

## Reactions of Alkenes II

**Reading:** Wade chapter 8, sections 8-9- 8-16

**Study Problems:** 8-47, 8-48, 8-55, 8-66, 8-67, 8-70

### Key Concepts and Skills:

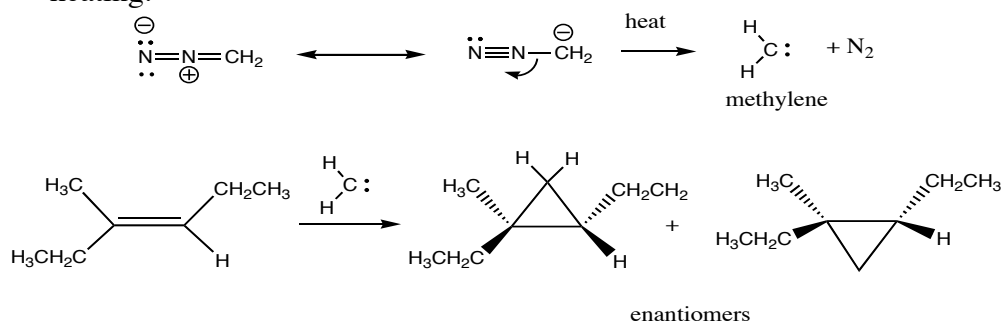
- Propose logical mechanisms to explain the observed products of alkene addition reactions, including regiochemistry and stereochemistry
- Use clues provided by the products of reactions such as ozonolysis to determine the structure of an unknown alkene
- When more than one method is available for a chemical transformation, choose the better method and explain its advantages

### Lecture Topics:

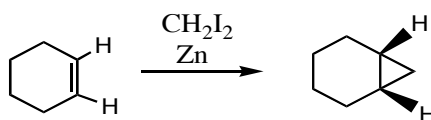
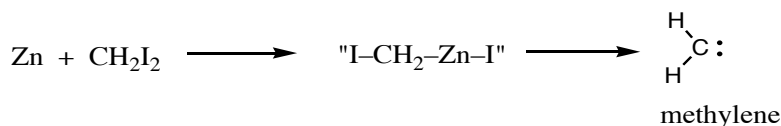
#### I. Additions to pi bonds: Carbenes

Carbenes react with pi bonds to form cyclopropanes. There are three methods for generating carbenes:

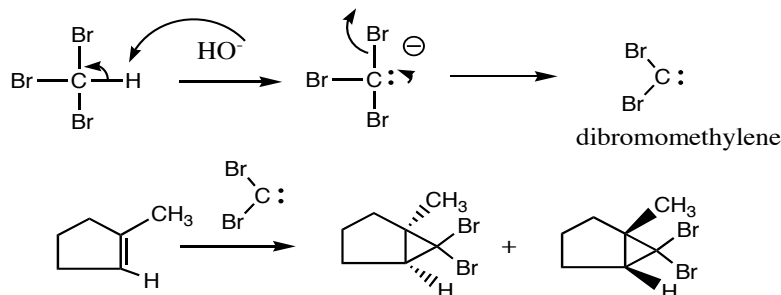
- heating of diazo compounds: Diazomethane produces methylene upon heating:



- Simmons-Smith Reaction: insertion of zinc into a dihaloalkane



- $\alpha$ -elimination reaction:



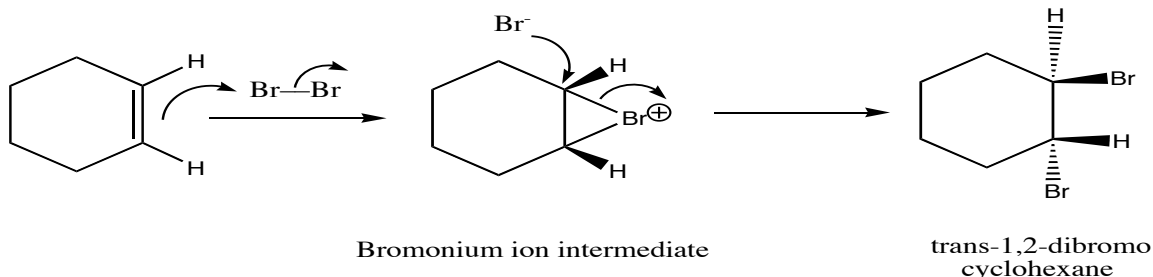
Stereochemistry of cyclopropanation: cis groups in the alkene remain cis in the cyclopropane; trans groups in the alkene remain *trans* in the cyclopropane

## II. Alkene Halogenation

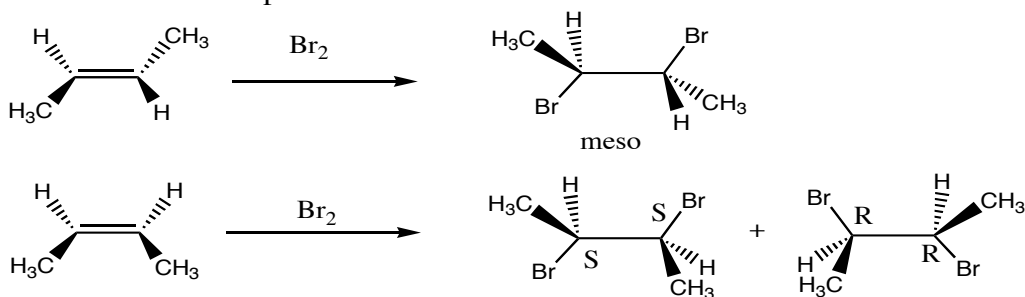
Addition of X-X across the pi bond

Pi bond acts as a nucleophile; a *bromonium ion* intermediate gets attacked by nucleophilic bromine; the resulting dibromide has trans stereochemistry:

Backside displacement

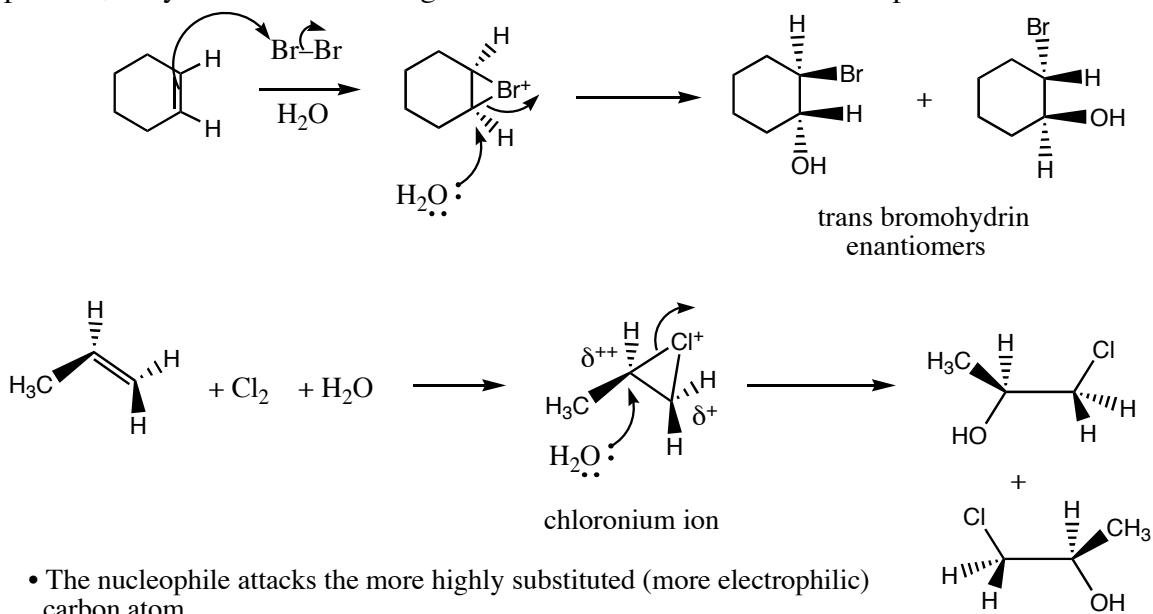


The reaction is stereospecific: different stereoisomers of starting material produce different stereoisomers of products:



### Halohydrin synthesis:

• Involves the interception of the bromonium ion by water (or alcohols), which are stronger nucleophiles than  $\text{Br}^-$ . Again, anti (trans) stereochemistry is observed in the product; unsymmetrical alkenes give Markovnikov orientation in the products:



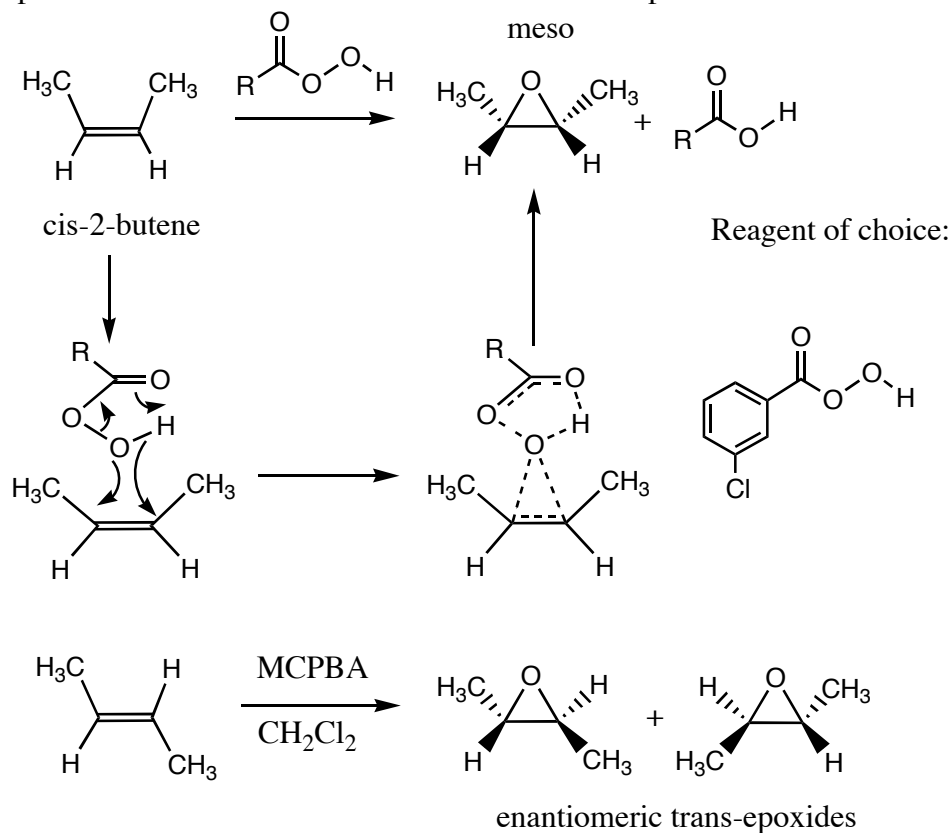
## II. Oxidation of Alkenes → Addition of oxygen

### Three flavors:

1. epoxidation
2. dihydroxylation
3. Oxidative cleavage

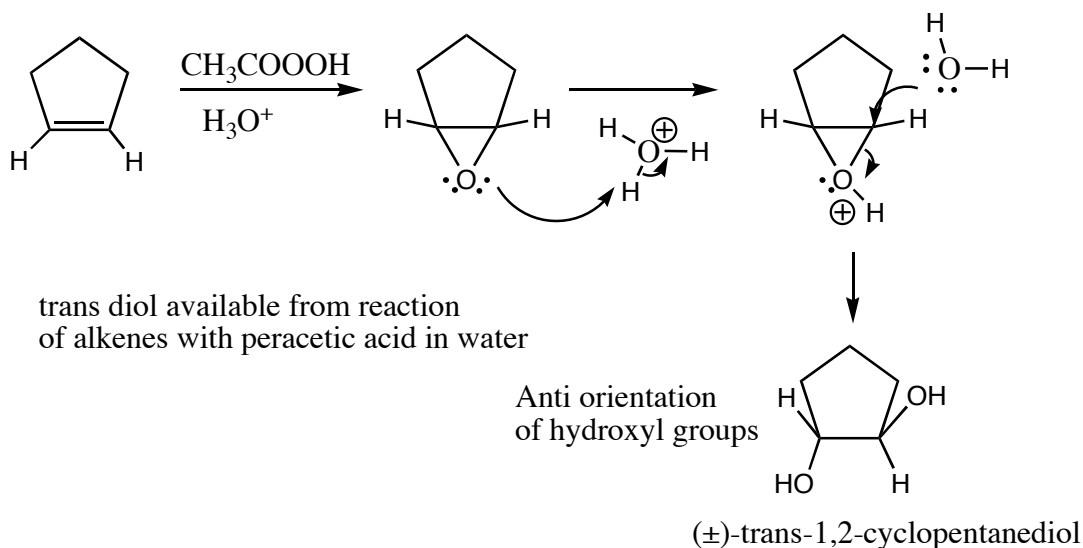
### 1. Epoxidation

Epoxide (oxirane) formation takes place when an alkene is treated with an organic peracid. In addition to the epoxide product, a carboxylic acid by-product is formed. Epoxidation is a one-step process (concerted bond formation and bond breaking), and the reaction is therefore stereospecific: groups that are *cis* in the alkene are *cis* in the epoxide, and groups which are *trans* in the alkene are *trans* in the epoxide.

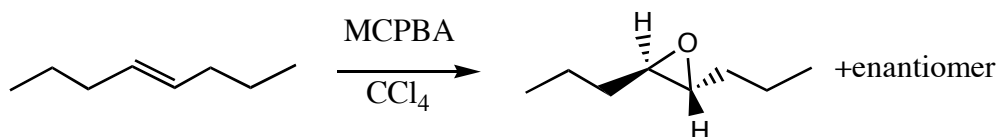


### Acid-catalyzed opening of epoxides: synthesis of *trans*-1,2-diols

Anti-diols are obtained by backside attack of water on activated epoxides formed by protonation of the epoxide oxygen. To favor formation of the *trans* 1,2-diol, peracetic acid is used in aqueous acid; to favor formation of just the epoxide, MCPBA is used in a non-polar solvent.



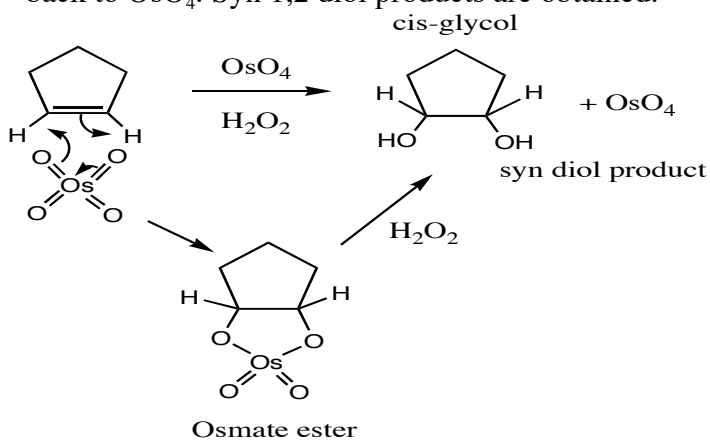
epoxides available from reaction of alkenes with MCPBA in  $\text{CH}_2\text{Cl}_2$



## 2. Direct Syn Hydroxylation of Alkenes

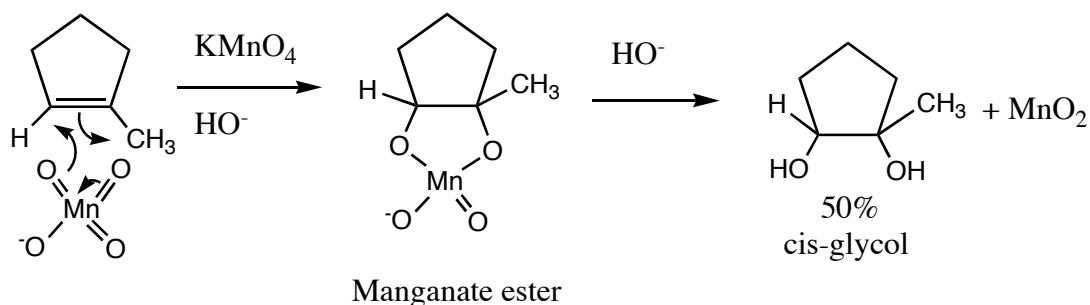
Two methods exist for syn hydroxylation:

- Osmium tetroxide is used in catalytic quantities in the presence of an oxidant to oxidize alkenes. An intermediate osmate ester is formed;  $\text{H}_2\text{O}_2$  hydrolyzes the osmate ester and oxidizes osmium back to  $\text{OsO}_4$ . Syn 1,2 diol products are obtained.



$\text{OsO}_4$  is expensive and toxic, but it gives excellent yields of the cis diol from alkenes.

- Permanganate hydroxylation: treatment of alkenes with dilute, cold aqueous  $\text{KMnO}_4$  gives moderate yields of the cis-1,2-glycol product.  $\text{KMnO}_4$  is cheaper and less toxic than  $\text{OsO}_4$



$\text{HO}^-$  serves to hydrolyze the intermediate Manganate ester

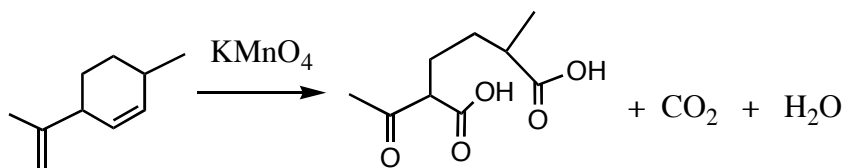
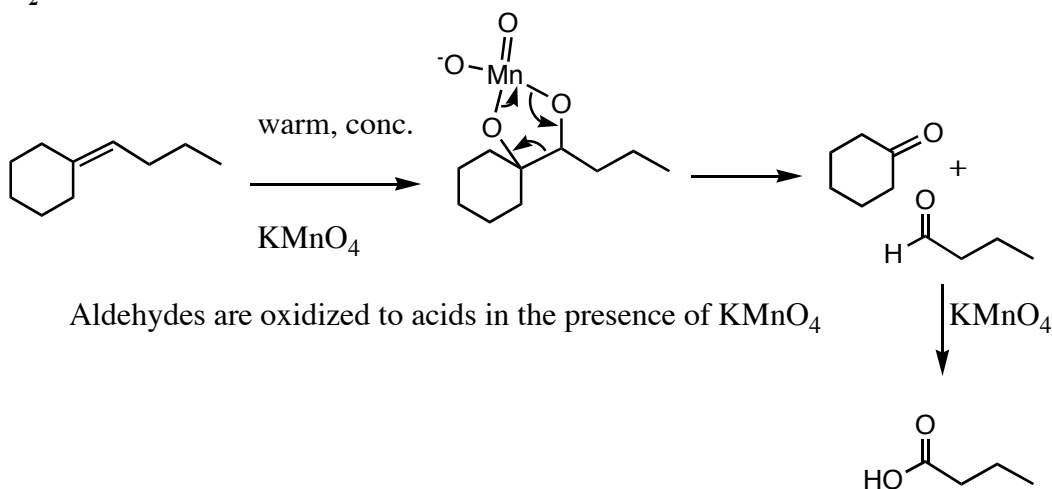
### 3. Oxidative Cleavage

a. Treatment of alkenes with a warm solution of concentrated  $\text{KMnO}_4$  leads to an oxidative cleavage of alkenes.

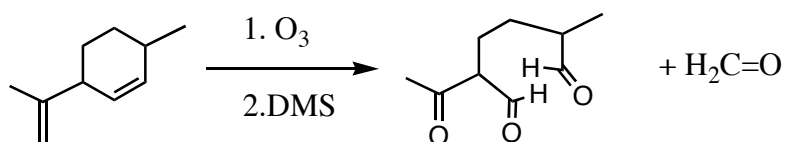
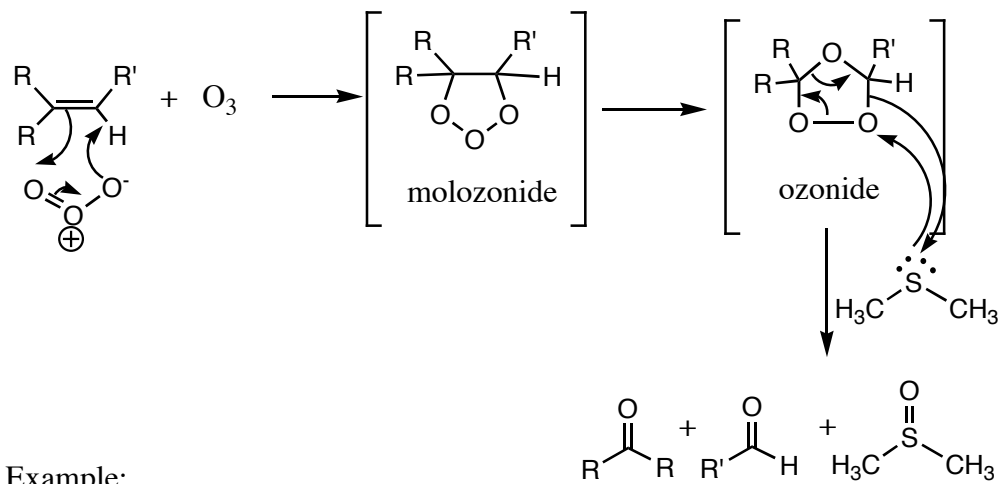
An alkene carbon with two alkyl groups is oxidized to a **ketone** ( $\text{R}_2\text{C}=\text{O}$ )

An alkene carbon with one alkyl group is oxidized to a **carboxylic acid** ( $\text{RC}(=\text{O})\text{OH}$ )

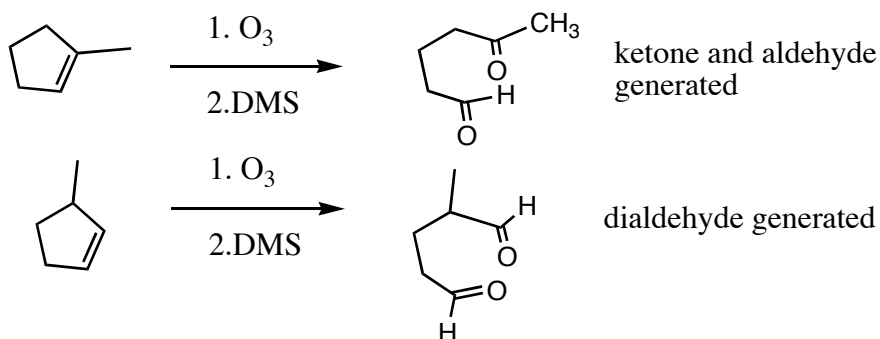
An alkene carbon with no alkyl groups and two hydrogen atoms is oxidized to  **$\text{CO}_2$  and  $\text{H}_2\text{O}$** .



b. Ozonolysis – Treatment of alkenes with ozone ( $\text{O}_3$ ) leads to oxidative cleavage, giving aldehydes and ketones. An intermediate ozonide is produced; dimethyl sulfide (DMS) is added in a second step to reduce the ozonide to aldehydes and ketones. Dimethyl sulfide prevents aldehydes from being further oxidized to carboxylic acids by ozone. To predict the products of an ozone cleavage, simply erase the double bond and put two carbonyls ( $\text{C}=\text{O}$ ) in its place.

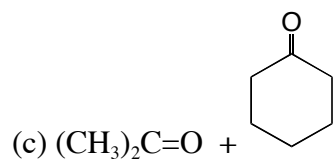
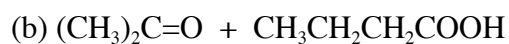


Ozonolysis provides confirmation of the location of olefins within a molecule

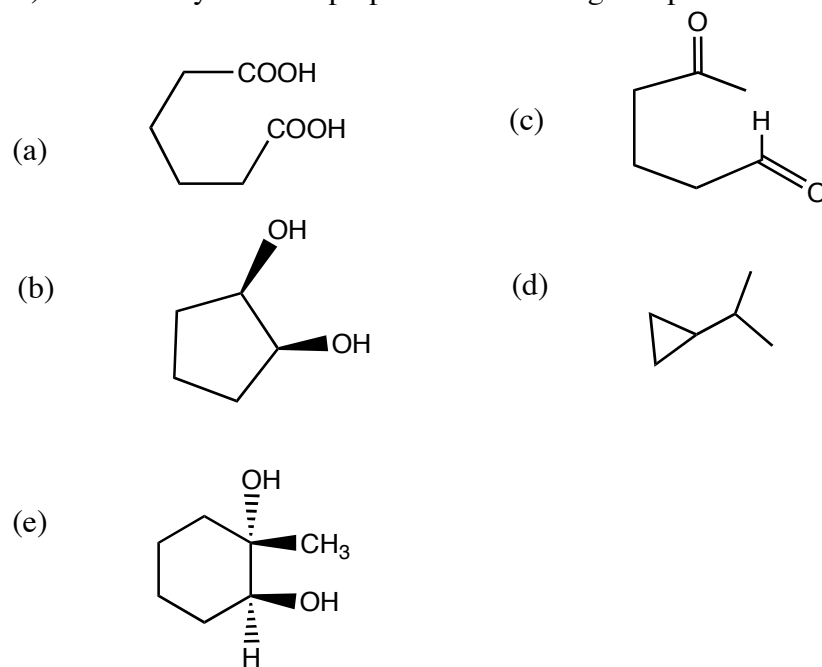


Additional Problems for practice:

1. Show the structures of alkenes that give the following products upon reaction with warm, concentrated  $\text{KMnO}_4$



2.) Show how you could prepare the following compounds from an alkene:



3.) Draw reasonable mechanisms for the following reactions:

