

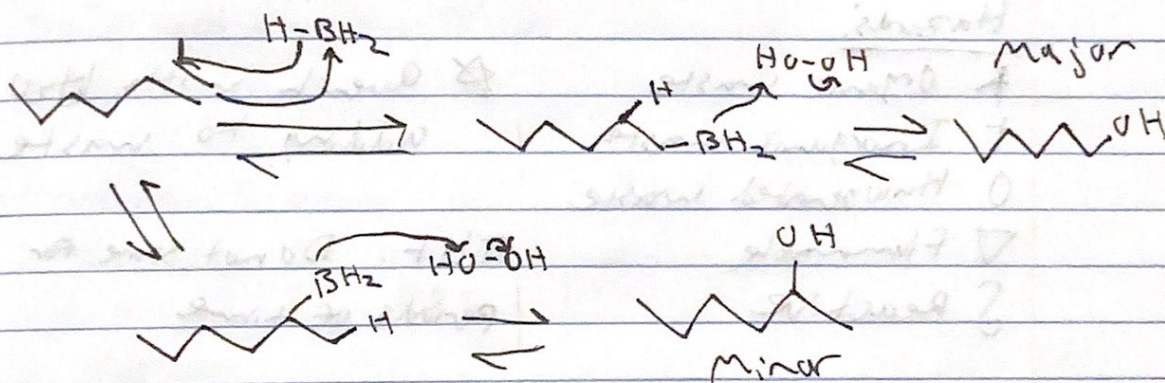
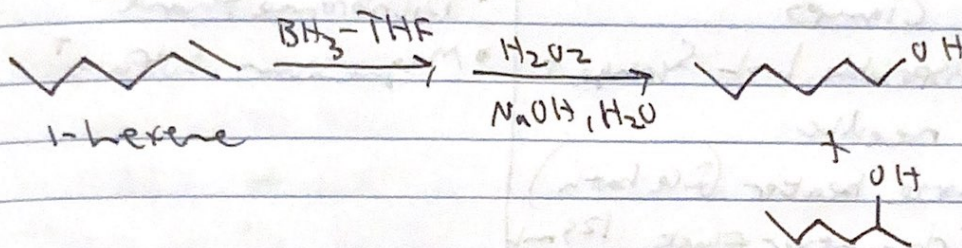
# Hydroboration/Oxidation of 1-Hexene

Purpose:

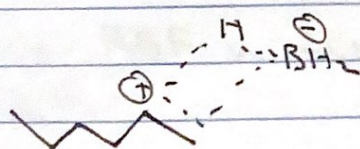
~~Determine major Product of Hydroboration/Oxidation~~

App

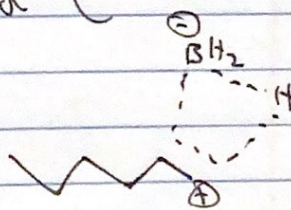
Synthesize an alcohol from an alkene by means of Hydroboration/Oxidation and determine major Product which should follow Anti-Markovnikov.



CCCCCO will be major Product because Hydroboration should follow anti-Markovnikov's rule which means  $\text{BH}_2$  will bond to less substituted C



OR



Less energy

More energy



## Procedure

### +1) Equipment:

- RB flask (dried)
- Magnet stir bar
- stir plate
- 19/22 Orange septum
- Sep Funnel
- Filter Paper
- 3 clamps
- Disposable 1mL Syringe + needle
- Large beaker (Ice bath)
- Erlenmeyer flask 125mL

### Chemicals

- Anhydrous THF \*  $\nabla$
- 1-Hexene \*  $\nabla$  0.6 mL
- $\star$  Borane-THF \*  $\nabla$   $\delta$  3 mL
- 3M NaOH  $\dagger$   $\delta$  0.6 mL
- 30%  $H_2O_2$   $\dagger$   $\delta$  0.6 mL
- Potassium Carbonate  $\dagger$  0.5 g
- Dichloromethane  $\nabla$  10 mL
- Magnesium Sulfate  $\dagger$  1 g

### Hazards:

- \* Organic waste
- $\dagger$  Inorganic waste
- $\emptyset$  Halogenated waste
- $\nabla$  Flammable
- $\delta$  Reactive

$\star$  Quench with  $H_2O$  before adding to waste

• THF: Do not store for long periods of time

- $H_2O_2$   $\rightarrow$  Causes severe burns and corrosive



TS

## Procedure

- 1) Collect Stir bar, Septum  
RBF flask



- 2) Add stir bar to RBF  
and cover immediately  
with Septum

- 3) In the hood, Flush  
RBF with Nitrogen

- Insert needle from N line  
in middle of septum

- Turn on  $N_2$  slowly

- Place open needle in  
top of septum for  $N_2$  to  
replace air

- 4) Measure 0.6 mL  
1-Hexene in Syringe  
and inject into RBF  
by Septum

- Dispose needle immediately

- 5) Add 2 mL anhydrous THF  
using Syringe

- 6) Place RBF in Ice bath  
and stir

- 7) Have TA add 3 mL of  
Bromo-THF using Syringe

$V_1 = 0.6$

$V_2 = 2.$

$V_3 = 3$



### Procedure

8.) Allow stir for  
5 min

9.) Remove Ice bath

10.) Stir another 30 min  
at room temp  
- Disconnect  $N_2$  and  
Septum

6:09

Oxidation

11.) Add 1 mL Gold water  
slowly dropwise  
with disposable pipet  
- If bubbles are too  
vigorous Immerse  
in Ice bath

Vol 2 1 mL

12.) Add 0.6 mL 3M  
 $NaOH$  using syringe

Vol 0.6

13.) add 0.6 mL 30%  $H_2O_2$   
using syringe  
- keep  $T < 40^\circ C$

Vol 0.6

- cloudy

14.) Stir 15 min

15.) Cool Rxn in Ice bath

16.) Add Potassium Carbonate  
until Saturated



## Procedure

- 17) Pour Rxn into  
Sep funnel  
- Rinse with 1-2 mL  
diethyl ether

- 18) 3 x 2 mL  $\text{Et}_2\text{O}$   
Separations

$V_1$  2  
 $V_2$  3  
 $V_3$  2

- 19) Dry with  $\text{MgSO}_4$   
- Stir well  
- Let sit for ~~10~~ 5-10 min

- 20) gravity filter into  
Pre weighed flask RBF

mass flask: 42.493  
mass top = 42.8

- 21) Add to Roto-vap  
- Don't increase T on  
water bath too high  
( $T_b \approx 38^\circ\text{C}$ )

- 22) weigh flask again

- 23) IR

IR anal ☒  
IR start ☒

- 24) GC

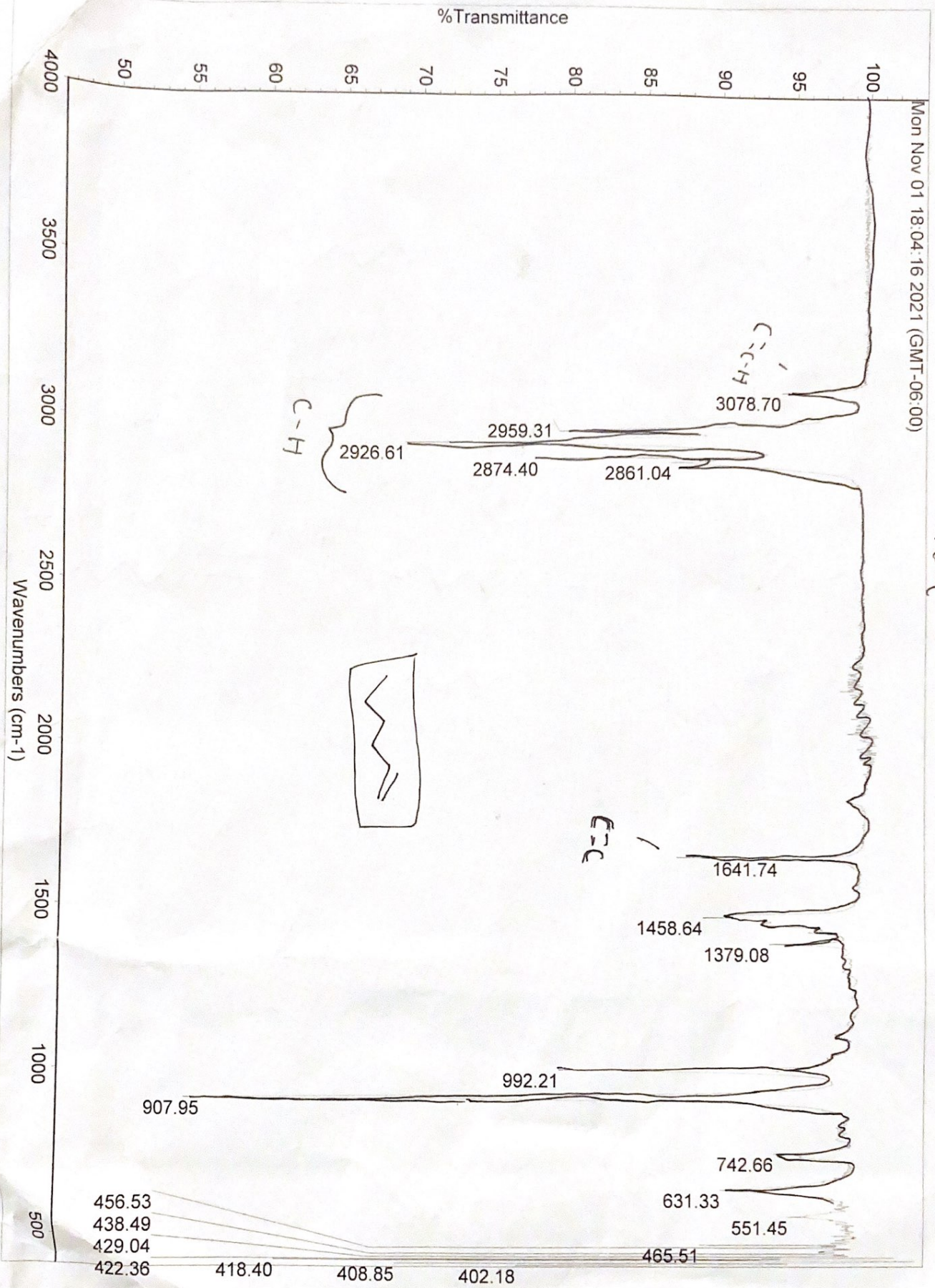
- Dissolve 1 drop product  
into 1 mL dichloromethane

GC: M] LO - )



	1-hexene	BH <sub>3</sub> ·THF	Hexanol Isomers
MW g/mol	84.16	1M	102.17
$\rho$ g/mL	0.67		0.81
Temp °C	63		140-159
amount used g/mL	0.6 mL	3 mL	0.307
amount used mol	$4.78 \times 10^{-3}$	$3.13 \times 10^{-2}$	$3.01 \times 10^{-3}$

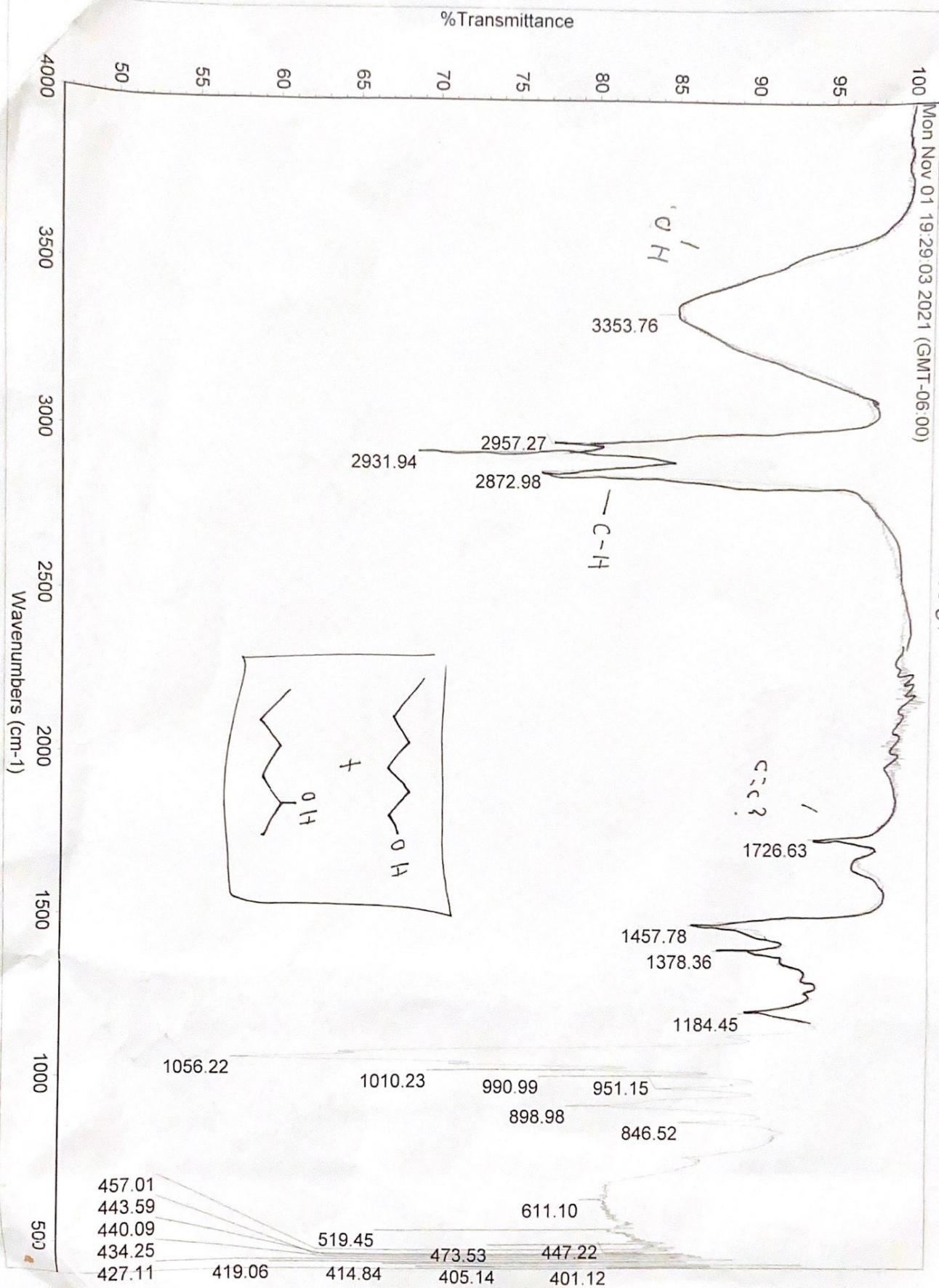




1 - Hexene



Product





# Qualitative Analysis Report

## User Chromatograms

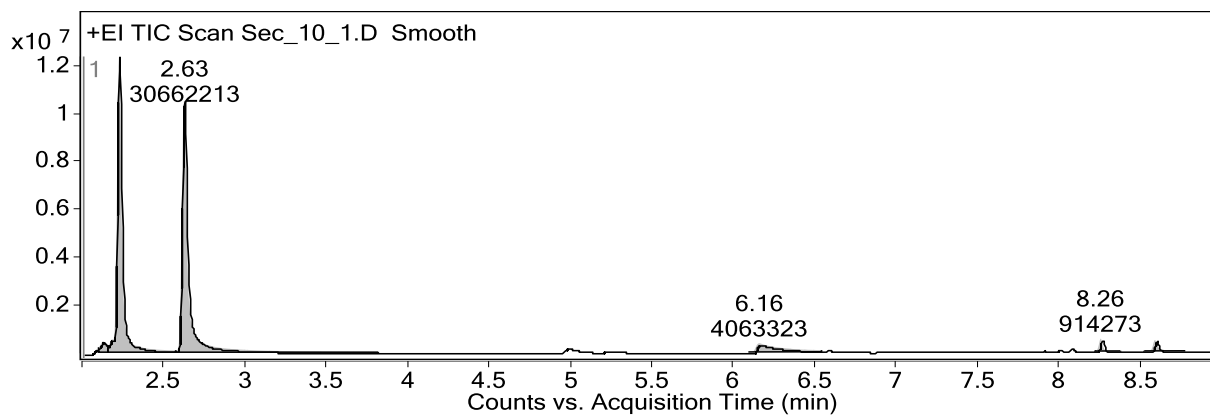
Fragmentor Voltage

Collision Energy

0

Ionization Mode

EI



### Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	2.1	2.13	2.16	454122	1219086	3.98
2	2.16	2.23	2.58	12324771	28910703	94.29
3	2.58	2.63	3.82	10520857	30662213	100
4	6.09	6.16	6.54	362422	4063323	13.25
5	8.22	8.26	8.38	520242	914273	2.98
6	8.53	8.59	8.78	454630	983967	3.21

THF

1-Butanol

1-Hexanol

Impurities

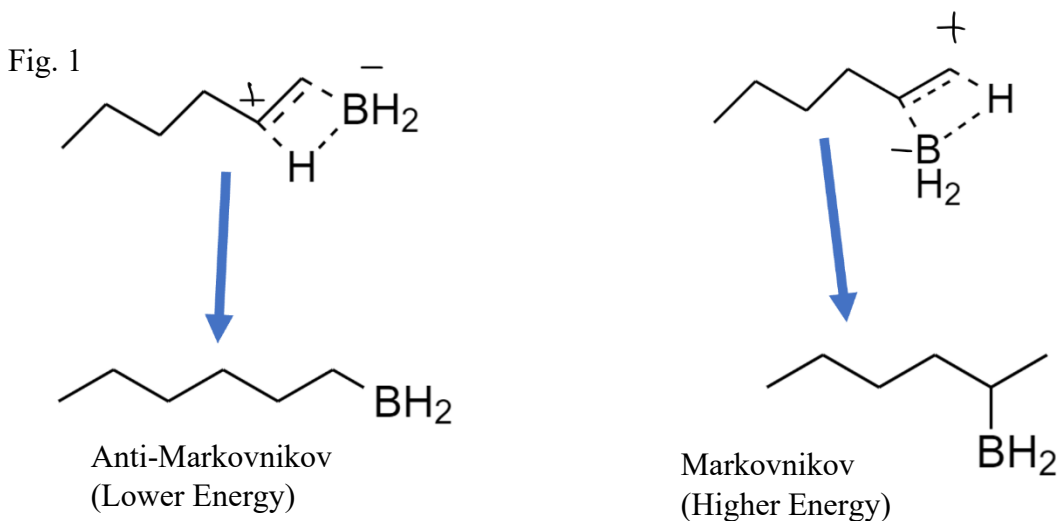
--- End Of Report ---



### Experiment 9 "Hydroboration-Oxidation of 1-Hexene"

Hydroboration-Oxidation is a common technique used to convert an alkene into an alcohol. This reaction has two steps. The first step involves the  $\text{BH}_3$  molecule attacking the  $\text{C}=\text{C}$  double bond on the alkene. One H bonds to one of the carbon atoms and the  $\text{BH}_2$  forms a bond with the other. The second step is to oxidize the organoborane which forms the alcohol. In this experiment, 1-Hexene was used as the starting alkene and IR spectroscopy and GC analysis was used to identify the major and minor products.

The original hypothesis was that the hydroboration step would follow anti-Markovnikov so the more stable intermediate alkylborane would have the  $\text{BH}_2$  bonded to the less substituted C. The reaction proceeds in this way for steric and electronic reasons. The  $\text{BH}_2$  bonds to the less substituted C because it is the more accessible C so the  $\text{BH}_2$  would be less sterically hindered. As for the electronic reason, although the mechanism involves a "concerted addition of H and  $\text{BH}_2$  from the same side of the planar double bond" (Smith 386) the bonds are not broken and formed at exactly the same time so there is a partial negative charge on B and a partial positive charge on one C as illustrated in Fig 1. The partial positive charge would be on the more substituted C because the positive charge is stabilized by alkyl groups. Therefore, the  $\text{BH}_2$  would bond to the C without the partial positive charge. The more stable intermediate would then be converted into the major product via the oxidation step.



The hypothesis was confirmed by analysis of the GC data. The instrument recognized six different peaks with RTs outlined in Table 1. These RTs are similar to those found in the reference GC data provided in the procedure (Zharov 5). The first two peaks may represent Tetrahydrofuran (THF). In the reference data there is only one peak representing THF but the first peak in the experimental data is very small and close to the second peak so it is likely they represent the same molecule. There is a peak for 2-Hexanol but it is so small that the instrument did not calculate its area so its product ratio is neglected. This data shows that there was much more 1-Hexanol present in the product than 2-Hexanol which confirms the hypothesis because 1-Hexanol is the least substituted Alcohol.



Table 1		
Molecule	RT (min)	Product Ratio (%)
THF	2.13, 2.23	45.1
1-Butanol	2.63	45.9
1-Hexanol	6.16	6.09
2-Hexanol	~5.2	0
Other	8.26, 8.59	2.84

The IR and GC data can both be used to infer the purity of the product. The IR data for 1-Hexene shows expected peaks correlating to the C=C and C-H bonds that make up the molecule. The C=C peak shows at around  $1642\text{cm}^{-1}$  and the C-H peaks range from  $2861$  to  $2959\text{cm}^{-1}$  with another peak at  $3079\text{cm}^{-1}$  which represents the C=C-H bonds. The IR data for the product shows peaks at a similar range as the starting material for the C-H bonds from  $2873$  to  $2957\text{cm}^{-1}$ . Instead of a peak at  $3079\text{cm}^{-1}$  however there is a broad peak at  $3353\text{cm}^{-1}$  which represents the alcohol. There also appears to be a peak at  $1727\text{cm}^{-1}$  which may correspond to a C=C double bond. If so, then there may have been some unreacted 1-Hexene leftover in the product. This peak could also represent THF because the GC showed that the product contained a high concentration of THF. In the GC data the actual “impurities” make up only 2.84% of the product which initially suggests that the product is pure. The majority of the product however, is not either of the Hexanol isomers, but THF. THF is included in the reaction solution because the  $\text{BH}_3$  that was used was provided as a  $\text{BH}_3$ -THF complex but it does not take part in the reaction. When all the components of the product are considered, then the product ratio of the desired product was only about 6% which signifies that the product was highly impure. Even if the THF and 1-Butanol peaks are ignored, then the remaining product consists only of 1-Hexanol and impurities but the product ratio of the impurities is almost half that of 1-Hexanol which also indicates that the product was very impure. This analysis indicates that whether unreacted reactants are included or ignored, the product was fairly impure.

A large amount of THF was found in the product because the reaction between 1-Hexene and  $\text{BH}_3$ -THF should be 1:1 but the number of moles of  $\text{BH}_3$ -THF was about 6.5x that of 1-Hexene so assuming 100% of the 1-Hexene reacted, according to the values in the following table, there was still about  $2.66\text{e-}2$  moles of  $\text{BH}_3$ -THF left in the solution. This suggests that much less  $\text{BH}_3$ -THF could have been used to produce the same amount of Hexanol Isomers while having less THF leftover in the product. This suggestion would not necessarily affect the purity of the product.

Table 2			
	1-Hexene*	1M $\text{BH}_3$ -THF <sup>a</sup>	Hexanol Isomers*
MW (g/mol)	84.16	85.94	102.17
Density (g/mL)	0.670	0.898	0.810
Amount Used (mL)	0.600	3.00	
Amount Used (mol)	$4.78\text{e-}3$	$3.13\text{e-}2$	
Amount Obtained (g)			0.307
Amount Obtained (mol)			$3.01\text{e-}3$

\*values obtained from procedure (Zharov 4)

<sup>a</sup>values obtained from sigmaaldrich.com (Borane tetrahydrofuran complex 1.0m tetrahydrofuran 14044-65-6)



The %yield for the impure product was about 63%. However, as discussed previously, the product consisted mostly of unreacted reactants and only about 6% of the desired product. This implies that the %yield for the pure product is much less than 63% and is calculated to be only 3.83%. It is possible that this incredibly small %yield is due to the inaccurate separation of layers during the extraction step of the experiment. When 2mL of Et<sub>2</sub>O was added to the solution in a separatory funnel, two distinct layers were not readily observed. It is possible that much of the desired product was drained out of the separatory funnel along with the aqueous phase and discarded. Since the two layers were not distinguishable, it is also possible that some of the aqueous phase was not drained entirely from the separatory funnel but remained in the product. The first scenario would explain the %yield of the impure product but it does not explain how impure the product was. Therefore, the second scenario is the more likely because 63% is not abnormal for a %yield but it would explain the abnormal concentration of impurities in the product.

One way to improve the %yield would be to use less BH<sub>3</sub>-THF. Theoretically, only about 0.457mL would be needed for 100% of the 0.60mL of 1-Hexene to react. This adjustment would decrease the amount of THF used in the reaction so it would be less prominent in the final product. If it is preferred that BH<sub>3</sub>-THF is the limiting reactant, then an acceptable amount to add could be 1-2mL instead of 3mL. Using just 1mL would supply about 1.04e-2 moles to the reaction which is more than twice the amount that is theoretically needed so there should still be plenty of BH<sub>3</sub>. Another improvement to the experiment would be to give the aqueous and organic layers more time to separate in the separatory funnel before trying to drain the aqueous layer.

As suggested by the GC and IR data and the theory governing this reaction, the major or anti-Markovnikov product was the less substituted alcohol while the minor or Markovnikov product was the more substituted alcohol. The product was not very pure and only a small amount of the expected product was obtained but the reaction itself proceeded as expected and 1-Hexanol was produced.

## References

“Borane Tetrahydrofuran Complex 1.0m Tetrahydrofuran 14044-65-6.” *1.0 M In THF* | 14044-65-6, <https://www.sigmaaldrich.com/US/en/product/aldrich/176192>.

Smith, Janice Gorzynski. *Organic Chemistry*. Third ed., McGraw-Hill, 2011.

Zharov, Ilya, *Hydroboration/Oxidation of 1-Hexene*. October 2021.