Conversions of Alkenes into Alcohols: Review of Alkene Hydration

• You already know one method for accomplishing the following transformation. What is that method? What is its mechanism?

• Now suppose you want to carry out the following transformation. Can you use the same method as you did above? Why or why not?

• What kinds of reactions might we want to *avoid* when carrying out organic synthesis in the laboratory?

Conversions of Alkenes into Alcohols: Oxymercuration-Reduction

• We can convert an alkene into an alcohol with the following *two-step* process:

• What is the mechanism of this reaction? Why are carbocation rearrangements not observed?

• Why might we say that this two-step sequence results in the "Markovnikov addition of water to an alkene"?

Forming and Opening 3-Membered Rings

• Let's take a close look at the mechanisms of the following reactions. Do you notice any similarities? Are there any generalizations you can make?

• What is the *stereochemistry* of the intermediate and product in the following reaction sequence?

Reading: Sections 5.3 and 7.9

Conversions of Alkenes into Alcohols: Hydroboration-Oxidation

• We can accomplish the "anti-Markovnikov" addition of water to an alkene with the following *two-step* process:

• Let's take a closer look at the first step of this reaction:

• Would you say that the first step of this reaction obeys "Markovnikov's Rule"?

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Conversions of Alkenes into Alcohols: Hydroboration-Oxidation

• Now, let's look at the mechanism of the *second* step of the hydroboration-oxidation sequence:

2. Consider the following chemical transformation. For **each step** in this mechanism, provide the **curved arrows** necessary to get from the reactants to the products. Be sure to indicate **lone pairs** on any species if necessary. (**Hint**: Focus on each step individually; we will grade each step independently. Also, please be aware that you may need to draw in a **hydrogen atom** if one is not shown...)

2

Name:

$$H_3C$$
 H_3C
 H_3C

Stereochemistry of Hydroboration-Oxidation

• Explain why hydroboration-oxidation of 1-methylcyclohexene gives only the product shown below:

Summary of Alkene Addition Reactions

• Show the product of each of the following alkene addition reactions, and include some *brief* notes about the mechanism of each reaction.

$$\begin{array}{c} & \\ & \\ \end{array}$$

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} 1. \text{ BH}_3 \text{ , THF} \\ \\ \hline \\ 2. \text{ H}_2\text{O}_2 \text{ , OH}^- \end{array} \end{array}$$

Ozonolysis of Alkenes

• Consider the following very interesting reaction sequence:

- What are the functional groups of the products of this reaction sequence?
- We won't worry (for now) about the *real* mechanism for this reaction, but we can write a *fake* mechanism:

• Using that fake mechanism, predict the product(s) of the following reactions:

Ozonolysis of Alkenes, With Oxidation

• If the second step of ozonolysis is *oxidative*, then slightly different products are obtained:

- What are the functional groups of the products of this reaction sequence? How is this different from the reductive "workup" (with Me₂S)?
- Predict the product(s) of the following reactions:

• Ozonolysis of a hydrocarbon (with oxidative workup) gave the following products. What are some possible structures for the original hydrocarbon?

Anti-Markovnikov Addition of HBr to Alkenes: Free-Radical Addition

• In the presence of certain compounds, notably *peroxides* (R–O–O–R), the addition of HBr (but *not* HCl or HI) takes place with *anti*-Markovnikov regiochemistry:

• Let's see if we can understand why this is so. First, we need to see the mechanism for HBr addition under these conditions. Note that this is not a mechanism that I would expect you to be able to guess or predict!

Anti-Markovnikov Addition of HBr to Alkenes: Relative Stability of Free-Radical Intermediates

• Now let's see if we can explain why the addition of HBr under *free-radical* conditions gives the "anti-Markovnikov" product. Consider the mechanisms for forming the Markovnikov and anti-Markovnikov products. What intermediates are formed in each case?

Markovnikov Regiochemistry:

Anti-Markovnikov Regiochemistry:

• How can we explain why the anti-Markovnikov product is preferred?

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How Can I Possibly Learn All of These Reactions?

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An Introduction to Organic Synthesis

• Propose a synthesis of the following product, starting with only hydrocarbons and inorganic reagents: