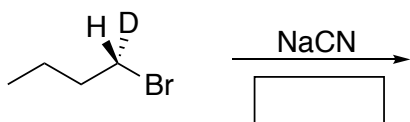


## Chem 51B (Pronin) Final Review

This worksheet is meant to help review the reactions you have learned so far by requiring you to fill out the information yourself. This should not be the only studying you do for the exam, but can help you identify things you should spend more time learning.

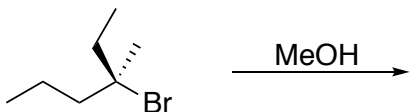
*Instructions: For each of the given reactions draw the mechanism (or part of the mechanism where indicated) with the substrates provided, draw all products (including byproducts), show relevant stereochemistry, and answer any additional questions.*

### $S_N2$

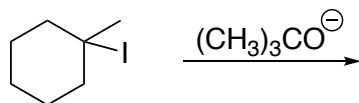


1. Fill in a polar aprotic solvent.
2. What is a general rate equation for a  $S_N2$  reaction?
3. Draw an energy diagram depicting an  $S_N2$  reaction. Draw the transition state.
4. Which alkyl halides ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ) undergo  $S_N2$  reactions?

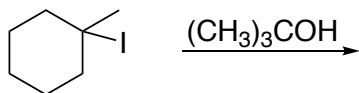
### $S_N1$



1. Do polar protic or polar aprotic solvents accelerate  $S_N1$  reaction?
2. What is a general rate equation for an  $S_N1$  reaction?
3. Draw an energy diagram depicting an  $S_N1$  reaction. Draw the transition states.
4. Which alkyl halides ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ) undergo  $S_N1$  reactions?

**E2**

1. Label the major product.
2. Draw the transition state for this E2 reaction.
3. Which alkyl halide ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ) undergoes E2 reactions the fastest?
4. What rule says the formation of the more substituted alkene is favored?
5. Do strong bases or weak bases favor an E2 reaction?

**E1**

1. Label the major product.
2. Draw the transition states for this E1 reaction.
3. Which alkyl halide ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ) undergoes E1 reactions the fastest?
4. Do strong bases or weak bases favor an E1 reaction?

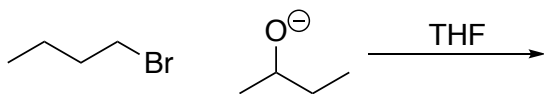
Answer the following questions with  $S_N2$ ,  $S_N1$ , E2, and E1. Some questions may have more than one mechanism.

- A. Primary alkyl halide, strong nucleophile.
- B. Primary alkyl halide, strong bulky base.
- C. Secondary alkyl halide, strong base and nucleophile.
- D. Secondary alkyl halide, strong bulky base.
- E. Secondary alkyl halide, weak base and nucleophile.
- F. Secondary alkyl halide, weak bulky base.
- G. Tertiary alkyl halide, weak base and nucleophile.
- H. Tertiary alkyl halide, weak bulky base.
- I. Tertiary alkyl halide, strong base.

Draw molecules that would fit the criteria given.

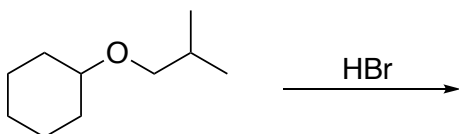
- A. An alkyl halide that gives four different products upon elimination. Draw the products.
- B. An alkene that can have cis and trans stereoisomers.
- C. An alkyl halide that only gives the cis product in an E2 elimination.

### Williamson Ether Synthesis



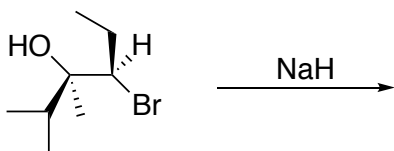
1. Draw another alkyl halide/alkoxide pair that would lead to the same product.
2. Which set of reagents is favored? Why?

### Reaction of Ethers with Strong Acid

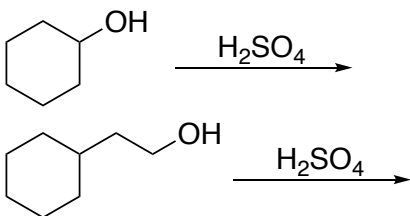


1. Draw the possible products of the reaction. Circle the two Markovnikov products.

### Epoxide Synthesis with Halohydrins

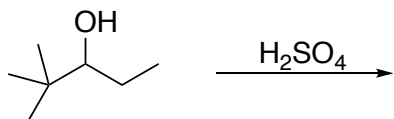
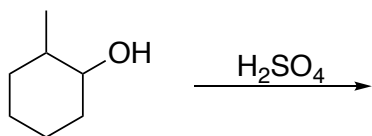


### Dehydration of an Alcohol in Acid



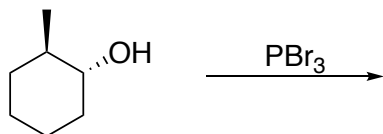
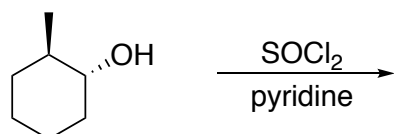
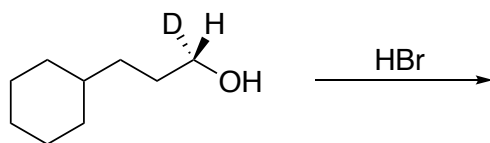
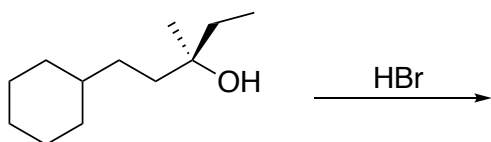
Note: The two mechanisms should be different.

## Carbocation Shifts



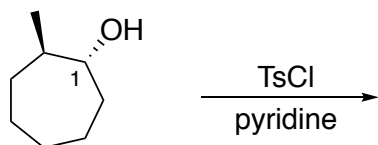
1. What drives a carbocation shift?
2. What are the two kinds of carbocation shifts shown above?

## Conversion of Alcohols to Alkyl Halides



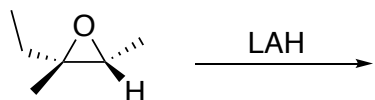
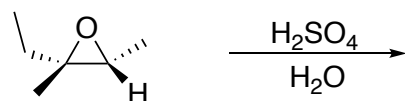
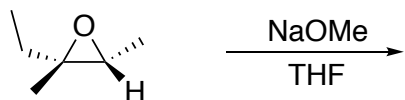
1. What happens to the stereochemistry at the reactive carbon in each reaction?
2. Which reactions replace an alcohol with an Iodine? Bromine? Chlorine?

## Tosylate



1. What is the resulting stereochemistry at carbon 1?

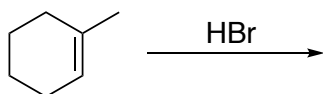
## Reactions of Epoxides



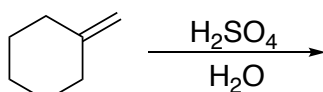
1. What is the regioselectivity of each reaction? Why?

## Alkene Addition Reactions

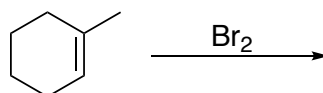
### Hydrohalogenation



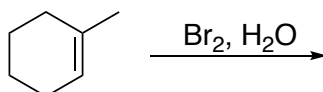
### Hydration



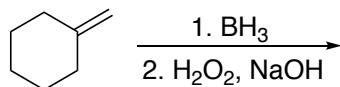
### Halogenation



### Halohydrin Formation



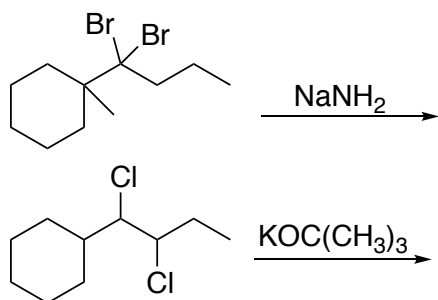
### Hydroboration-Oxidation



Note: Do not show the oxidation mechanism for hydroboration oxidation.

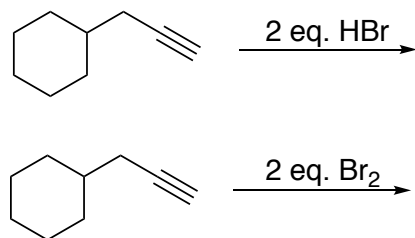
1. When would you use hydration vs. hydroboration oxidation?
2. Which reactions proceed with syn addition? Anti addition? Unselective?

### Alkyne Synthesis



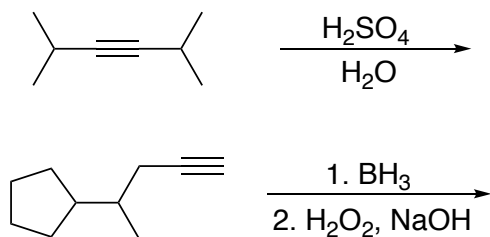
1. Label each dihalide as “vicinal” or “geminal”.

### Hydrohalogenation and Halogenation of Alkynes



Note: Do not show the mechanism for the first addition of  $\text{HBr}$  across the alkyne.

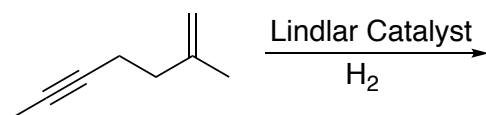
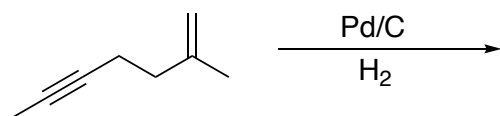
### Hydration and Hydroboration Oxidation of Alkynes



Note: Do not show the oxidation mechanism in hydroboration oxidation.

1. What new functional group is made as a result of each reaction?
2. If the product is an enol, show the tautomerization to a ketone or aldehyde.

### Reduction of Alkenes and Alkynes

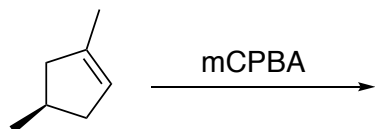


Note: It is unnecessary to show the mechanism for these reactions.

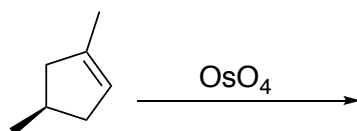
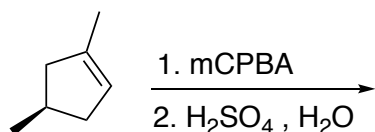
1. Does the second reaction form a cis or trans alkene?

### Oxidation of Alkenes

#### *Epoxidation*



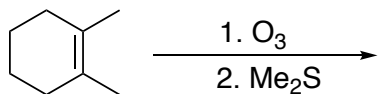
#### *Dihydroxylation*



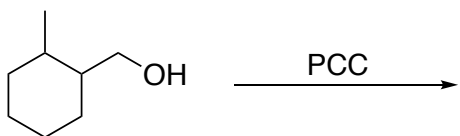
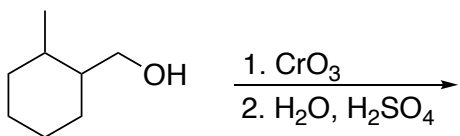
Note: Do not show the fragmentation mechanism in  $\text{OsO}_4$  oxidation.

1. What is the difference in products between the two dihydroxylation reactions?

### *Ozonolysis*



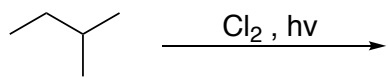
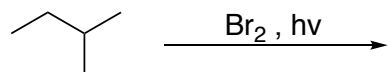
### **Oxidation of Alcohols**



1. What functional groups are formed as a result of each reaction?
2. What other way have you learned to make aldehydes?

### **Radical Reactions**

#### *Halogenation of Alkanes*



1. Include initiation, propagation, and three termination mechanisms.
2. Why is radical bromination highly selective while radical chlorination is not?  
Reference energy diagrams if necessary.

#### *Allylic Bromination*

