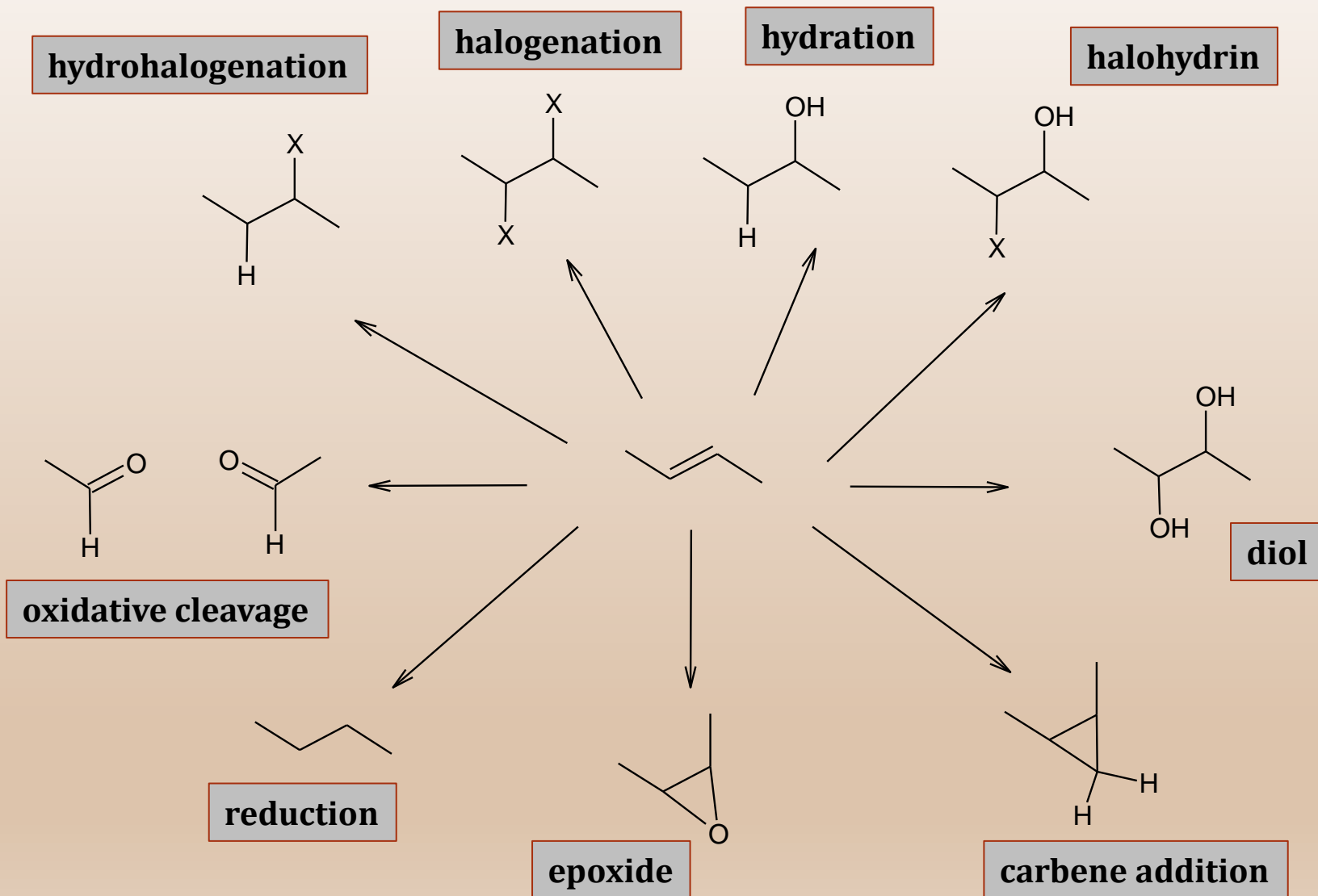


Alkene Reactions

2- Addition Reactions – Synthesis of Alcohols

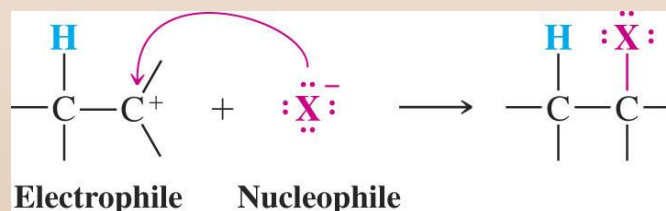
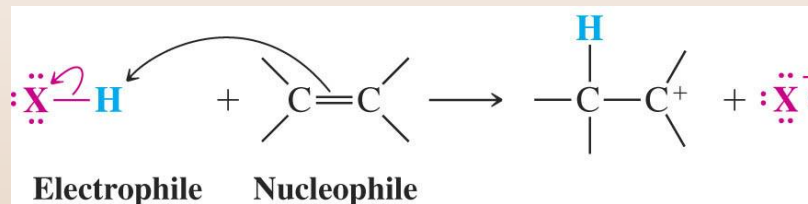
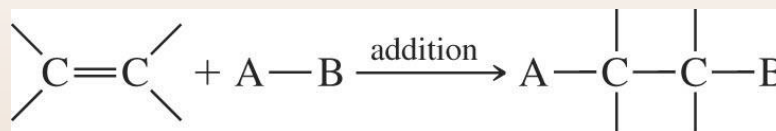
Dr. Sapna Gupta

All Reactions

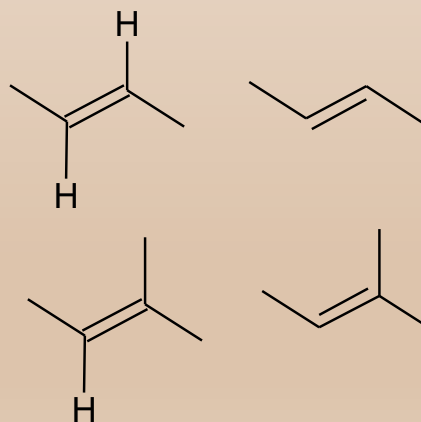


General Mechanism

- The alkene is the nucleophile.
- The reagent is the electrophile

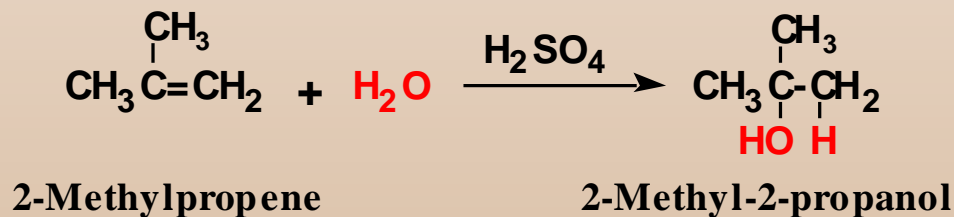
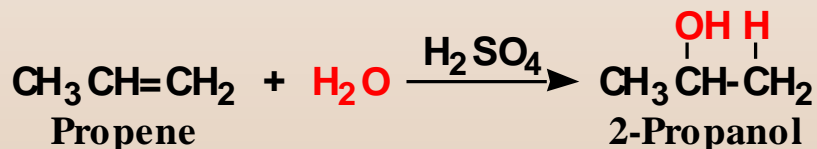


- Alkene types: symmetric – where alkene has equal number of carbons on the double bond and asymmetric where one carbon of the double bond has less carbons.



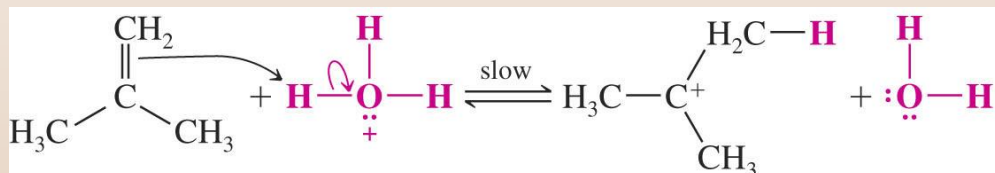
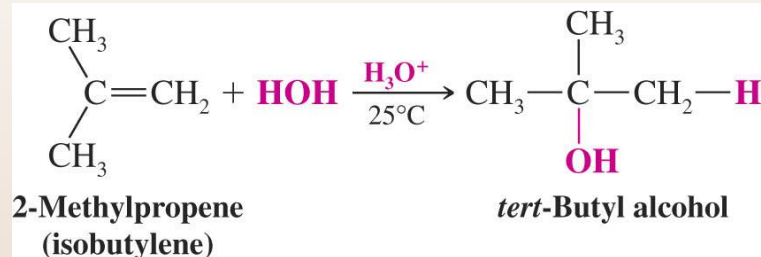
Hydration - 1 - Addition of H₂O

- **Hydration of an alkene** is the addition of H-OH to give an alcohol
- Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol
- HOH adds in accordance with *Markovnikov's rule*.

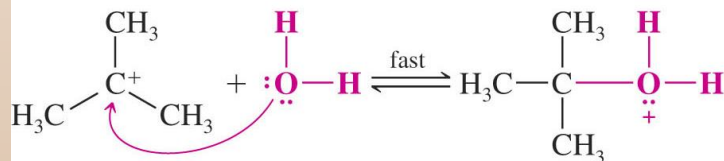


Hydration - Mechanism

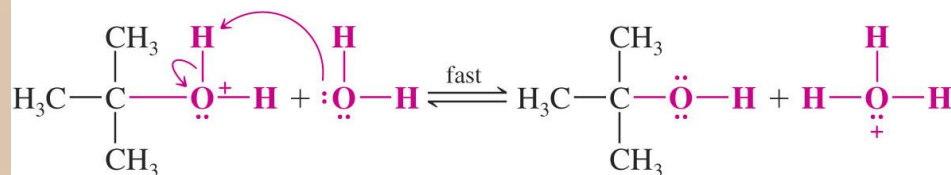
- **Markovnikov's addition**
- Note: rearrangement can occur where applicable



The alkene donates an electron pair to a proton to form the more stable 3° carbocation.



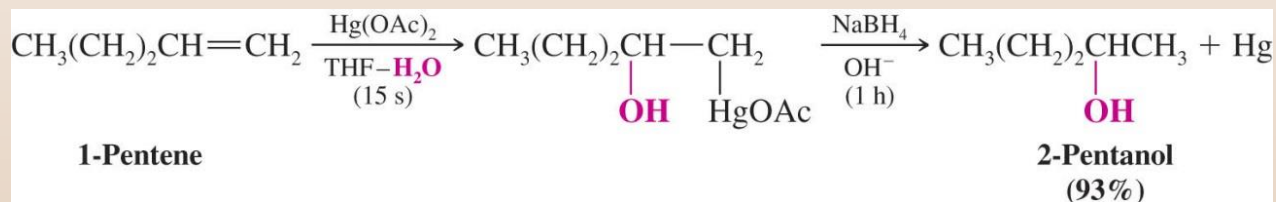
The carbocation reacts with a molecule of water to form a protonated alcohol.



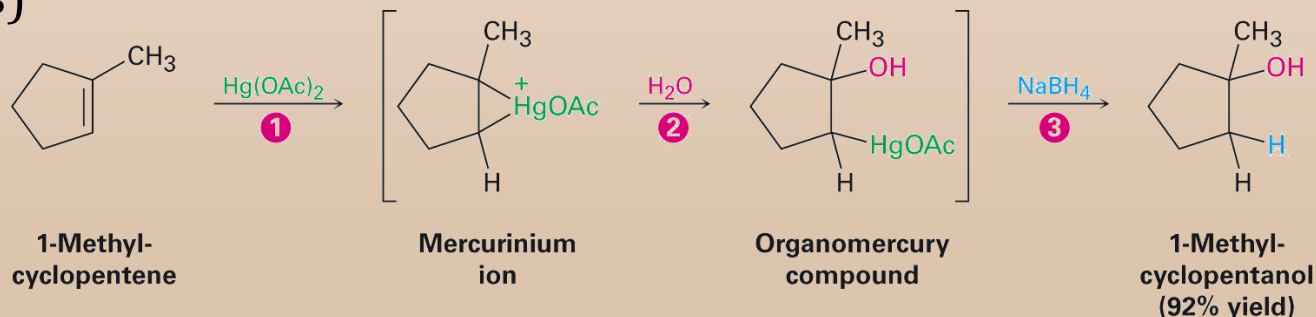
A transfer of a proton to a molecule of water leads to the product.

Hydration – 2 – Oxymercuration

- **Markovnikov's addition**
- There is no rearrangement (unlike acid catalyzed hydration)
- Reagent is $\text{Hg}(\text{OAc})_2$ followed by NaBH_4 and $\text{OH}^-/\text{H}_2\text{O}$

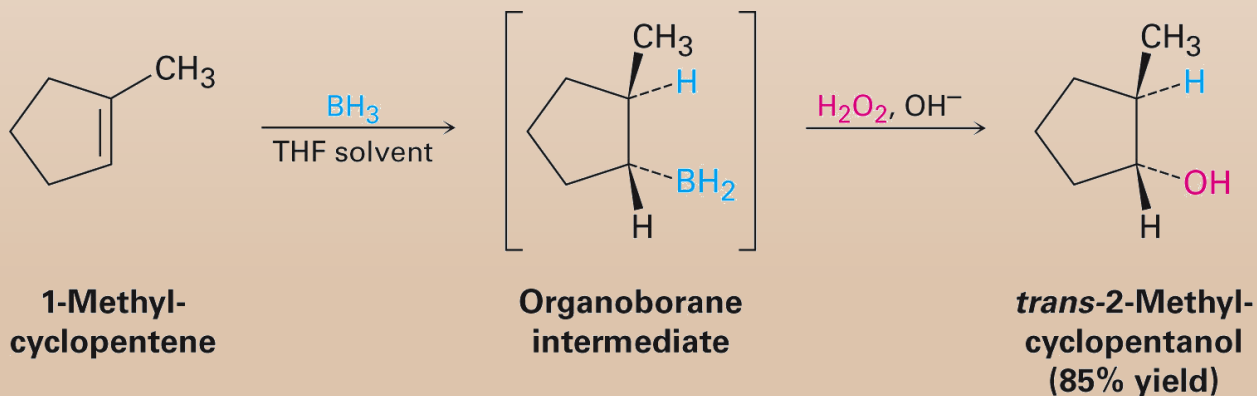
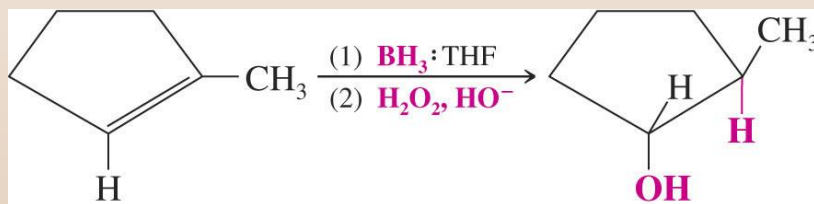


- Mechanism (**trans or anti addition** – H and OH are on the opposite sides)



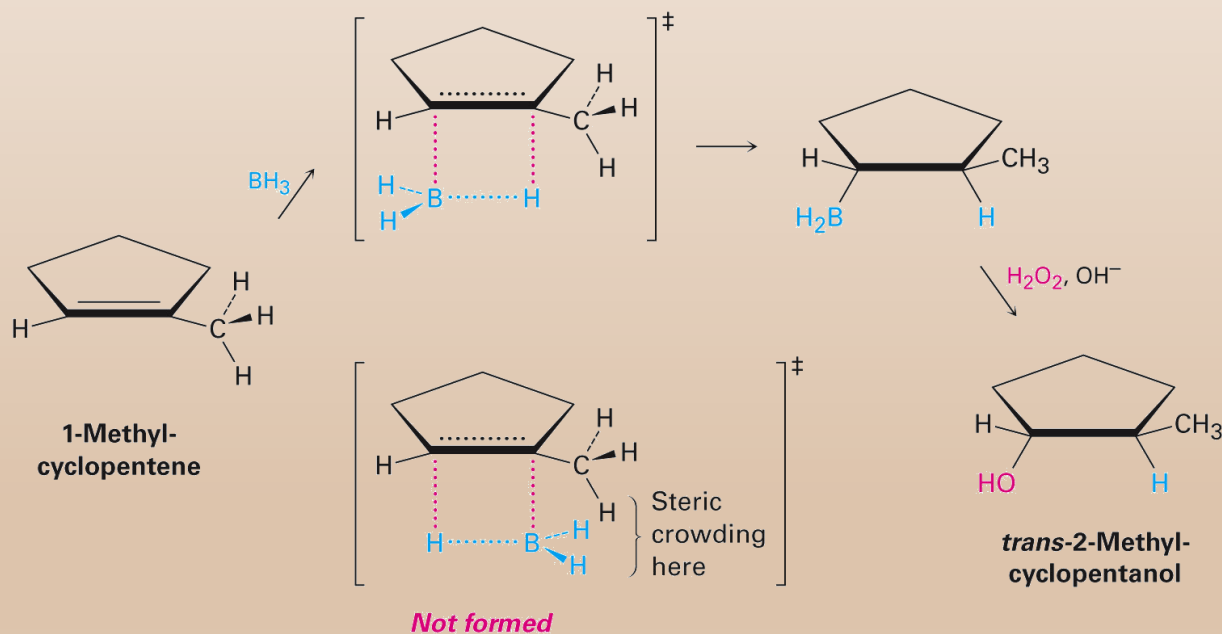
Hydration – 3 – Hydroboration

- **Anti-Markovnikov's addition**
- Needs borane reagent ($\text{BH}_3:\text{THF}$ – where THF is the solvent that stabilizes the BH_3) followed by $\text{OH}^-/\text{H}_2\text{O}_2$ (hydrogen peroxide)
- **SYN addition** (addition on same side)



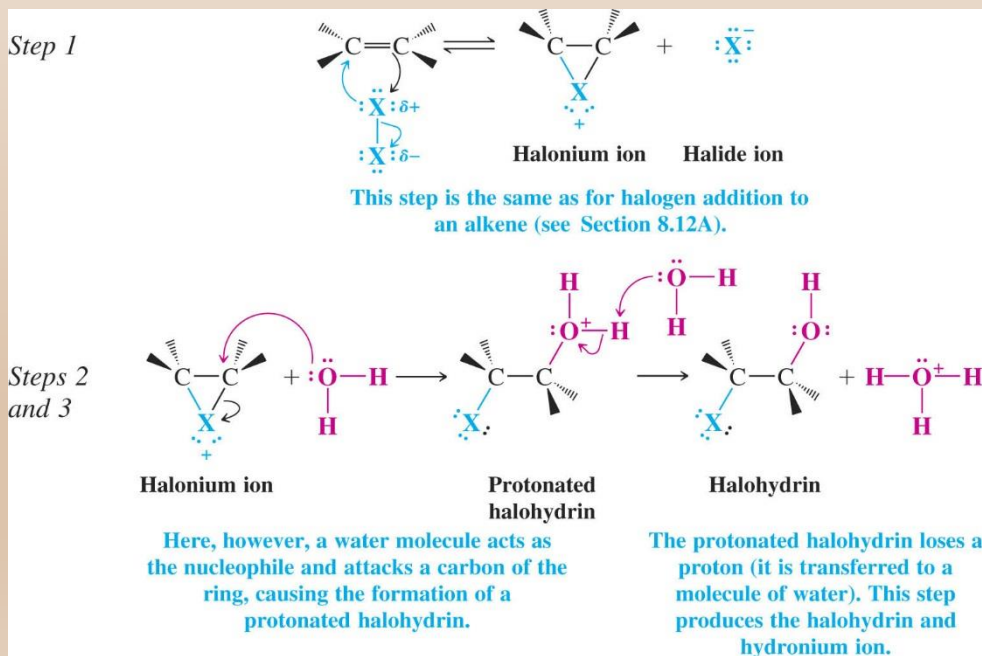
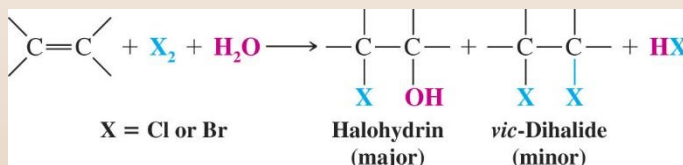
Hydration – Hydroboration Mechanism

- Borane is a Lewis acid
- Alkene is Lewis base
- Transition state involves BH_3 adding across $\text{C}=\text{C}$
- More stable carbocation is also consistent with steric preferences



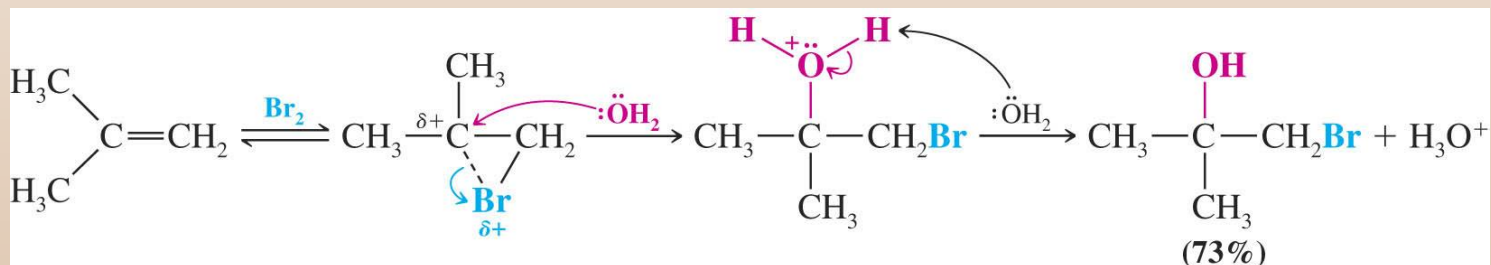
Halohydrins from Alkenes

- This is formally the addition of HO-X to an alkene to give a 1,2-halo alcohol, called a halohydrin. **Addition is ANTI.**
- The actual reagent is the dihalogen (Br₂ or Cl₂) in water in an organic solvent)



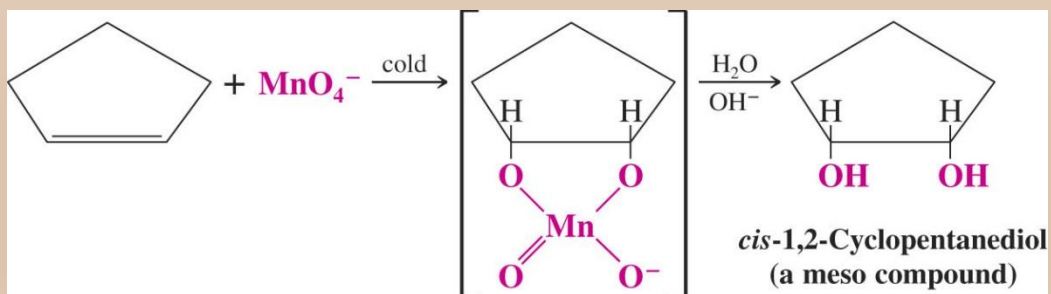
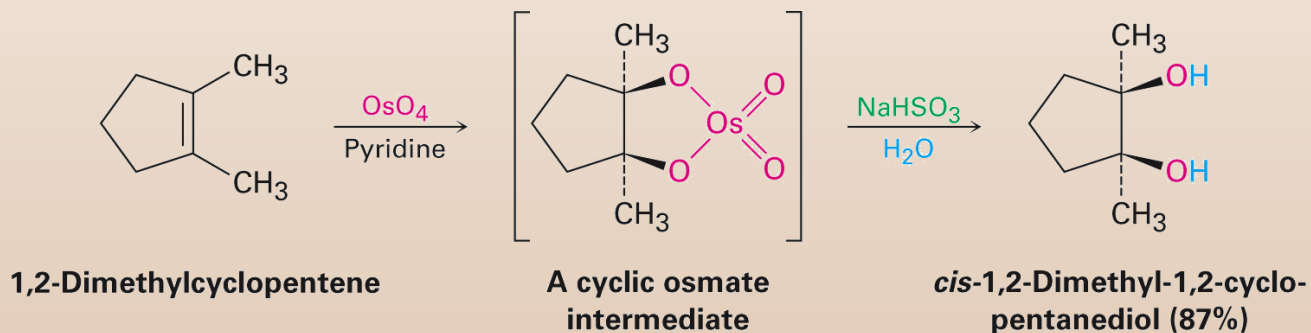
Halohydrin - 2

- In unsymmetrical alkenes, the bromonium ion will have some of its $\delta+$ charge density on the most substituted of the two carbons
 - The most substituted carbon can best accommodate $\delta+$ charge
- The water nucleophile will tend to react at the carbon with the most $\delta+$ charge – i.e. the more substituted carbon.



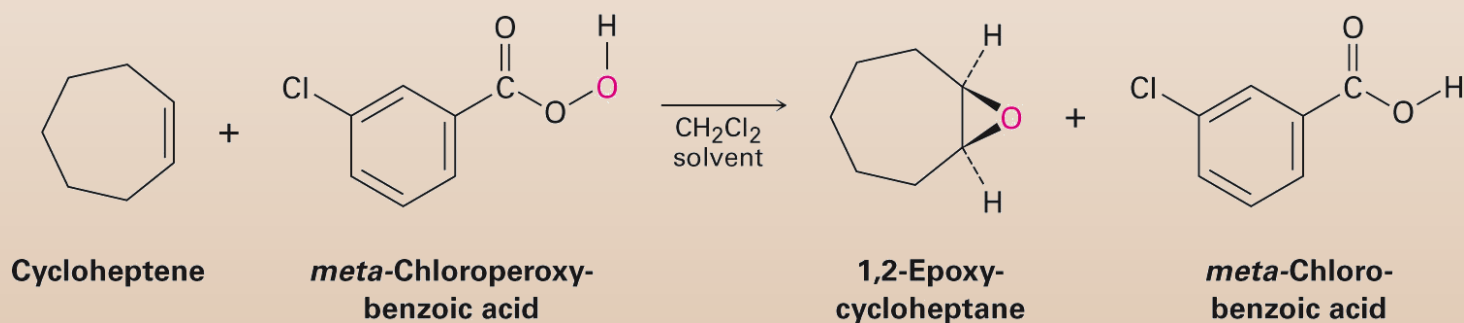
Diols from Alkenes

- **Hydroxylation – addition is SYN**
- Osmium tetroxide, then sodium bisulfite
- Can also use KMnO_4 (cold) (*QUALITATIVE TEST*)



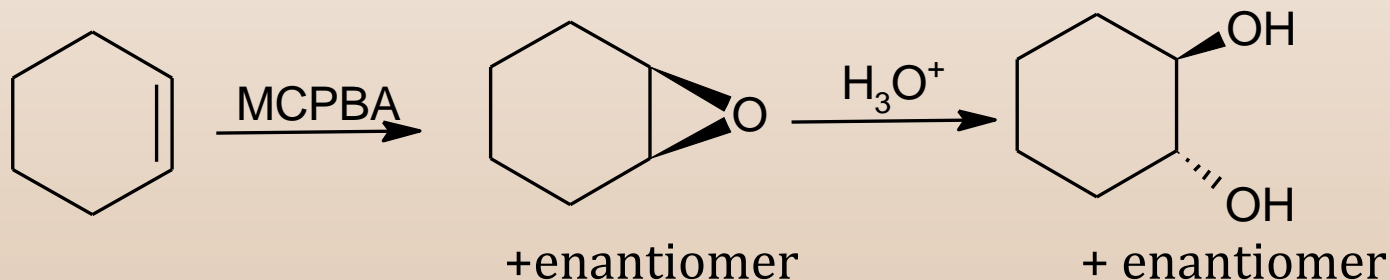
Epoxide Formation

- Epoxidation results in a cyclic ether with an oxygen atom
- Reagent is CH_3COOOH or any peracid (meta perbenzoic acid – MCPBA is a common acid)
- Stereochemistry of **addition is SYN**



Diol Formation

- **Dihydroxylation – *addition is ANTI***
- Form an epoxide and then treat with weak acid or base to give the diol.

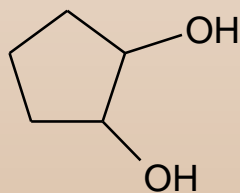
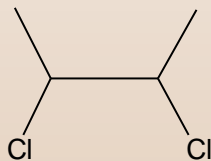


Location of Groups

Vicinal

On adjacent carbons

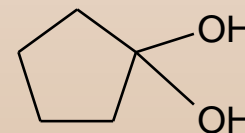
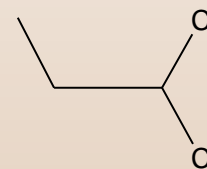
(1,2)



Geminal

On the same carbon

(1,1 or 2,2)



Key Words/Concepts

- Electrophilic addition
- Markovnikov's addition
- Syn addition
- Anti addition
- Hydration (water-acid, oxymercuration and hydroboration)
- Halohydrin
- Epoxides
- Diols