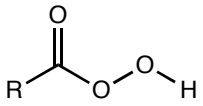
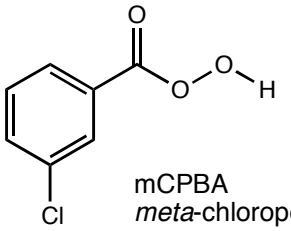
Synthesis of Epoxides With Peroxycarboxylic Acids

- A much more convenient, one-step synthesis of epoxides from alkenes uses peroxycarboxylic acids, often called "peracids." Some examples:

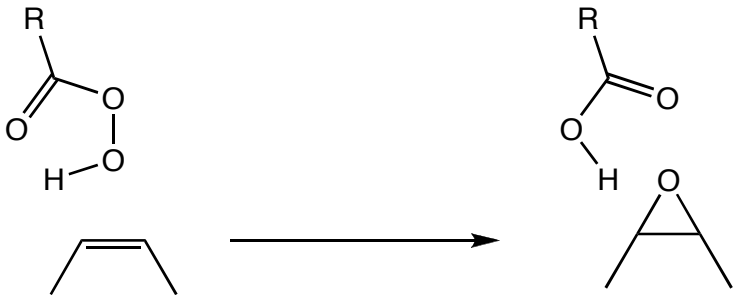


a general peracid



mCPBA
meta-chloroperoxybenzoic acid

- Draw the curved arrows for the following single-step synthesis of an epoxide from an alkene:

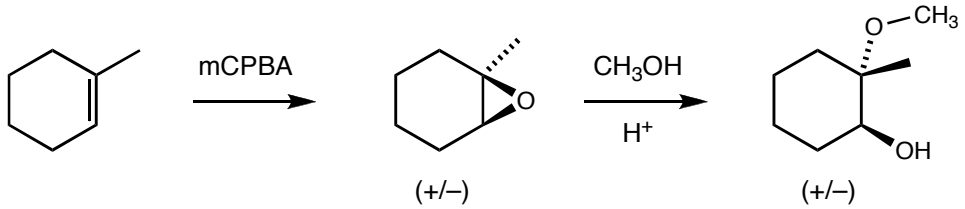


- Identify the molecular orbitals involved in this reaction. Is this mechanism similar to any other reactions you have seen before?

Reading: Section 11.2

Opening Epoxides: Acidic Conditions

- Provide a mechanism and explain why the indicated product is formed selectively in each of the following reactions:

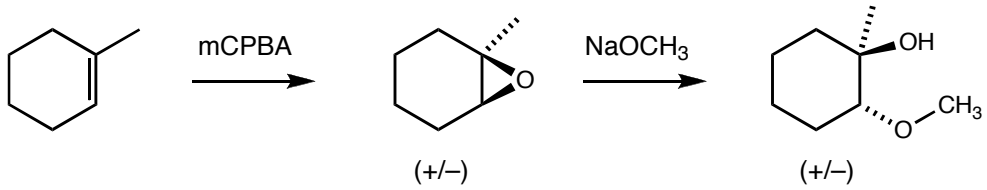


(+/–) (+/–)

Reading: Section 11.4

Opening Epoxides: Basic Conditions

- Provide a mechanism and explain why the indicated product is formed selectively in each of the following reactions:

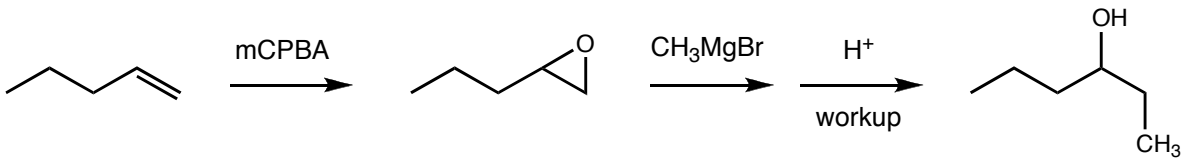


(+/–) (+/–)

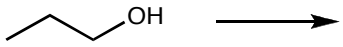
Reading: Section 11.4

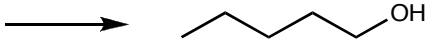
Opening Epoxides with Grignard Reagents

- Provide a mechanism that shows how the following epoxide reacts with the indicated Grignard reagent:



- This reaction is quite useful for synthesis, because it forms a new **carbon-carbon bond**. Provide a synthetic route for the following transformation:

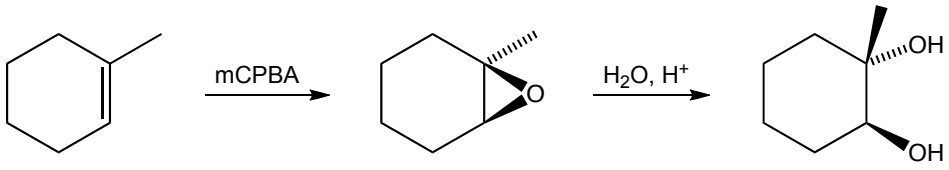




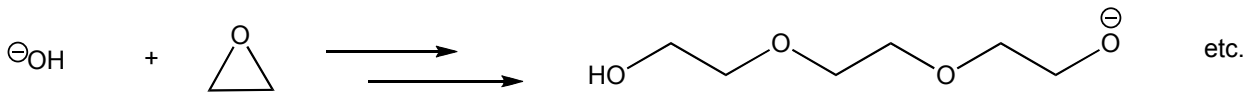
Reading: Section 11.5

Synthesis of Glycols (Vicinal Diols) from Epoxides

- Glycols can be synthesized from epoxides. What is the overall stereochemistry of the following transformation?



- In general, acid-catalyzed hydrolysis of epoxides is preferable to base-catalyzed hydrolysis, because base-catalyzed hydrolysis can result in **polymerization**:

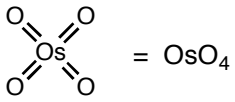


This polymerization reaction is extremely exothermic, and can be dangerous!

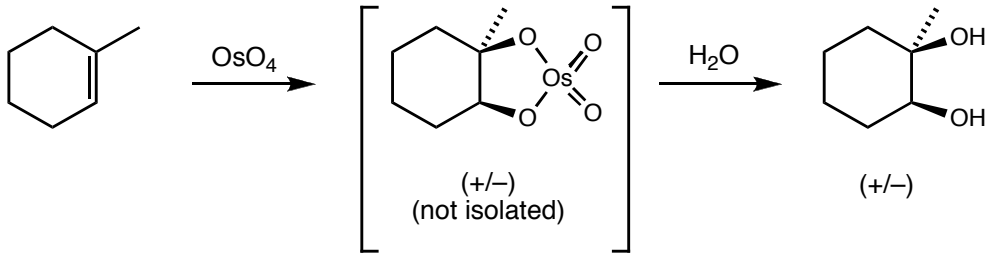
Reading: Section 11.5

Synthesis of Glycols (Vicinal Diols) from Alkenes

- There is a *direct* route to synthesis of glycols from alkenes using osmium tetroxide, OsO_4. Draw the curved arrows for the following reaction. What is the overall stereochemistry of this reaction?



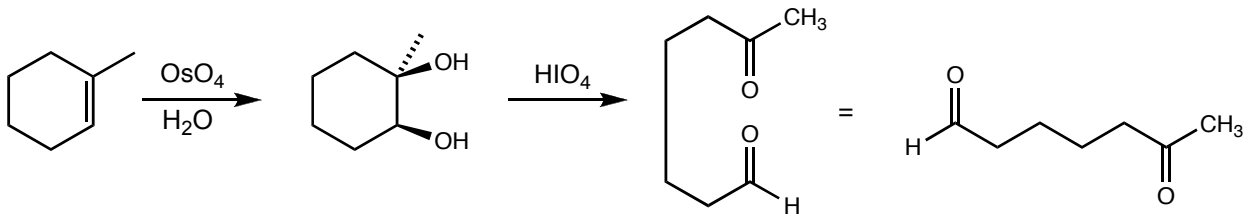
= OsO_4



Reading: Section 11.5

Cleavage of Glycols: It's Kinda Like Ozonolysis

- Glycols react with HIO_4 (periodic acid . . . how do you pronounce that?) to give products in which the C–C bond of the glycol has been cleaved:



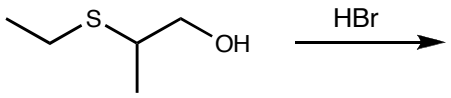
- Is this overall transformation reminiscent of anything?

Reading: Section 11.5

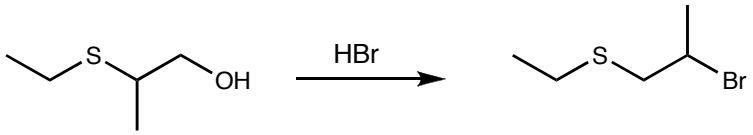
Neigboring-Group Participation

- When an alkyl halide has a nucleophilic atom (often S or N) nearby in the same molecule, the molecule can undergo an **intramolecular** S_N2 reaction that may then be followed by an **intermolecular** S_N2 reaction!

- What product would you expect to be formed by the following reaction: (Include a curved-arrow mechanism)



- The actual product is shown below. Draw a curved-arrow mechanism that can account for the unusual product. (Note that this is *not* a simple methyl shift!)

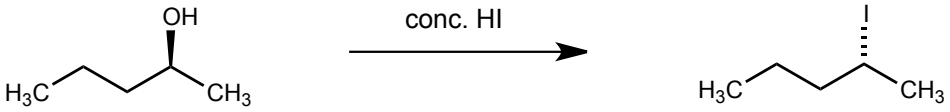


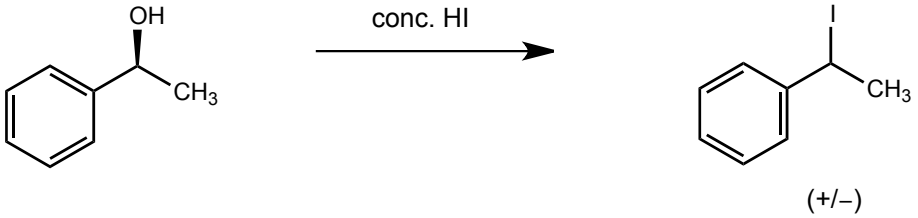
- What is one experiment you could do to prove that this mechanism is not a simple methyl shift?

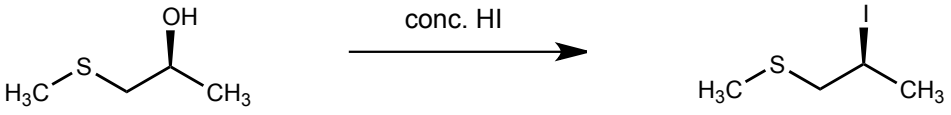
Reading: Section 11.7

Test Yourself Now!

The following three reactions are very similar, yet each has a different stereochemical result. For each reaction, provide a complete curved-arrow mechanism **and** explain briefly how the observed stereochemistry arises as a result of that mechanism.







Test Yourself Now!

Provide a complete synthesis of the desired product from the indicated starting material. You may use any organic or inorganic reagents in your synthesis.