 4:

Figure 4: Proposed Reaction Mechanism for a Wilkinson's Reagent Catalyzed Hydroboration Reaction

According to the above mechanism, only the regiospecific incorporation of deuterium at C2 of the product alcohol should be expected. After isotope labeling studies carried out on the rhodium catalyzed olefin hydroboration reaction by Evans and Fu, it was found that the mechanism of these reactions is not as straightforward as Figure 4 above suggested. When they used Wilkinson's catalyst to catalyze hydroboration of 1-decene with deuteriocatecholborane (2 mol % catalyst, THF,
20°C) followed by oxidation, they did not find simple regiospecific incorporation of deuterium at C-2 of the isolated 1-decanol as the mechanism in Figure 4 suggests. Instead, a significant proportion of the deuterium in the product alcohol was found at the hydroxyl-bearing carbon. But when they used Wilkinson's catalyst to catalyze the hydroboration of styrene with deuteriocatecholborane, they found deuterium incorporation exclusively in the terminal carbon position of the Markovnikov product. These results indicated that the mechanisms of the hydroborations of the 1-decene and styrene are not completely the same. The different hydroboration results are rationalized in Figure 5.

In the case of 1-decene, the regioselectivity determining step is reductive elimination step. To explain the incorporation of deuterium at C-1, the hydride migration step should be considered to be a reversible step. In the case of styrene, the regioselectivity determining step is an irreversible hydride migration step. Since these two reactions have different regioselectivity determining steps and different reversibility, the labeling study showed different results.
Recently, Zhang et al. also proposed the mechanism of hydroboration for styrene promoted by Wilkinson's catalyst. It is shown in the Figure 6. In this proposed mechanism, the insertion of an olefin to M-H bond or (M-Bbond)
mechanism, the insersion of an olefin to M-H bond or (M-Bbond) may occur in two different ways: primary insertion and secondary insertion.

Our observations led us to believe that the secondary insertion (to form the secondary system, ArCH(CH₃)MB was the predominant step, since hydroboration-oxidation of styrene with catecholborane promoted by Wilkinson's catalyst (for half an hour), gave 96.9% Markovnikov product and only 3.1% anti-Markovnikov product. The domination of the insertion on the secondary carbon can be explained by the formation of η³-benzyl complex as illustrated in Figure 7.
Figure 6: Proposed Mechanism for Hydroboration of Styrene Promoted by Wilkinson's Catalyst:

secondary insertion  primary insertion
The enhanced stability of $\eta^3$-benzyl complex makes the secondary insertion a preferred step. Such $\eta^3$-complexs have been reported. This mechanism explains why the hydroboration of styrene mainly gave the Markovnikov addition product as observed in our experiments.

**Hydroboration of 2,3-Dihydrofuran Promoted by Wilkinson’s Catalyst**

The main purpose of this part of the project is to study the effect of Wilkinson’s catalyst on hydroboration of heterocyclic olefins in an attempt to find the optimum conditions for these systems.

In 1985, Brown’s research group studied the hydroboration of 2,3-dihydrofuran with BH₃·SMe₂. They found that the hydroboration of 2,3-dihydrofuran with BH₃·SMe₂ (3:1 molar ratio) at 0°C for 2 hours proceeded to give a mixture of trialkylborane and borinate (14). Oxidation afforded a mixture of 3-hydroxytetrahydrofuran (10, 88%) 3-buten-1-ol (11, 4%) and 1,3- and 1,4-butanediols (12 and 13, 6%). The formation of these products can be rationalized in
the following Figure 8 (the mechanism has been outlined on p. 13 of the introduction section):

**Figure 8 : Hydroboration-oxidation of 2,3-dihydrofurane**

\[
\begin{align*}
\text{BH}_3 \cdot \text{THF} & \rightarrow \text{MeO} \quad \text{2 h} \\
\text{H}_2\text{O}_2 + \text{NaOH} & \rightarrow \text{MeO} \\
\text{HOCH}_2\text{CH}_2\text{CHCH}_3 & + \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\end{align*}
\]
We applied Wilkinson’s catalyst to 2,3-dihydrofuran and the results are summarized in Table 2 and Table 3 of the experimental section.

These results indicate that Wilkinson’s catalyst caused different effects when the ratio of reactant to hydroboration reagent was changed from 3:1 to 1:1. When the ratio of 2,3-dihydrofuran to BH₃·THF was 3:1, the ratio of main product (3-hydroxytetrahydrofuran, 10) in the product mixture was 73.4% in the absence of the Wilkinson’s catalyst. In the presence of Wilkinson’s catalyst, the ratio was 81.5%. However, when the ratio of 2,3-dihydrofuran to BH₃·THF was changed from 3:1 to 1:1, the ratio of 3-hydroxytetrahydrofuran in the product mixture was 55.0% in the absence of Wilkinson’s catalyst. It was changed to 50.0% in the presence of Wilkinson’s catalyst. Since the mechanism of hydroboration-oxidation of heterocyclic olefins is not yet known, we are still unable to explain these results.

The product yield was lower with Wilkinson’s catalyst than without Wilkinson’s catalyst. The possible reason for this may be the following: since 2,3-dihydrofuran has an electron rich oxygen and Wilkinson’s catalyst has a vacant site, the electron rich oxygen might bind to the Wilkinson’s catalyst such that further reaction may be suppressed. In other words, the Wilkinson’s catalyst might be deactivated by 2,3-dihydrofuran. Further evidence is needed to test the above suggestion. Evans has also printed out that Wilkinson’s reagent is subject to oxidation which can affect the product ratios.

These results also showed that in the presence of excess hydroboration reagent, the ratio of the main product (3-hydroxytetrahydrofuran, 10) in the total product mixture was much lower. This is because the presence of excess hydride cause ring cleavage of the alkylboranes, which leads to side products.
Hydroboration of the Cyclopropane Ring in a Quadricyclene System

promoted by Wilkinson's Catalyst

Other research workers in our group were studying Wilkinson's catalyst promoted hydroboration of a cyclopropane ring in quadricyclene. One of my research projects was to hydroborate a cyclopropane ring in quadricyclene dimethylester or quadricyclene dicarboxylic acid. The new reaction that we plan to perform is:

\[
\begin{align*}
\text{COOCH}_3 & \xrightarrow{1) \text{BH}_3, \text{THF} \text{ or CB, WILK. Cat.}} \\
& \xrightarrow{2) \text{H}_2\text{O}_2, \text{NaOH, H}_2\text{O}} \\
\end{align*}
\]

We prefer to use diester rather than diacid as a substrate for this reaction, because the hydroborated diacid intermediate might be susceptible to protonolysis by
the rest of the diacid\textsuperscript{58}. One typical example to illustrate the above point is shown below.

\[
\text{RSCH}_2\text{CH} = \text{CH}_2 \rightarrow \text{RSCH}_2\text{CH}_2\text{CH}_2\text{EtCOOH} \xrightarrow{\triangle} \text{RSCH}_2\text{CH}_2\text{CH}_3
\]

Therefore, we may not be able to use the diacid for the hydroboration experiment because the following reaction may happen.

We first attempted to prepare the quadricyclene dimethylester as the starting material for the hydroboration reaction. In principle, the synthesis can be achieved through the (2+2) addition of norbornadiene dimethylester.

Norbornadiene dimethylester was successfully prepared by reaction of cyclopentadiene with dimethyl acetylenedicarboxylate. The Diels-Alder addition (2+4) of two reactants gave us norbornadiene dimethylester. The product was verified by 200 MHz \textsuperscript{1}H NMR spectra.

Norbornadiene dimethylester synthesized in the previous experiment was placed in 1-liter Pyrex® photochemical reaction apparatus and irradiated for 4.5 hours. The $^1$H NMR spectra indicated that the expected (2+2) addition had not happened. To study whether the reaction time had an effect on the addition, we performed our experiments with the different irradiation time ranging from 4.5 hours to 8 hours, 24 hours, 48 hours and 72 hours. The $^1$H NMR analysis still indicated that the (2+2) addition product was not present in the mixture. We also experimented with different (more dilute) concentrations of norbornadiene dimethylester to avoid polymer formation. The amount of starting norbornadiene dimethylester decreased from 100 g (0.48 M) to 50 g (0.24 M), and then the solution was irradiated for 8 hours, 24 hours and 48 hours respectively. An analysis of the product mixture using 200 MHz $^1$H NMR still showed none of the desired 2+2 addition product.

The above results suggested that we may not be able to use norbornadiene dimethylester directly to synthesize quadricyclene dimethylester. One possible reason is that norbornadiene dimethylester may form polymer under irradiation, although the concentration study did not show this.

Because of the difficulty in synthesizing quadricyclene dimethylester from norbornadiene dimethylester, we decided to use quadricyclene dicarboxylic acid for the hydroboration study despite the possible problem mentioned above.

First, we successfully prepared norbornadiene dicarboxylic acid by a 2+4 Diels-Alder addition of cyclopentadiene and acetylene dicarboxylic acid. The product was verified by $^1$H NMR spectrum.

Norbornadiene dicarboxylic acid prepared in the above experiment was irradiated for 10 hours. The reaction product was analyzed by $^1$H NMR. The $^1$H NMR indicated that there was no norbornadiene dicarboxylic acid present. The olefin
proton signal at 8 7.0 had disappeared which proved only quadracyclene dicarboxylic acid was present.

**Hydroboration-oxidation of quadracyclene dicarboxylic acid with BH₃·THF promoted by Wilkinson's catalyst**

The precipitate from reaction mixture could not dissolve in THF, methanol, and DMSO. Good reaction and workup procedures are needed for the study

**Future work**: first someone can hydroborate quadracyclene dicarboxylic acid directly using hydroboration reagent BH₃·THF, catecholborane or other reagents to study the hydroboration of cyclopropane ring with and without the presence of Wilkinson’s catalyst. Secondly, we can synthesize quadracyclene dimethylester from quadracyclene dicarboxylic acid and then hydroborate quadracyclene dimethylester.
200 MHz $^1$H NMR of Norbornadiene diacid in CD$_3$COCD$_3$
200 MHz $^1$H NMR of quadricyclene diacid in DMSO
GC - Mass spectrum of the reaction of styrene and BH\textsubscript{3}-THF without Wilkinson's catalyst
GC - Mass spectrum of the reaction of styrene and BH3·THF
with Wilkinson's catalyst

Scan 71 (1.770 min) of DATA:STYRENE2.D

Scan 77 (1.902 min) of DATA:STYRENE2.D

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GC - Mass spectrum of the reaction of styrene and catecholborane without Wilkinson's catalyst.

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The images show mass spectra and TIC (Total Ion Current) traces for scans at different times: 1.987 min, 1.982 min, and 2.289 min. The spectra display peaks at various masses, indicating the reaction products and their abundance over time.
GC - Mass spectrum of the reaction of styrene and catecholborane

with Wilkinson's catalyst (reaction time 0.5 hr.)

Scan 82 (1.864 min) of DATA:PINGCB2.D

Scan 98 (2.026 min) of DATA:PINGCB2.D

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GC - Mass spectrum of the reaction of 2,3-dihydrofuran and BH₃·THF without Wilkinson's catalyst
GC - Mass spectrum of the reaction of 2,3-dihydrofuran and BH₃·THF

with Wilkinson's catalyst

---

Scan 77 (1.582 min) of DATR:PING.D

Scan 85 (1.628 min) of DATR:PING.D

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TIC of DATR:PING.D

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70
Capillary GC spectrum of authentic α - phenylethanol sample
Capillary GC spectrum of authentic β-phenylethanol sample

![Chemical structure of β-phenylethanol](image)

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Capillary GC spectrum of the reaction of styrene and catecholborane with Wilkinson's catalyst (reaction time 1 hr.)

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Capillary GC spectrum of the reaction of styrene and catacholborane with Wilkinson's catalyst (reaction time 0.5 hr.)

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