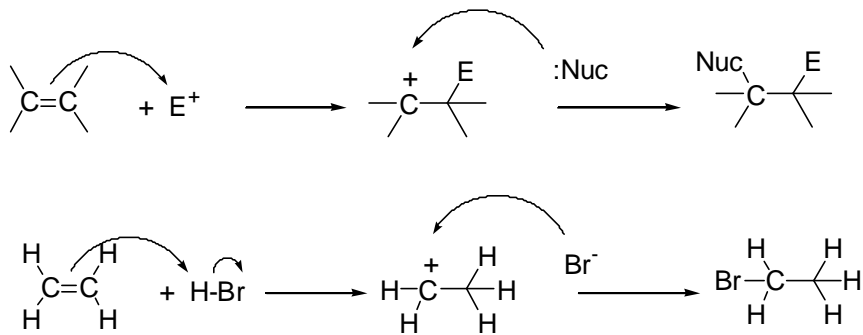


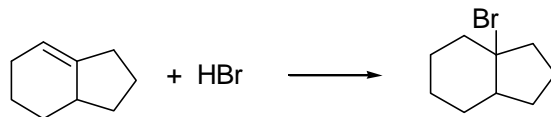
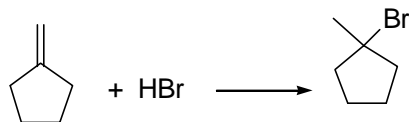
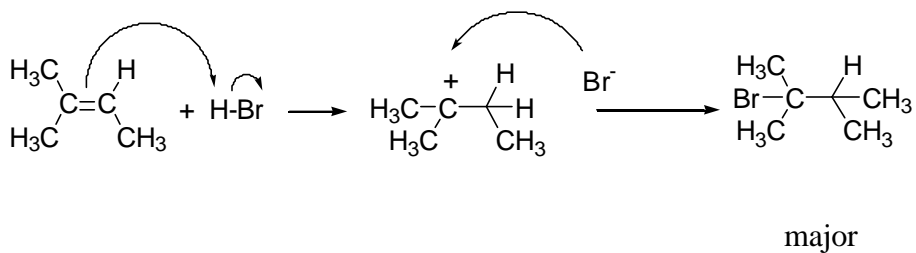
# Chap 8

## Reactions with Alkenes

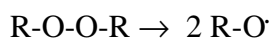
### 1. Electrophilic addition to alkenes.

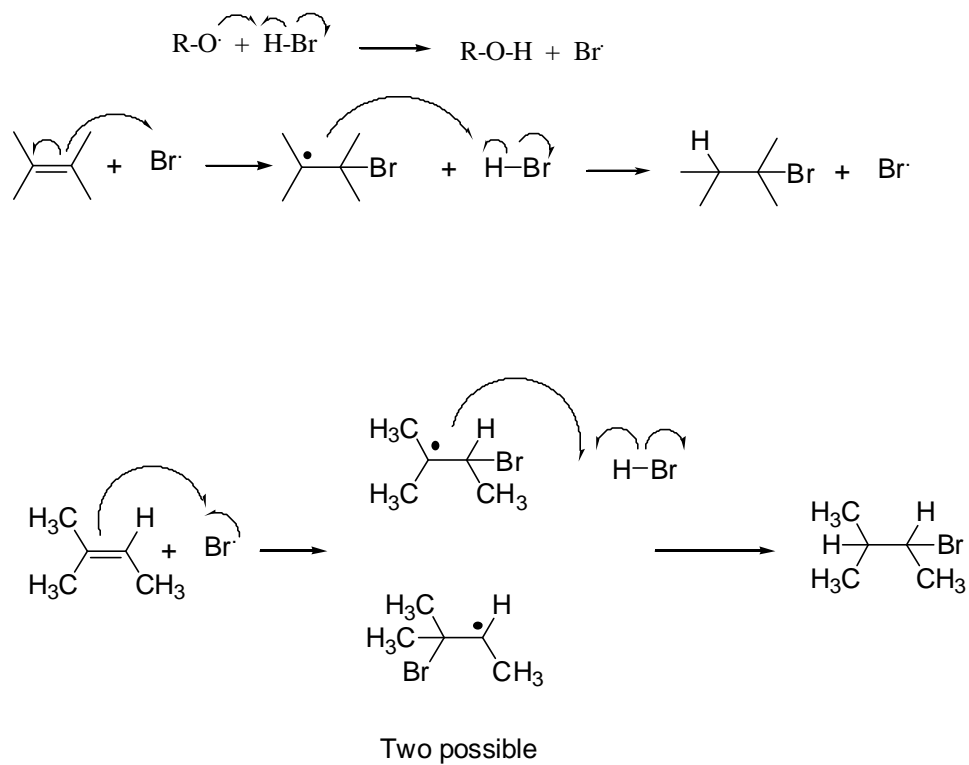


A) Markovnikov's rule- (1869) addition of a proton to an alkene results in the proton bonded to the carbon that has the most hydrogens (more substituted carbon gets the addition) more stable intermediate.

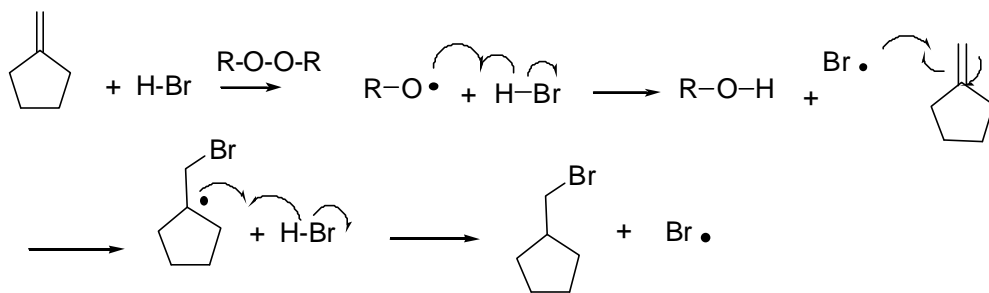


B) Anti-markonikov addition.



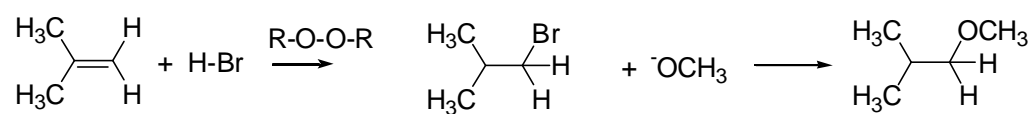
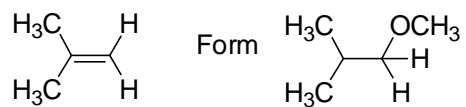


Ex.

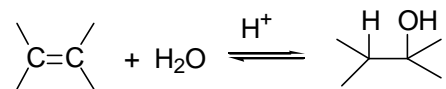


Only HBr works for the radical rxn. Very endothermic for HI, HCl.

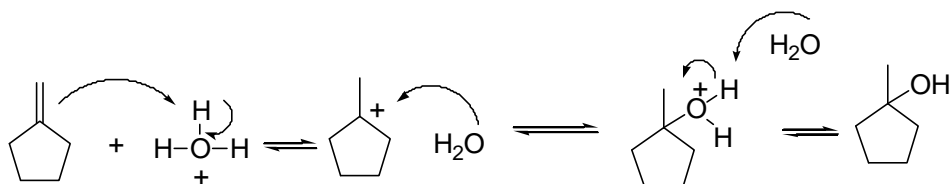
Anti-mark addition of ethers. R-O-R



c) Hydroboration of Alkenes.

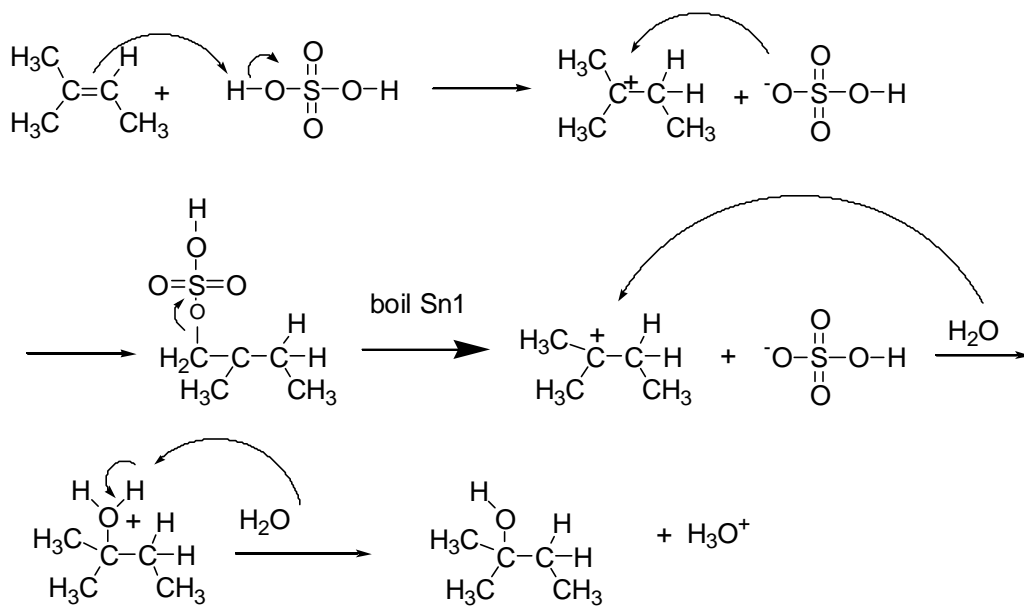


opposite of dehydration



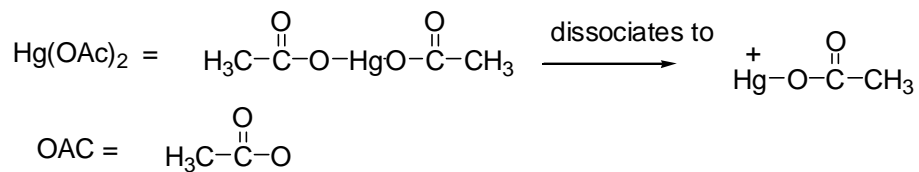
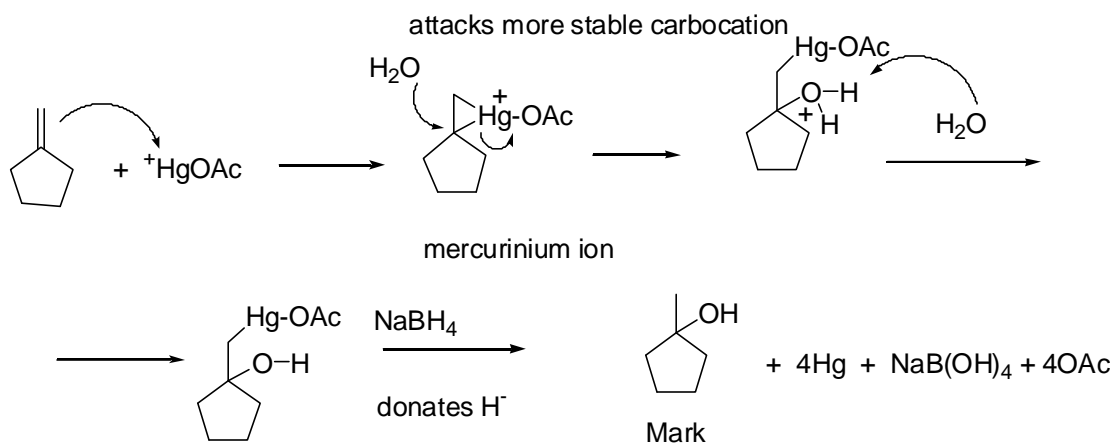
Mark addition

d) Addition of sulfuric acid.



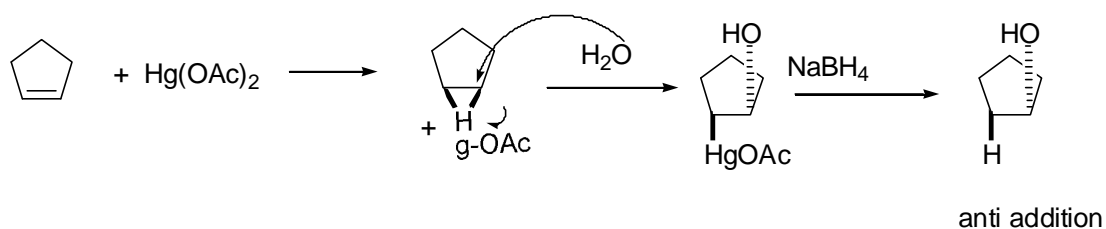
mark addition

e) no rearrangements.

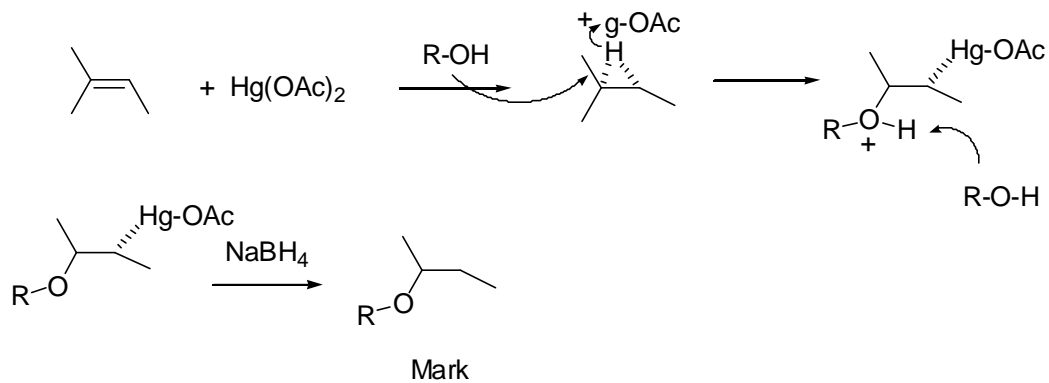


1. Better yields than acid catalyzed.
2. no rearrangements.
3. no harsh conditions.
4. Bad, organomercurial reagents are highly toxic.

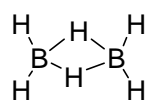
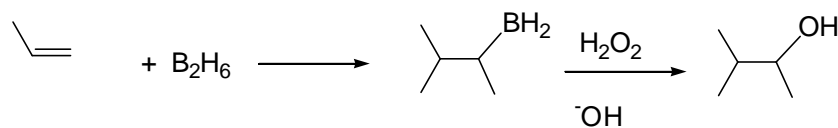
### Stereochemistry- anti-addition



### 2) Formation of an ether Alkoxymercuration-demercuration

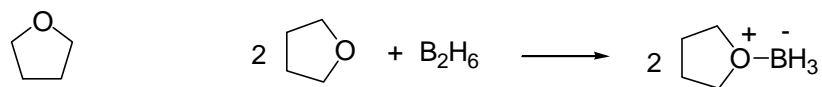


### f) Anti-mark, Hydroboration of alkenes.

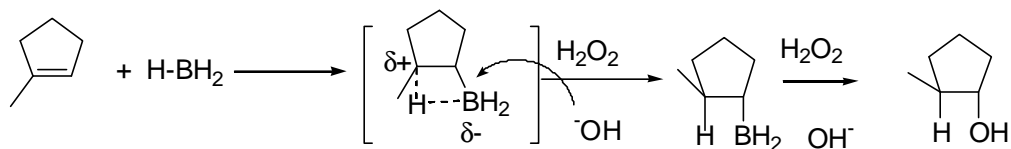
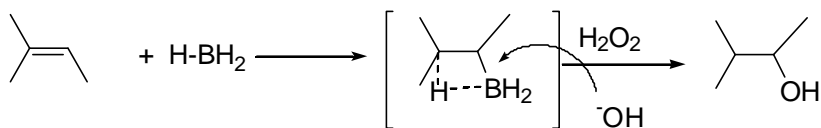


toxic, flammable  
explosive

diborane



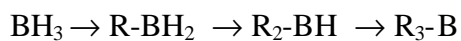
use THF  
tetrahydrofuran



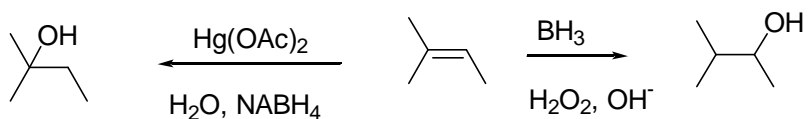
syn - addition, same face

stereochemistry racemic R,R and S,S

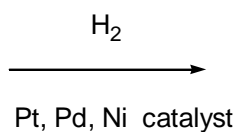
stoichiometry- 1 mole  $\text{BH}_3$  reacts with 3 moles of alkene.

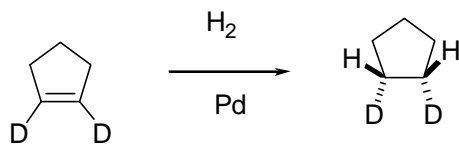


Summary-

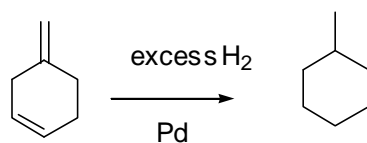


Catalytic hydrogenation of alkenes-



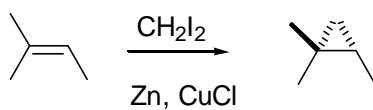


syn addition



b) carbenes.

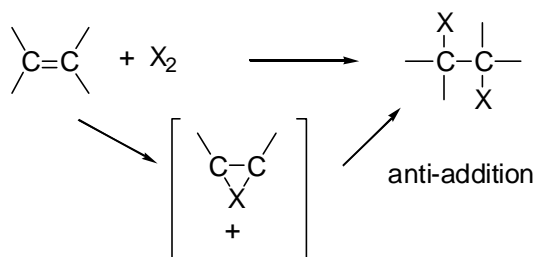
1.  $\text{N}_2\text{-CH}_2$
2.  $\text{CHBr}_3 + \text{Base} \rightarrow \text{:CBr}_2 + \text{Br}^- + \text{Hbase}$
3.  $\text{CH}_2\text{-I}_2 + \text{Zn, CuCl}$  (Simmons-Smith Rxn)



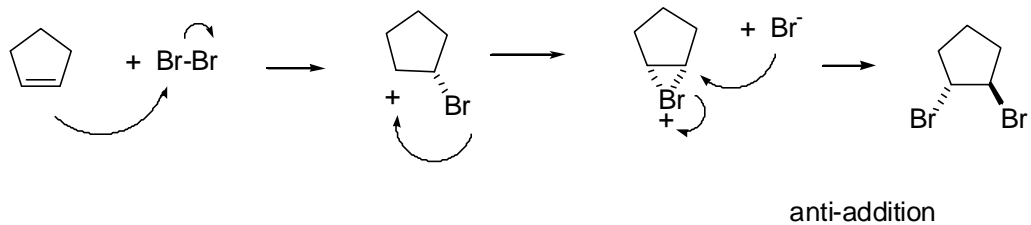
reagent formed by  $\text{CH}_2\text{I}_2 + \text{Zn(Cu)} \rightarrow \text{ICH}_2\text{ZnI}$

Simmons Smith Reagent  
(carbenoid)

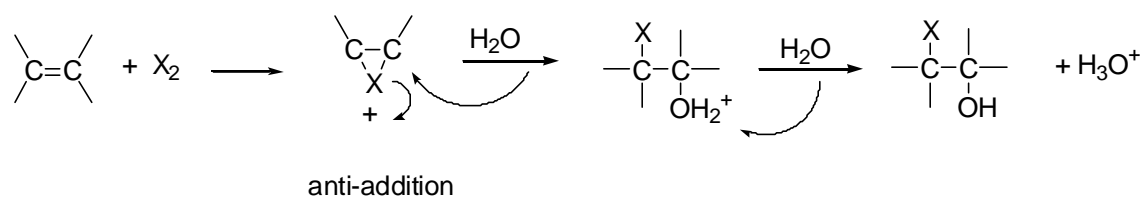
3) Halogen addition



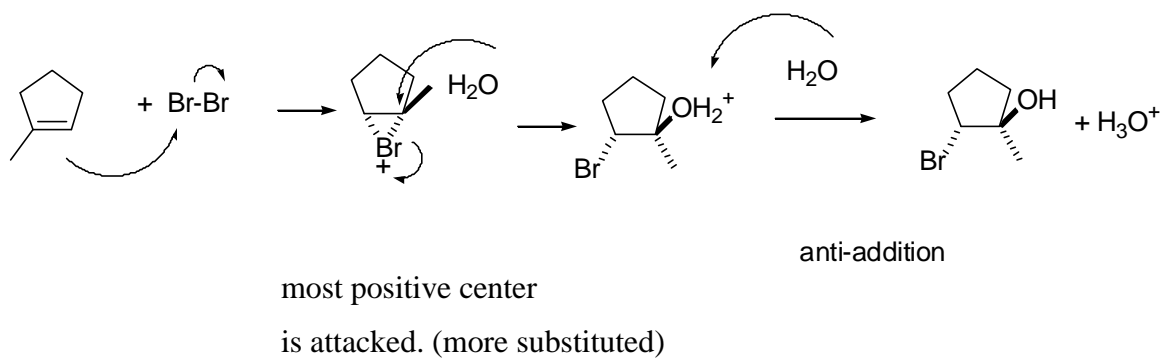
Ex.



#### 4) Formation of Halohydrins



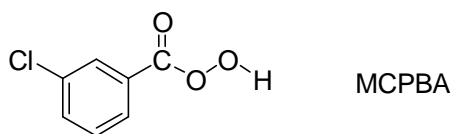
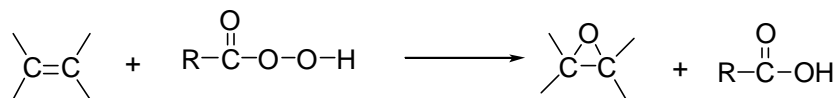
Ex.



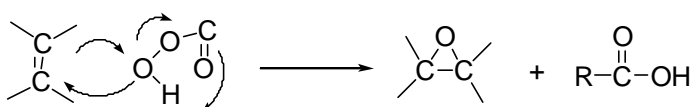
#### 5) Epoxidation of Alkenes

a) Epoxide-

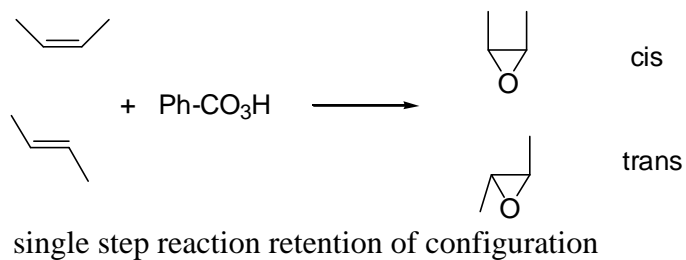




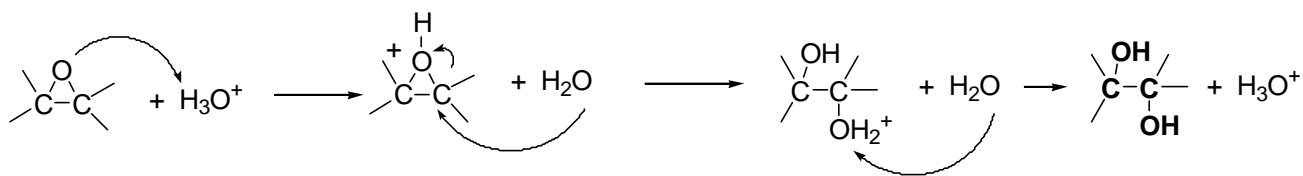
### Mechanism



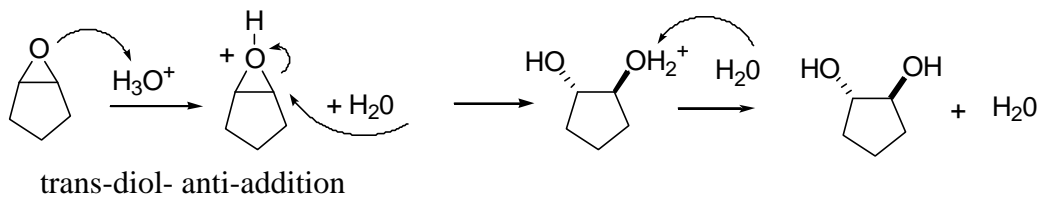
### Stereochemistry



### b) Acid-catalyzed opening of epoxides.

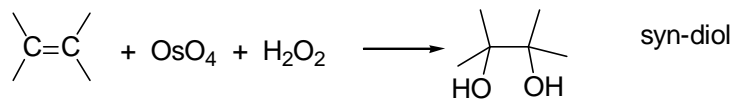


Ex.

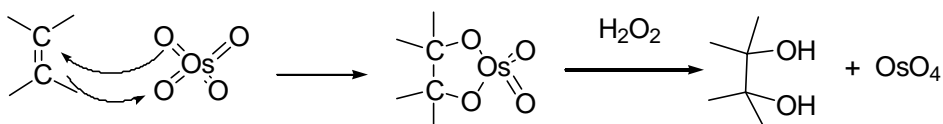


6) Syn hydroxylation of alkenes, syn diol.

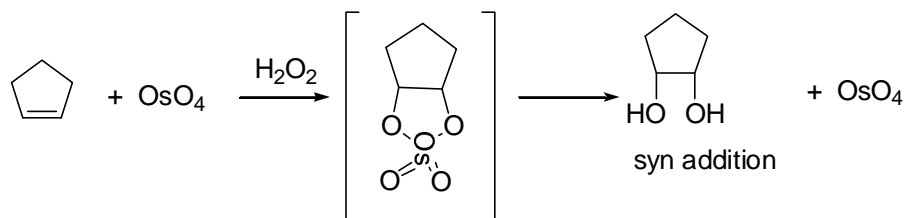
a)



mechanism.

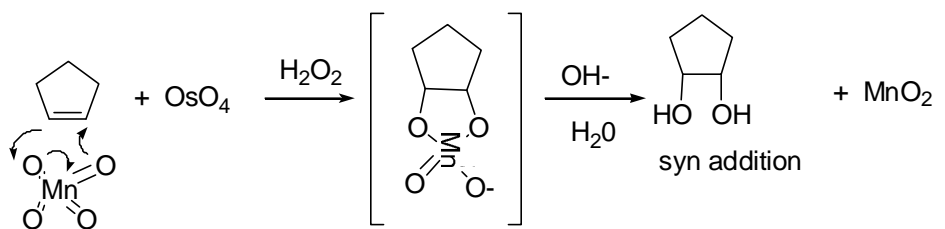


Ex.



expensive, toxic, volatile

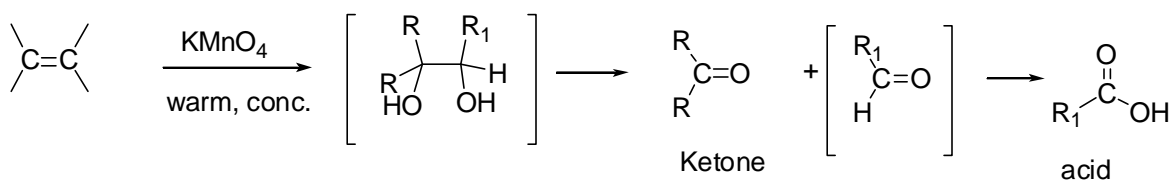
c)  $\text{MnO}_4^-$ , cold, dilute.



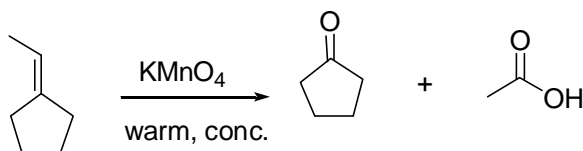
lower yield.

## 7. Oxidative cleavage of Alkenes

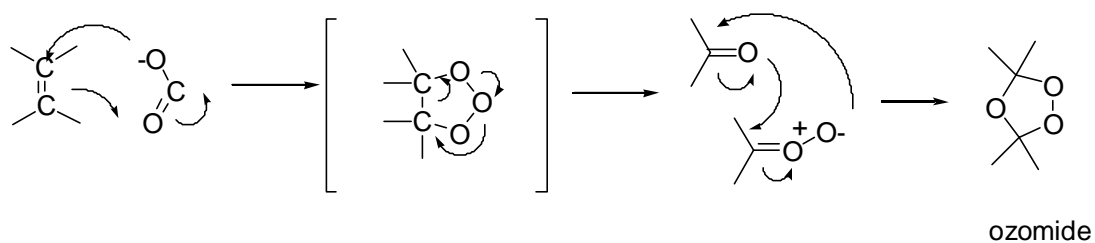
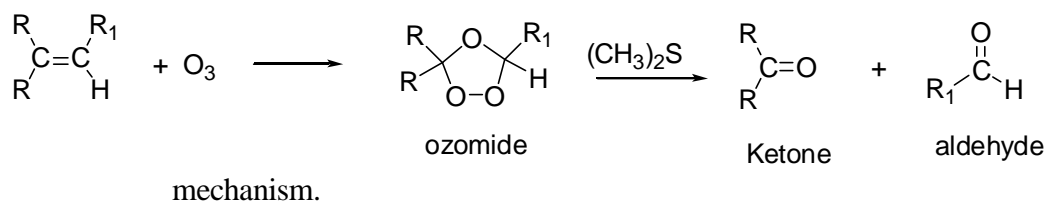
a)  $\text{KMnO}_4$  warm concentrated.



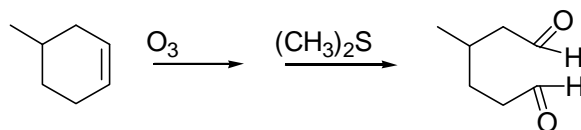
Ex.



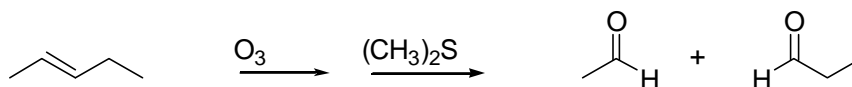
b) Ozonolysis.  $\text{O}_3$



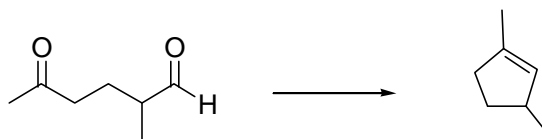
Ex.



Ex.



Ex.

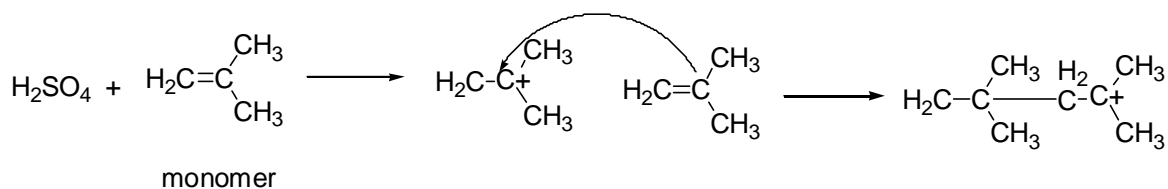


Where from

## 8. Polymerization of Alkenes.

Polymer is made up of monomers (small repeating units)

a) cationic polymerization.



other initiator  $BF_3$  good Lewis acid

