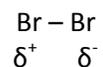


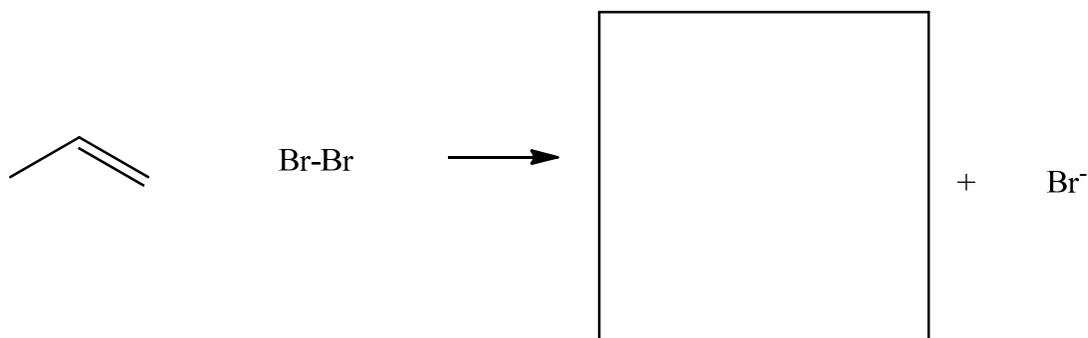
## Addition with Cyclic Intermediate

### Model 1: Electrophilic Addition of Br<sub>2</sub>

In the molecule Br<sub>2</sub>, one of the bromines is partially positive and the other is partially negative, due to the electronegativity of Br. The electrons constantly flow back and forth between the bromines, so that there is always a dipole.



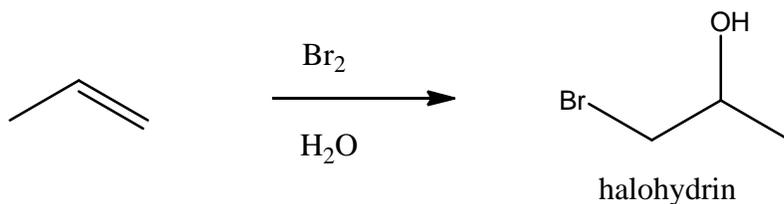
The partially positive Br acts as an electrophile; the partially negative Br acts as a leaving group and becomes fully negative.



Question 1. Draw arrows, and show the intermediate carbocation that is most likely to form in the above reaction.

Question 2. Then draw an arrow from the Br<sup>-</sup> to the carbocation, and draw the product.

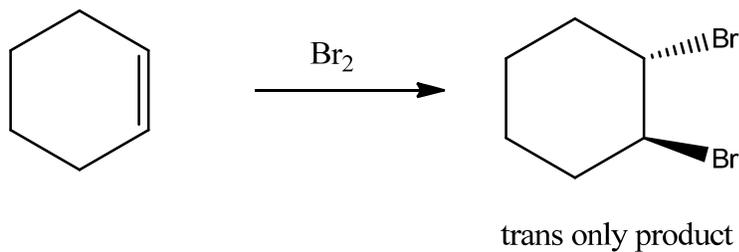
Question 3. If a large excess of competing nucleophile is present, such as  $\text{H}_2\text{O}$ , it will compete with the  $\text{Br}^-$  and win out. Draw a mechanism that shows the formation of the halohydrin:



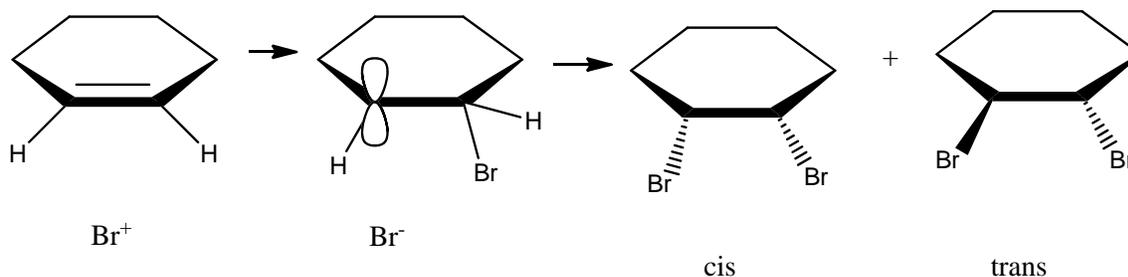
Question 4: Is the above reaction Markovnikov or anti-Markovnikov?

**Model 2:** Trans-only Stereochemistry Explanation

When  $\text{Br}_2$  is added to cyclohexene, the cis stereoisomer is NOT observed.



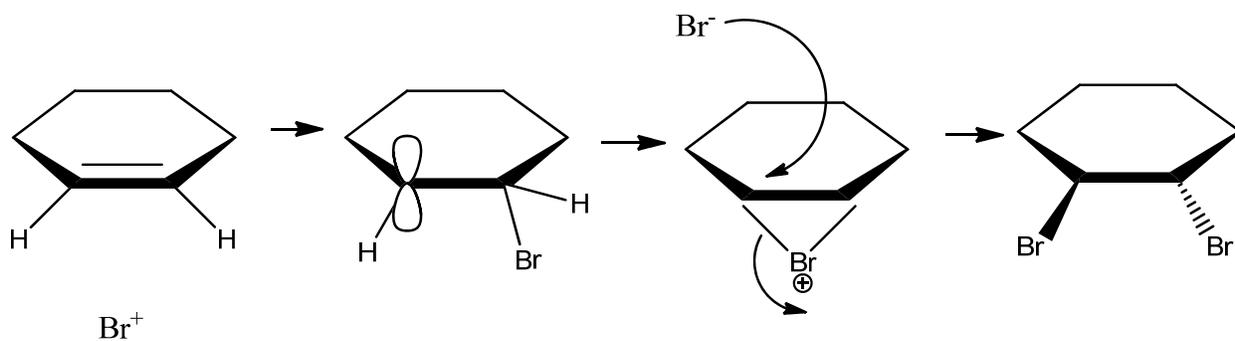
Question 1. Add curved arrows to show that the  $\text{Br}^-$  could attack either the top or the bottom lobe of the empty p-orbital of the carbocation, giving both cis and trans products:



The above mechanism cannot account for the stereoselectivity of the reaction.

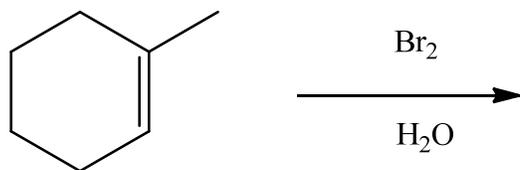
**Model 3:** Bromonium ion

In 1937, chemists suggested that the trans-only stereochemistry of this reaction could only be explained by a three-membered ring called a **bromonium ion**.



Question 1. Why is it easier for the  $\text{Br}^-$  to attack the top face of the ring, rather than the face with the bromonium ion?

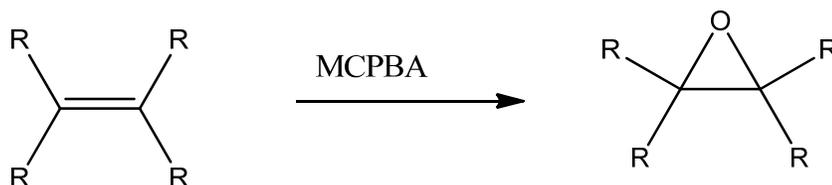
Question 2. Draw the product of the reaction below, and label it Markovnikov or anti-Markovnikov.



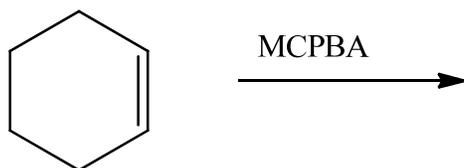
## Other addition reactions to alkenes

### Model 1: Epoxides

Three-membered ring cyclic ethers, called epoxides, are highly strained and reactive. They are formed by the addition of m-chloro perbenzoic acid (MCPBA) to an alkene.



Question 1. Draw the product of the following reaction:



### Model 2. Addition of a carbene to an alkene

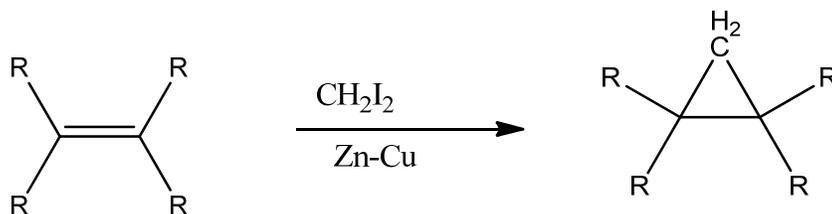
A carbene is a highly reactive species that has a carbon with two bonds, and a lone pair. There are two carbenes that we work with:

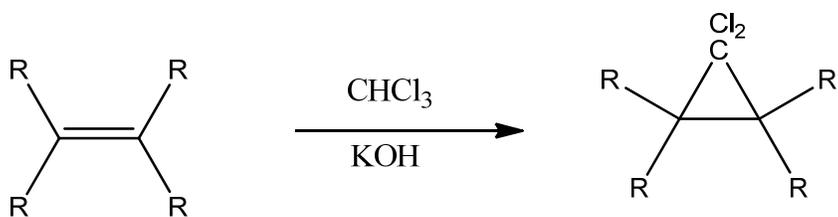


Carbene A is produced from the reagent  $\text{CH}_2\text{I}_2/\text{Zn-Cu}$

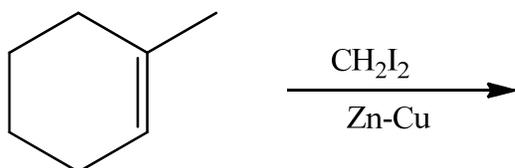
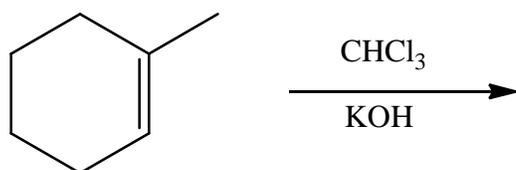
Carbene B is produced from the reagent  $\text{CHCl}_3/\text{KOH}$

Carbenes add across a double bond to form a three-membered ring product.



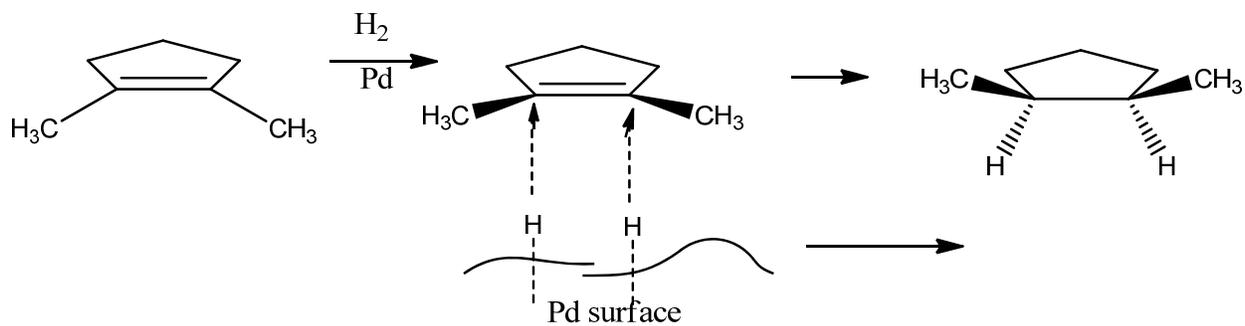


Question 1. Draw the product of the following reactions:

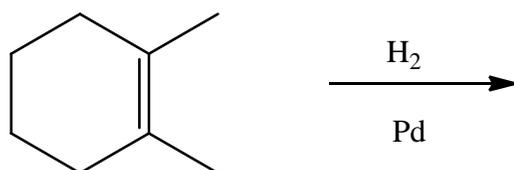
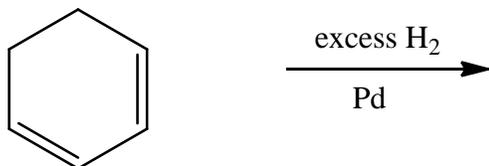
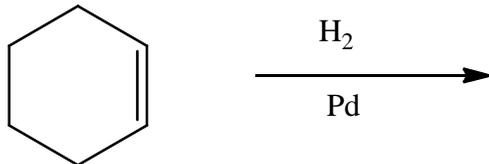


**Model 3:** Hydrogenation. Addition of hydrogens to a double bond.

Hydrogens add to the double bond using the reagent  $\text{H}_2/\text{Pd}$ . These hydrogens always go on cis.

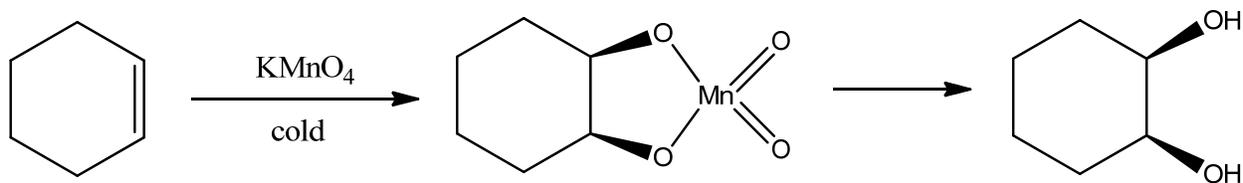


Question 1. Draw the product of each of the following reactions:

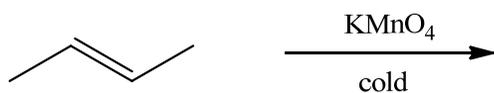
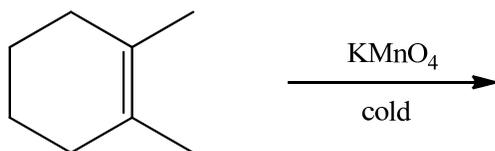


**Model 4.** Oxidation of an alkene. Addition of two OH groups across the double bond.

The reagent  $\text{OsO}_4$  (or cold  $\text{KMnO}_4$ ) will add two OH groups across the double bond. The OH's always go on cis.

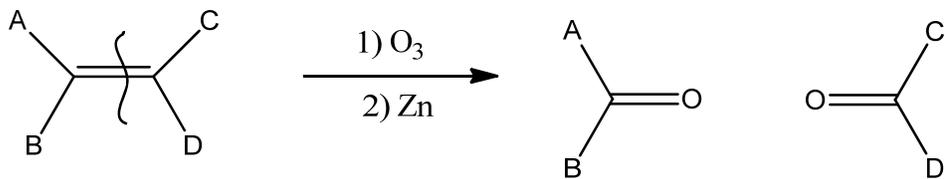


Question 1. Draw the product of each of the following reactions:

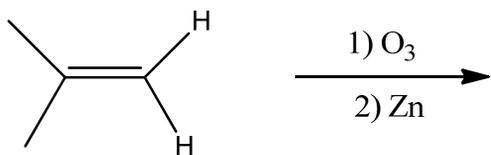
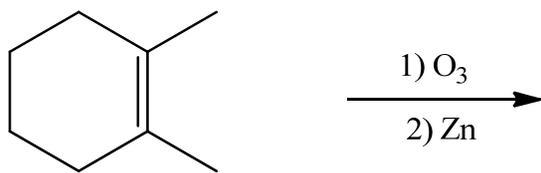


**Model 5:** Ozonolysis. Oxidative Cleavage of the C=C double bond.

Ozone “cuts” and “cauterizes” the double bond of an alkene:

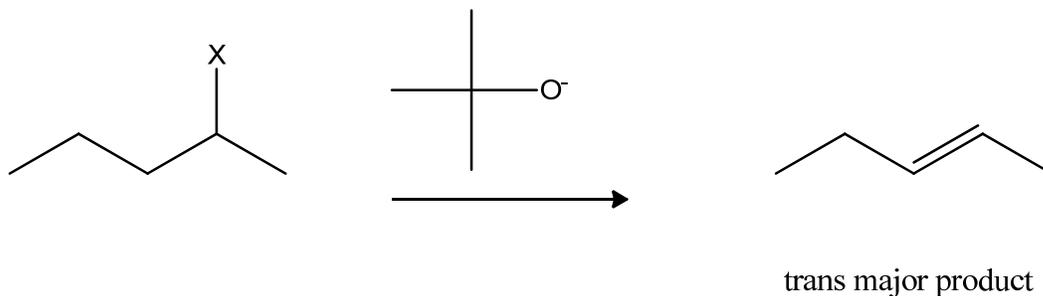


Question 1. Draw the products of the following reactions:

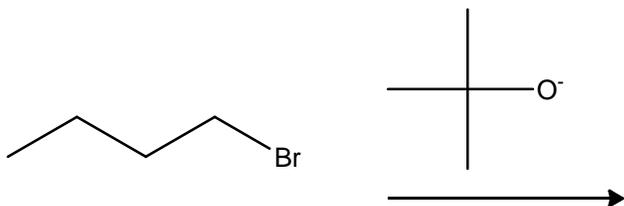
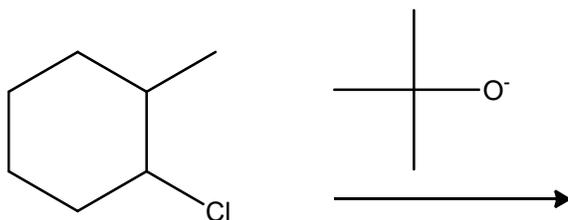
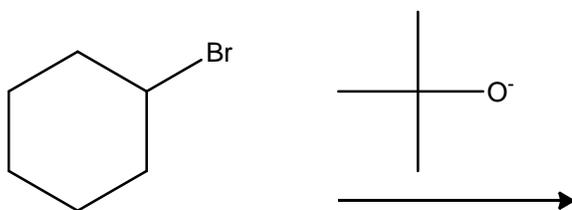


## Formation of Alkenes via Elimination Reactions of Alkyl Halides and Alcohols

**Model 1.** The major product of the elimination of HX from an alkyl halide with potassium t-butoxide is the most stable alkene product of all possible products.

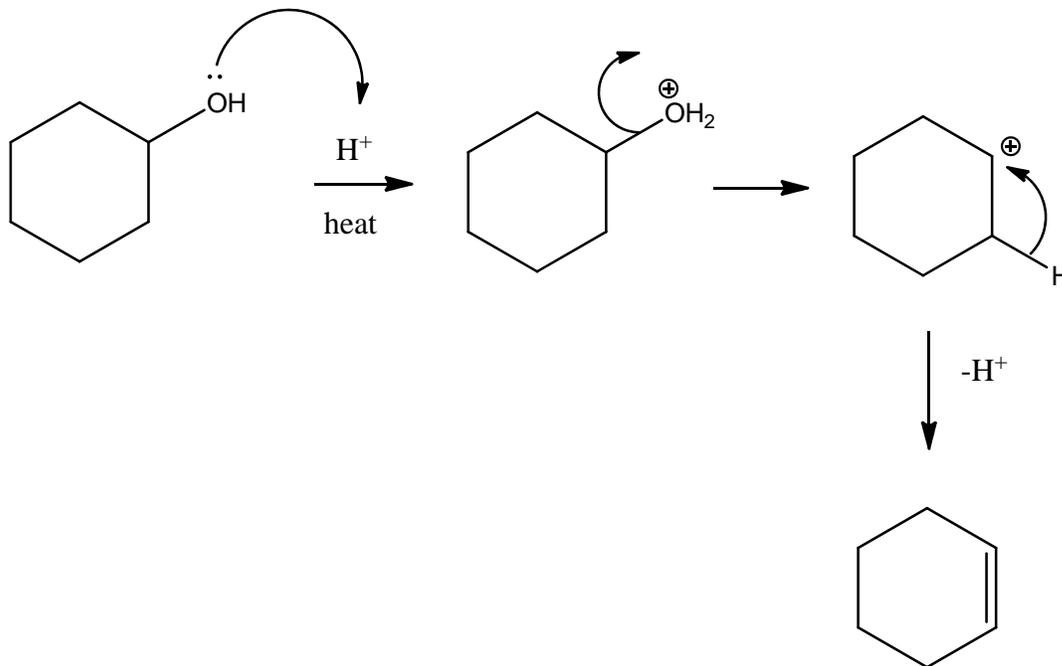


**Question 1.** Draw the major product of each of the following reactions:



**Model 2.** Formation of Alkenes from 2° or 3° Alcohols.

Alkenes can be produced from 2° or 3° alcohols using acid (usually  $\text{H}_3\text{PO}_4$  or  $\text{H}_2\text{SO}_4$ ) and heat. The mechanism involves a carbocation intermediate, which then loses a proton to form the double bond.



Question 1. Draw a mechanism and give the product of the following reactions:

